Adhesion Studies of Polymers: (I) Autohesion of Ethylene/1-Octene Copolymers; (II) Method Development and Adhesive Characterization of Pressure Sensitive Adhesive in Paper Laminates for Postage Stamps

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(Abstract)

Autohesion is defined as the resistance to separation of two bonded identical films that have been joined together for a period of time under a given temperature and pressure. Studies on the autohesion phenomenon can provide fundamental insights into the physical processes of adhesive bond and failure, as well as the practical engineering issues such as crack healing, elastomer tack, polymer fusion, self-healing, and polymer welding. In the first part of this dissertation work, four ethylene/1-octene (EO) copolymers were used in the present study consisting of molecules with linear polyethylene backbone to which hexyl groups are attached at random intervals. These copolymers have similar number-average molecular weight (Mn) and polydispersity, but different 1-octene content. These hexyl groups act as the short branches and hinder the crystallization, reduce density to some extent in the solid state, lower the melting temperature, and decrease the stiffness of the bulk materials. A full understanding of the autohesion behavior of the ethylene/1-octene copolymers involves investigations at three different length scales: 1) the molecular scale which controls the interfacial structure; 2) the mesoscopic or microscopic scale which can provide information on the formation of interfaces and on how the energy is dissipated during a fracture process; and 3) the macroscopic scale at which the mechanical properties such as fracture energy can be obtained for a particular test geometry. In the present study, the effects of the branch content on the formation and fracture of the interface of these ethylene/1-octene assemblies were evaluated at bonding temperatures (Tb) and bonding times (tb). The correlation among these three length scales was also investigated and modeled.

The adhesion strength of these symmetric interfaces of EO copolymers was investigated by T-peel fracture tests. The fracture of the interface is an irreversible entropy creating process which involved a substantial amount of energy dissipation. The results of such mechanical tests with respect to the bonding temperature (Tb), bonding time (tb) and peel rate indicated this energy dissipation is the result of a complicated interplay between the ability of the interface to transfer stress and its plastic and viscoelastic deformation properties. When Tb is much higher than the characteristic temperature (Tc), the interfaces were completely healed and cohesive failure was observed in T-peel tests. In this case, the fracture strength decreased with increasing branch content. In contrast, when Tb is very close to Tc, the fracture strength showed an increase with the branch content with either interfacial failure or cohesive failure being observed depending on the branch content and Tb. At higher peel rates, it is observed that higher peel energies are required to fracture the surfaces. Transmission electron
microscopy (TEM) showed that the interfacial/interphase structure changed from amorphous to crystalline with an increase in the $T_b$.

The results from the bonding time effect studies showed that the peel energy is proportional to $t_b^{1/2}$ regardless of $T_b$. But the branch content and the $T_b$ play an important role on the seal rate. Thus, higher seal rate was found for higher $T_b$ and higher branch content. These results also suggest that the autohesion of ethylene/1-octene copolymers are strongly associated with the interactions of melted chains. The chain compositions of these Zeigler-Natta EO copolymers are highly heterogeneous with the branches concentrated in the lower molecular weight portion. Long linear chain segments could form large, well-ordered crystals that provide strong anchors for the tie molecules and therefore determine the density of inter-crystalline links. Short chains with lots of branches could behave as protrusions along the chain to obstruct chain disentanglement and limit a chain from sliding through a crystal. Due to these reasons, the short chains with branches would contribute much less than the long linear chains to the full peel strength after complete sealing. However, higher peel strengths could be obtained only at the higher temperatures or longer bonding times at which the long linear chains begin to melt and diffuse across the interface. On the other hand, the higher branch content samples have the lower crystallinity and could obtain the higher chain mobility at the lower bonding temperatures and with shorter bonding times. Therefore, higher seal strength was observed for the higher branch content samples at lower $T_b$.

Following T-peel fracture tests of ethylene/1-octene copolymer assemblies which showed interfacial failures, the fractured surfaces were investigated by using Atomic Force Microscopy (AFM) and characterized by fractal analysis together with the original films. The AFM images showed strong dependence on the peel rate and branch content. Quantitatively, the fractal analyses demonstrated fractal characteristics at the different finite scales. Two regimes showing fractal features were identified for each surface. In regime I (low magnifications) the fracture test did not change the fractal dimensions much. But there were significant changes in regime II before welding and after T-peel fracture tests. The length scale that separated these two regimes is very close to the size of lamellar structures. The characteristic sizes at which the fractal characteristics emerge were shown to appear at larger scales for surfaces fractured at higher peel rates. This suggests that the appearance of fractal behavior at larger scales requires higher fracture energies. The characteristic sizes and fractal dimensions were shown to depend on the molecular structure. Because the fractal analysis suggests at least some crystalline lamellae on the surfaces still existed during T-peel fracture tests, a “Stitch-welding” has been therefore proposed as the autohesion mechanism in which only chains in the amorphous portions could inter-diffuse.

In the second part of this dissertation work, a multi-layer lap-shear geometry has been designed and proven as a reliable testing method in evaluation of the dynamical mechanical properties of polyacrylic pressure sensitive adhesive (PSA) in paper lamination for postage stamp applications. In-situ testing of four different PSA stamp laminates constructed by laminating water-based polyacrylic PSAs to the stamp face papers were carried out using a dynamic mechanical analyzer (DMA) in the temperature range from -50 to 60 °C at frequencies 0.1, 1, 10, and 100 Hz. This geometry requires the tension mode on the DMA, but the results which were recorded as tensile properties were
converted to shearing properties of the PSA layers in the laminate. The effect of the thickness (layers of laminates) on the dynamical mechanical properties has been studied and the results suggested that a multi-layer geometry with 5-10 layers could be an appropriate structure to produce enhanced responses. Therefore, the geometry with 8-layer laminates was used for frequency sweep/isothermal temperature and frequency sweep/temperature step tests. The results showed three relaxation responses that is, glassy, transition, and flow regions with respect to the frequencies and temperatures. These results also implied the viscoelastic characteristics of these PSA products. The tensile properties of the face papers were also tested using the same parameters as those of the multi-layer geometry. Significant differences were found between the shearing behaviors of the multi-layer geometry and the tensile behaviors of the elastic face paper. This suggests that the tensile deformation of the face paper in the multi-layer geometry could be ignored and the elastic paper did not contribute to the shearing properties of the PSA layers. Time-temperature superposition curves have been produced with reference temperature set at 23 °C, which can be used to predict the long term and short term performances of these samples at this temperature.

This method can be utilized as a standard testing method on the PSA adhesives in the laminate form. In addition to the dynamic mechanical properties, it can also be developed to be a general standard method on testing the rheological properties of adhesives, polymer melts and other viscous materials.
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Adhesion Studies of Polymers:

Part (I)

Autohesion of Ethylene/1-Octene Copolymers
Chapter 1

INTRODUCTION

Polymer welding is a common process encountered in polymer processing and is usually generated between two surfaces of polymers. Autohesion is defined as the resistance to the separation of a bonded interface of two identical polymers\(^1\). Studies on the autohesion phenomenon can provide fundamental insights into the chain dynamics and thermodynamics as well as the practical engineering issues such as crack healing, elastomer tack, polymer fusion, self-healing, and polymer welding. This information may help product and process design because the interfacial structures can play a critical role in determining final properties, reliability and the function of polymeric materials. In the framework of the present work, the most important property of a polymer interface was investigated, which is its ability to transfer stress from one side of the bond to the other. This ability is the prerequisite for any measurable macroscopic fracture energy for separating the original substrates. However, the ability to sustain initial stresses, a purely interfacial property tells only the thermodynamic part of the story. In most applicable cases one is also concerned with the amount of the energy which is irreversibly dissipated during the propagation of an interfacial crack. This energy that is referred as fracture toughness, fracture energy, or the work of adhesion, is not only dissipated in the plane of interface, but also in volume elements near the interface which can vary in size for polymers with different structures. As a result, the fracture toughness/energy of a particular interface is not only a unique property of the plane of interface itself, but also depends on the mechanical properties of a bulk material of polymer near the interface.
A full understanding of the autohesion process of the ethylene/1-octene copolymers interfaces involves investigations at three different length scales: 1) a molecular scale which controls the interfacial structure; 2) a mesoscopic or microscopic scale which can provide information to describe how the energy is dissipated during a fracture process; and 3) a macroscopic scale at which the mechanical properties such as fracture energy can be obtained for a particular test geometry. Recently, the availability of surface analysis techniques and of polymers with controlled molecular structure has provided a much better understanding of the molecular structure at the polymer interfaces. This acquired knowledge is a very useful tool for correlating the interfacial structure and its ability to sustain a measurable energy without failing, or during crack growth.

Semicrystalline polymers play a very important role in adhesives applications. However, they are less understood in both their mechanical properties in general, and their interfacial properties in particular, as compared to the glassy materials. This is mainly because these semicrystalline polymers typically have two-phase structures (amorphous and crystalline domains) and their deformation mechanisms are much more complicated than those of glassy polymers and depend strongly on the processing conditions.

Linear and lightly branched polyethylene materials constitute the vast bulk of commodity plastics and form a major class of semicrystalline polymers. The architecture of individual polyethylene chains is usually described in term of linear, branched or cross-linked structures. The chain architecture can have profound effects on properties. For example, linear PE chains like strings can pack closely in the solid state and have a relatively high degree of crystallinity, such as in high density polyethylene (HDPE).
Typical examples of items made of HDPE are gallon milk jugs and large chemical containers, where rigidity and strength are important properties. The chains with multiple branches of varying lengths do not pack as closely together or crystallize as readily, and the result is low density polyethylene (LDPE). LDPE plastic is used to make baby bottles, butter tubs, and other objects that must have flexibility as well as strength. PE chains with small branches typically four to nine carbon atoms in size can not pack closely; the resulting plastic is linear low density polyethylene (LLDPE). This material is excellent for high-strength plastic bags. Linear PE chains that have very high molecular weight ($M$ of about $10^7$) may have difficulty crystallizing due to self-entanglement and high viscosity; the resulting polymer is called ultra high molecular weight polyethylene (UHMWPE). These materials have excellent fatigue and wear resistance and are often used in artificial hip joints.

The subjects of adhesion between polyethylenes can be very rich if one considers the broad variety of possible pairs having different crystalline and amorphous content, molecular weight, and chemical composition, etc. Generally, they fall into two basic categories of interfacial combinations of polyethylenes; symmetric interfaces or asymmetric interfaces. Symmetric interfaces involve the identical polymer on both sides of interface; thus, the chains on the ensemble average are in the same molecular construction. The surfaces wet each other, and then interpenetrate toward the opposite substrate and can even co-crystallize to form a single crystallite. This results in the autohesion process of polyethylene materials. For polyethylenes, if the degree of the interpenetration is sufficient, the interpenetrated interfaces can transfer a significant amount of stress even if there are only van der Waals interactions between the...
interpenetrated chains, However, co-crystallization can also give rise to a very large increase in adhesion energy for a short time of contact, even without any significant interdiffusion of polyethylene chain across the interface. Overall, the mechanical properties (fracture energy) and rheological properties (viscosity) of bulk polymer can play an important role in the autohesion of polyethylenes.

The purpose of the current study is to investigate the correlation that exists between the interfacial structure and its ability to sustain a measurable crack growth energy among polyethylene, especially when the short hexyl branches are introduced into the chain topologies. Branched polyethylenes nearly resemble linear ones in many aspects, for example, they often dissolve in the same solvent with linear ones in thermodynamic equilibrium and not kinetics is considered. However, they can be sometimes distinguished from linear polymer by their lower tendency to crystallize and by their different solution viscosity and light scattering behavior. In term of the practical applications, short branches seem to be important for solid polyethylene properties: as their presence reduces the melting point and extent of crystallinity. Autohesion of ethylene/1-octene copolymers is typical the technique used for sealing packages or forming bags, in which the heat transfer process is involved with the phase change. To achieve a reasonable bond, the surfaces must be pressed together at an adequate temperature and pressure for a sufficient time so that the polymer chains can diffuse across the interface to form seal. Within the context of autohesion of ethylene/1-octene copolymers, the lower degree of crystallization versus other polyethylene due to the increment of branches could introduce three important aspects that need to be taken into account when interpreting the experimental data: Firstly, the formation of interface
occurs either through chain entanglement or through incorporation of both chain in the same crystallite; Secondly, the microstructure near the interface is highly dependent on thermal treatment, which is function of temperature, time and pressure. Finally, these microstructures will strongly influence the interfacial failure and therefore the fracture toughness.

This thesis is organized as following. The first part includes 7 chapters involving the autohesion of ethylene/1-octene copolymers. Chapter 1 gives introduction and states the problem. In Chapter 2, a brief literature review is given on the adhesion, fracture testing and microscopic characterization methods. Chapter 3 describes the experimental approaches. In Chapter 4, the bulk properties of ethylene/1-octene copolymers are included. Chapter 5 reports the mechanical properties of the interfaces with respect to bonding temperature, bonding time and peel rate. In Chapter 6, the interfacial structures are studied qualitatively and quantitatively using TEM and AFM. Chapter 7 concludes this work and provides recommendations for future works in this area.

![Figure 1.1](image.png)

**Figure 1.1** Three different length scales involve in polymer-polymer adhesion. From bottom to top, the smallest scale is the polymer architecture; the median scale is the microscopic scale and the largest scale is macroscopic scale.
Chapter 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

Polyethylenes are one of the major classes of semicrystalline polymers. Formation of adhesion bonds between branched polyethylenes is typically useful for package sealing, among other important applications. Investigation of the mechanical properties of interfaces between branched polyethylenes is complicated and requires knowledge of the interfacial structure at different length scales: (1) a molecular scale for entanglement and co-crystallization effects, (2) a microscopic or mesoscopic scale for understanding the localized deformation mechanism, and (3) a macroscopic scale for correctly interpreting the results obtained from fracture testing, and for understanding crack propagation in mixed mechanism model. Such detailed investigations require the use of several analytical methods. These include the quantitative evaluation of fracture testing, atomic force and electron microscopy, surface analysis, and the use of sealing models. This chapter will provide the theoretical background and a review of experimental works related to these topics.
2.2 Mechanical Properties of Interfaces -- Macroscopic Scale

Autohesion of branched polyethylenes can be achieved by heat-welding two identical thermoplastic materials. To achieve a reasonable bonding, the surfaces must be pressed together at an adequate temperature and pressure for a sufficient time so that the polymer chains can diffuse across the interface and transfer stress to form a seal through entanglement and co-crystallization. The bonding temperature and bonding time are the most important parameters to the formation of interfaces because they can as well as the chain mobility in the amorphous/molten phase. The residual crystallinity also govern the degree of chain mobility for inter-diffusion and co-crystallization. In addition, recrystallization of the melted chains that occurs near the interface during cooling will also contribute to the autohesion strength.

A fracture energy/fracture stress is used to quantitatively evaluate the mechanical properties of polyethylene interfaces after autohesion formation. However, the fracture energy of such polymer interfaces is not only a representation of the intrinsic properties of the polymer interface, for example, thermodynamic work of adhesion, but its value will also depend on the testing geometry and conditions. These are usually chosen to basically probe the energy necessary to develop the crack propagation along the plane of interfaces. Such a fracture energy is the most common way to characterize a bonded interface at macroscopic scale. The following sections will discuss the test geometries and the temperature and time dependences.
Figure 2.1. Illustration of T-Peel test and different failures (Adapted from Figure 1, Meka et al. J. Applied Polym. Sci. 1994, 51, 90.)

2.2.1 Test Geometry

A variety of mechanical tests have been developed to determine the fracture energy of polyethylene to polyethylene interfaces. One of the test geometries often used
is the T-peel geometry as shown in Figure 2.1(A)\textsuperscript{8,9}. In a T-peel test, one or both beams are pulled apart and the force necessary to achieve this movement is directly measured and converted to work. In particular, this is a valid way to probe strong adhesion between relatively soft adhesive materials, such as polyethylenes, which are typically flexible and ductile plastics having a yield stress less than 20 MPa\textsuperscript{10,11}. This is also the main reason that other test geometries, e.g. the double cantilever beams (DCB) are not appropriate to obtain the fracture energy of polyethylene interfaces since they are only suited for the brittle interfaces and relatively high yield stress materials (20 MPa)\textsuperscript{12-15}. On the other hand, the major drawback of a T-peel test is that some energy is dissipating to bend the beams and to extend the beam in tension which subsequently may be incorporated in the fracture energy evaluation. However, a careful analysis of the experimental data determined using this T-peel geometry can generate meaningful values of the work of the adhesion which is directly related to the structure of the interfaces\textsuperscript{16}.

Figure 2.2. Schematic plot of apparent peel strength vs. bonding temperature for semicrystalline polymer (Adapted from Figure 2, Meka et al. J. Applied Polym. Sci. 1994, 51, 91)
Stehling and Meka\textsuperscript{8} reported and interpreted the different failure modes in T-peel fracture tests. As illustrated in Figure 2.1(A), as the two arms of a test piece are pulled at a constant rate, a peeling force versus extension (distance) curve is obtained. The maximum value of this peeling force divided by the width of the specimen obtained in such a test (Figure 2.1 (B)) is commonly defined as the peel strength. At sufficiently high extension, several types of failures of the test piece may occur. The elongation of the test piece at failure (peel elongation) and the area under the curve (peel energy) are commonly taken as indicative of the peel quality of the seal. Figure 2.1 (C-E) schematically illustrates three types of failures that commonly occur. They are, 1) peeling failure along the initial contact surface, 2) tearing failure, and 3) a combination of peeling and tearing failure. When peeling failure mode occurs, suitably conducted peel tests can be used to measure the intrinsic work of adhesion of the polyethylene interfaces. However, under some typical circumstances, the apparent peel strength comes at least partially, from the bulk deformation of the test beams. In particular, when tearing failure mode occurs, the interface formed between the beams is not separated, and the peel strength as defined above, indeed, represents more of the tensile properties of the bulk material than those of interfacial attachment. Therefore, such a value is referred to as the apparent peeling force. Figure 2.2 is a schematic plot of the apparent seal strength versus seal bar temperature for a polyethylene sample just to provide an example. The apparent seal strength is low and peeling failure mode is observed when the seal bar temperature was substantially lower than the melting point of the polymer. At high temperatures, the apparent seal strength reaches a plateau level and tearing failure mode was found. However, in the cited work\textsuperscript{8}, the influences of peel rate on the crack propagation were not
considered. This rate has a strong effect on the peel energy and also the type of the failure modes as pointed out by Mueller et al. in a different study\textsuperscript{17}.

![Figure 2.3](image)

**Figure 2.3.** Effect of peel rate on the measured peel strength of 1000s bonding (Reprinted from Figure 3, Mueller et al. *J. Applied Polym. Sci.* 1998, 70, 2024. Copyright 1998 John Wiley & Sons, Inc.)

Figure 2.3 shows a schematic plot of the peel strength dependence on the bonding temperature and peel rate in autohesion of polyethylenes, which is reprinted from the work by Muller et al.\textsuperscript{17}. At constant peel rate, a rapid increase in the peel strength with increasing bonding temperature was followed by a plateau in most cases. A strong dependence of the measured peel strength on peel rate was also reported and demonstrated in this work. This strong dependence was most pronounced in the temperature range at which the seals began to attain significant peel strength. For example, seals made at 115°C were determined to be very weak if peeled slowly, but very strong if peeled rapidly. Even for the weakest seals, which were those made at 110°C, the measured peel strength increased from 20 to 85 N/m with an increase in the peel rate from 0.5 to 50 mm/min. However, even though the higher value of the fracture
energy may reflect the viscoelastic properties of polyethylene interfaces, it is also possible that some higher observed energy is due to the energy dissipation when the beams are bended and extended. This may also possibly lead to alternative failure modes, which have been discussed in Stehling’s paper. The slower rates of about 2 ~ 5 mm/min have been chosen for most reported works on autohesion of polyethylenes.

### 2.2.2 Bonding Temperature Effects

The interfacial temperature achieved during the bonding process between two polyethylene films has one of the strongest effects on the final peel strength. The crystal domains in polyethylenes are considered as the barrier to chain interdiffusion. It is believed that only the chains in the amorphous region are available for interdiffusion and for formation of adhesives bonds. The PE material can be partially or fully molten depending on the bonding temperature and the time, which will be discussed in next section. The residual crystallinity determines the number of chains available for diffusion and co-crystallization across the interface. In general, the final adhesion strength of polyethylenes is very low which will result in the interfacial failure when the bonding temperature is lower than the melting temperature. This fracture energy could dramatically increase with an increase of bonding temperature, and finally reach a plateau seal strength which will no longer change with further increase of the bonding temperature. The amorphous fraction required to achieve a measurable seal strength appears to be in the range of 75–80%. Beyond this amorphous fraction, the adhesion strength increases approximately linearly with the amorphous fraction. This is verified in the later work of Meka and Stehling where the fraction of the amorphous phase at the bonding temperature was reported to strongly influence the peel strength. The peel
strength versus bonding temperature curves for several polyethylenes covering a wide range of density and the fraction of the amorphous phase at the room temperature is given in Figure 2.4. The bonding initiation temperature (the start point at which a measurable adhesion strength is achieved), the bonding plateau temperature (the start point at which the adhesion strength reaches the full strength) and the full adhesion strengths differ widely for these materials. These results imply that the relationship of the amorphous fraction with the adhesion strength mentioned above applies to various structurally heterogeneous polymers, but this empirical approach does not consider the parameters of the melted chains such as molecular weight, branch content, and/or comonomer content. Nevertheless, an approach that relates the melting distribution of the polymer, as determined by differential scanning calorimetry (DSC) measurements, to the normalized seal strength promisingly appears to follow this empirical description.

The interfacial temperature during the bonding process of branched polyethylenes is not only a function of the dwell time of contact, but also is a function of the heat transfer between the plateau and the polymer film surface. Micro-thermocouples were used to measure the interfacial temperatures during the bonding process by Meka and Stehling. They also developed a finite element analysis (FEA) model to predict the interfacial temperature as a function of time.

Mueller et al. also studied the effect of peel rate on the measured peel strength for the autohesion of LLDPE, which is illustrated in Figure 2.5 for films bonded for 1 and 1000 s at temperatures from 100 to 125 °C. A 1 s bonding time produced a very low strength seal until the bonding temperature reached 115 °C; then, the peel strength increased rapidly between 115 and 125 °C. The same tendency occurred for the films...
bonded for 1000 second. The rapid increase in peel strength occurred between 110 and 115°C with a bonding time of 1000s.

**Figure 2.4.** Peal Strength vs. bonding temperature and amorphous fraction vs. temperature of very low density polyethylene (VLDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) (Adapted from Figure 4 & 5, Stehling et al. *J. Applied Polym. Sci.* 1994, 51, 112)

For ultrahigh molecular weight polyethylene (UHMWPE), the bonding temperature has a strong influence on the occurrence of co-crystallization, which directly affects the final peel energy of the films\textsuperscript{18}. The peel energy of these prewetted films, bonded at different temperature, is depicted in Figure 2.6. From this figure it is clear that, after bonding at 125°C where doubling of the lamellae occurs (the mechanism of cocrystallization, which will be discussed later), the film cannot be separated anymore. At low bonding temperatures, the fraction of melted chains is not enough to generate interdiffusion and, therefore, to double the lamellae across the interfaces. This results in a very low peel energy. When the temperature is above the melting temperature, the
cocrystallization does greatly enhance the peel energy to a cohesive failure level, even though a large amount of chain diffusion was prohibited for these polymers due to the high molecular weight.

![Figure 2.5](image)

**Figure 2.5.** Effect of bonding temperature on peel strength of LLDPE measured at a rate of 5 mm/min. (Reprinted from Figure 9, Mueller *et al.* *J. Applied Polym. Sci.* 1998, 70, 2027. Copyright 1998 John Wiley & Sons, Inc.)

### 2.2.3 Bonding Time Effects

Similarly to the bonding temperature, the bonding time, $t$, is an important parameter for the autohesion of polyethylenes. For the bonding of amorphous polymer interfaces, an interface can be achieved by chain diffusion and the formation of a “bridge”. Therefore, the adhesive fracture energy will be determined by the number of a chain to cross the interface. It has been suggested from a contour length model by Wool that this number is 3 per chain in the melt state\(^{27}\). Several experimental and model works\(^{28-30}\) indicate that the number of bridges established in a glassy polymer should be proportional to $t^{1/2}$. As a result, this also leads to the same rule for the fracture energy (~
Ignoring the chain disentanglements, the situation may be modified for a semicrystalline polymer, in which a molecule can create a bridge by diffusing across the interface in the melt and then crystallizing into crystalline anchors on either side of the interface upon cooling and, thus becoming a tie molecule\(^{32,33}\).

**Figure 2.6.** Peel energy of prewetted films annealed for 15 min at different temperatures (O). The two dots (●) refer to prewetted films of which one side was “preannealed” before wetting and final annealing, so that cocrystallization across the interface is prohibited. (Reprinted from Figure 4, Xue et al. *Macromolecules*, 2000, 33, 7086. Copyright 2000 American Chemical Society.)

Xue et al.\(^{19}\) investigated the development of peel energy \(G_a\) at 135\(^\circ\)C as a function of bonding time for various films of UHMWPEs which was prepared by melt-crystallization, solution casting and prewetting before welding, respectively. These results are depicted in Figure 2.7. The prewetted films could achieve their full peel strength in a very short time (about 1 minute), however, the fracture energy for melt-crystallized and solution-casted films increased slowly with the bonding time. Although the buildup of peel energy and the possible explanation of the adhesion mechanism are distinctly different with respect to bonding time among these three types of film preparation, it is evident that the peel energy increases with the bonding time by a the
half-power law. The rate of autohesion for each type of films was sensitive to the preparation method as described in their work.

Figure 2.7. The adhesive fracture energy $G_a$ as a function of bonding time, for melt-crystallized (●), solution-cast (■), and prewetted films (♦). (Reprinted from Figure 5, Xue et al. Macromolecules, 1998, 31, 3078. Copyright 1998 American Chemical Society.)

Muller et al.\textsuperscript{17} also studied the influences of bonding time on the peel strength for the autohesion of linear low density polyethylene (LLDPE) films. The increase in peel strength as a function of bonding time for various bonding temperatures is shown in Figure 2.8. At 120°C, a bonding time of 100 s was required to create a full strength bond, that is, the peel crack did not follow the seal, rather than the arms necked and tore. At 115°C, this time increased to 5000 s. At 110°C, the peel strength gradually increased with bonding time but did not reach full strength even after 100,000 s (more than 1 day). Again, the peel strength conformed reasonably well to the $t^{1/2}$ dependence in their results. A strong temperature effect on the seal rate was also noted with a transition at about
115°C between lower temperature seals that formed very slowly without achieving full seal strength and higher temperature seals that achieved full strength very rapidly.

Figure 2.8. Peel strength versus $t^{1/2}$ for various bonding temperature (Reprinted from Figure 8, Mueller et al. *J. Applied Polym. Sci.* 1998, 70, 2026. Copyright 1998 John Wiley & Sons, Inc.)

2.3 Interfacial Structures – Microscopic and Mesoscopic Scale

In the case of autohesion of branched polyethylenes, there is a link between the mechanical properties of the assembly and the polymer parameters in the interfacial region and polymer structures, i.e. the interface. This “interphase” volume determines the final adhesion energy at the macroscopic scale. On the other hand, the morphology and topography of the fractured interfaces will reflect the processes in which the macroscopic energy irreversibly was dissipated during the propagation of an interfacial crack. The wide availability of sophisticated surface analysis and microscopic techniques$^{34-36}$ has
aided a much better understanding the fractured interfacial structures, and therefore some clue of the interfacial structures before fracture. This section will give a brief review of the different experimental techniques used for characterization of the surfaces.

2.3.1 Qualitative Analysis --- Imaging

Microscopy has been widely used for various aspects on studies of the fracture of bulk materials as well as adhesives joints. An image of the fractured surfaces or the cross-section of the sealed structures will provide direct information of the history of the fracture and bonding process. Visualization of the formation of polymer interfaces and fractured interfaces can be obtained by applying the microscopy techniques. Use of an electron beam for microscopic observation in transmission electron microscopy (TEM), scanning electron microscopy (SEM), plus atom force microscopy (AFM), and other related techniques helped researchers to overcome the optical diffraction limit and to get images at close to the molecular resolution.

In the bonding of isotactic polypropylene (iPP)/polyethylene (PE) laminates, considering are two representative TEM images obtained from the interfacial regions of Ziegler- Natta-catalyzed PE/iPP and metallocene PE/iPP specimens (Figure 2.9). In these images, the contrast was created via different degrees of absorption of the heavy metal strain in different phases. The crystalline regions almost completely exclude the heavy metal oxide (RuO₄) and appear lighter in these images, while the amorphous phases absorb more RuO₄ and appear darker. White strips (about 10 nm wide) in both the PE and iPP regions correspond to fold-chain crystalline lamellae. Because the PE layer has a lower overall degree of crystallinity, they appear darker than the iPP layer. At first glance, the morphology of the two specimens seems to be identical. However, a
more careful inspection reveals a critical difference in the interfacial structures. The metallocene PE/iPP interface displayed a clean transition from one phase to the other, with lamellae evident right up to the juncture, even protruding across the boundary in some places. In contrast, there is a distinct area of black stained region, about 10 nm wide, separating the Ziegler-Natta catalyzed PE and iPP phases. Considering the expected staining characteristics, these black strips represent the amorphous region, and will result in the weaker adhesion energy for these systems.

Figure 2.9. TEM images of the interfacial region in welded PE/iPP laminates. The metallocene-based polymers (A) exhibit a relatively sharp phase boundary virtually free of noncrystallizable material. In contrast, the interface between the welded Ziegler-Natta–based plastics (B) contains a heavily stained band, about 10 nm wide (arrow), indicating that amorphous material has collected at the phase boundary. (Reprinted from Chaffin et al. Science, 2000, 288, 2187. Copyright 2000 The American Association for Advancement of Science.)

In supporting the autohesion mechanism of the UHMWPE films, Xue et al found from the TEM images\textsuperscript{18} shown in Figure 2.10 that the thickness of the regular stacked lamellae of the solution-casting films was about 107 Å for unannealed samples, while the thickness was exactly doubled when the samples were annealed at 125 °C for 15 min. This is a strong evidence to support a proposed co-crystallization process during the autohesion in Xue’s work; That is, the regular stacked lamellae whose thickness doubled upon annealing below the melting temperature could provide a special way to introduce a
well-defined amount of cocrystallization across the interface. As a result, the annealed films could not be separated any more by T-peel tests. The conclusion is that the films are sealed completely.

**Figure 2.10.** Transmission electron micrographs showing the lamellar doubling in solution-cast UHMWPE films upon annealing: (a) not annealed, (b) after 15 min annealing at 125 °C. (Reprinted from Figure 1, Xue *et al.* *Macromolecules*, 2000, 33, 7085. Copyright 2000 American Chemical Society.)

In a bonding investigation of polypropylene and high density polyethylene (HDPE), the jointed samples were crystallized at 136 °C and the interfacial structures were found sensitive to the various crystallization times. In SEM images of etched sections which were cut perpendicular to the interface, the shape of interface of PP/HDPE was flat if the crystallization time was short; however, an irregular wave shape was obtained with the increase of the crystallization time, some pear-like interface shapes even occurred. The distortion of the interface plane apparently leads to higher surface roughness after fracture; this also results in the higher fracture energies. These results are shown in Figure 2.11.
Figure 2.11. SEM photos of a PP/HDPE interface crystallized isothermally at 136 °C for the different times. A) 0.5 h. B) 1.0 h. C) 1.5 h. The surfaces were etched for 30 min. (Reprinted from Figure 4, Yuan et al. *Polymer Engineering and Science*, 1990, 30, 1458. Copyright 1990 Society of Plastics Engineers.)

The PP surface of a fractured PP/HDPE interface was also examined with SEM44, and the results are shown in Figure 2.12. With increasing crystallization time, the size of spherulites at the interface increased, but their number decreases appreciably. For example, when crystallized at 0.5 hour, the SEM images showed one spherulite and some fine fiber-like structures. There are bigger spherulites growing near the interface when crystallized at 1.0 hour. A well-developed spherulite with “clean” shell debonded surfaces and interstitial areas due to polymer segregation and volume contraction appeared in the SEM images with 1.5 hours of crystallization. The mechanical testing showed that a stronger interface formed with fewer nuclei or spherulites.
Figure 2.12. SEM micrographs are shown of PP surface of a fractured PP/HDPE interface with the different crystallization times at 136 °C. A) 0.5 h. showing one spherulite and fine fibers; B) high magnification of fibers in (A); C) 1.0 h. showing many more spherulites growing near the interface; D) 1.5 h. well developed spherulites with “clean” shell debonded surfaces and interstitial areas due to polymer segregation and volume contraction. (Reprinted from Figure 5, Yuan et al. Polymer Engineering and Science, 1990, 30, 1458. Copyright 1990 Society of Plastics Engineers.)

Muller et al.\textsuperscript{17} have investigated the morphological features of the peeled surfaces with changes in the peel rate, bonding temperature and time for LLDPE films. The surface features observed were found to reflect to these different experimental conditions from the micrographs of SEM. At the lowest peel rate, plenty of small and craze fibrils appeared in the images. The size of fibrils increased and the number of fibrils decreased with the increasing peel rate. At the highest peel rate, a porous texture appeared in the micrographs; this consists of much thicker and longer fibrils with some thick, membrane-like connections between fibrils. The possible explanation for these morphology changes, as the author suggested, is that the lower peel rates led to the higher contributions of
chain disentanglement and creep in craze fibrils. The loss of entanglements was equated with reduced effective surface energy and smaller fibrils resulted. Meanwhile, as the creep component in fibril rupture increases, the stable length of the craze fibril decreases. When examining the effects of bonding time on the morphology of peeled surfaces, these authors found that the shorter bonding time would result in an “isolated fibrils morphology” of the fractured surfaces, which corresponded to the low peel energy. However, longer bonding times resulted in “three dimensional cellular structures” on the peeled surfaces, which indicated a good seal. The changes in the surface morphology and the increase in the peel energy were consistent with an increase in the number of entanglements. The SEM images also showed that the changes in surface morphology with increasing bonding temperature were analogous to those morphologies observed with increasing bonding time. All fractured surfaces from the low bonding temperature studies contained small and isolated fractured fibrils. At high bonding temperatures, the fractured surfaces exhibited some evidence of the membrane-like connections between fibrils indicating the beginning of a three-dimensional cellular structure. The broken fibrils on the fractured surface were noticeably thicker and longer as the seal temperature was increased to 120 and 125 °C. Meanwhile, the fibril density decreased and the membrane-like connections became more dominant. The increasing density of chain entanglements indicated by these changes in the surface morphology led to significantly higher peel strengths. These results are shown in Figure 2.14.
Figure 2.13. SEM micrographs of peel surfaces from a film bonded at 115°C for 1000 s. The peel rate is indicated. (Reprinted from Figure 5, Mueller et al., J. Applied Polym. Sci., 1998, 70, 2025. Copyright 1998 John Wiley & Sons, Inc.)

Although these electron microscopes are essential for visualization of polymer fracture surfaces with highly corrugated features, they have definite limitations. First of all, an electron beam might cause the sample modification and damage. Second, the SEM cannot be efficiently applied for examining the structure of surfaces with nanometer-
scale corrugations. Third, the convolution of structures obtained from TEM might complicate the image analysis. And finally, there is no substantial off-line analysis of images in electron microscope for digitized information to supplement the images\textsuperscript{45}. Another microscopic technique widely used now is the atomic force microscope (AFM). In this technique, the repulsive force between a sharp probe fixed on a sensitive cantilever and the sample was used for imaging. The cantilever’s bending, which is caused by tip-sample forces, is measured with a deflection of a laser beam, which reflects from the backside of the cantilever. In the AFM tapping mode, the probe oscillates vertically; and during imaging, it contacts the sample surface intermittently. The height images of AFM revealed the film topography while the phase images at smaller scale reveal their nanometer scale details such as difference in modulus.

This technique simplifies the sample preparation and can be operated in various environments when examining the fractured surfaces\textsuperscript{46}. Another remarkable feature of this microscope is its ability to examine the surfaces in nanoscopic and mesoscopic scales, and to analyze the surfaces feature quantitatively after imaging processing.

Some work has been done to investigate the surface features of polyethylenes by applying AFM. Images of some high density polyethylene films showed a corrugated surface with biaxial oriented lamellar structures. Images of some linear low density polyethylene film showed a “bumpy” surface, which was formed from the lamellar aggregates embedded in the amorphous overlayer. Individual lamellae with the amorphous surrounding were seen in the phase image\textsuperscript{37}. 

Figure 2.14. SEM micrographs of peel surfaces from films bonded at 115°C. The bonding time and the peel strength are indicated. (Reprinted from Figure 7, Mueller et al. J. Applied Polym. Sci. 1998, 70, 2026. Copyright 1998 John Wiley & Sons, Inc.)

2.3.2 Quantitative Analysis --- Fractals

An introduction to the concepts of fractal geometry was pioneered by Benoit Mandelbrot in his book\textsuperscript{47}. Fractals are disordered systems having some correlations
whose disorder could be described in terms of non-integral dimension. One of the remarkable features about fractal geometry is that it is a powerful tool in which simple rules can be applied to build up realistically complex objects, whereas conventional Euclidean geometry does not actually describe the objects found in the nature just by drawing straight lines and/or circular arcs. Fractal geometry also treats the disorder as an intrinsic property rather than a perturbative phenomenon. Furthermore, fractal dimensions can be related to physical processes or mechanisms that operate to produce the real objects and surfaces. These processes are iterative and may operate at many different dimensional scales. There are generally three types of fractal surfaces. The first one is a dense object with a fractal surface, which displays a self-similar or self-affine characteristic; the second type is a mass fractal such as network or cluster and the third one is a pore fractal in which a distribution of holes or pores existing on the surface of a dense object. In most cases, fractured surfaces or interfaces of polymer materials fall in the first category.

An example illustrating fractal analysis is depicted in Figure 2.15. This is the result of fractal analysis concerning the apparent perimeter of a boundary line in Richardson’s work. The measured perimeter was plotted against the value of the stride length (measuring scale) using logarithmic axes; the results were shown as a straight line between curved ends. The increase in the perimeter length as the measuring scale reduced indicated that the real boundary is composed of irregularities at all scales. As the magnification of examination is increased, more of the roughness is revealed. In this Richardson analysis, the linear portion of the log-log plot implies the roughness of the boundaries is self-similar; it also means that the amount of increase in the observed
boundary length is the same at any scale. Given an image of the boundary of the above object with no scale marking, the visual appearance of the roughness would give no clue to the actual magnification. This kind of self-similarity is the hallmark of a fractal, and has a positive impact on the interpretation of natural sciences. One would not expect to find real objects which exhibit this behavior from the infinitely large to the infinite small, but many real-world objects are observed to be describable as fractals over some ranges of length scales. There are two limits in this plot, the upper limit typically corresponds to the maximum size of the object, while the lower limit may either be set by the available image magnification finer details observed with a microscope of higher resolution or by some changes in the physical process that produces the surface. The slope of this line (Figure 2.15) is negative, since the largest value for the perimeter length was obtained with the shortest stride length. The slope of this line is between zero (the Euclidean limit) and one. The fractal dimension is defined as the sum of the magnitude of the slope and 1.0 for a plane in this Richardson plot, or the magnitude of the slope and 2.0 for a three-dimensional surface. Fractal dimension are expected to different for different objects, because the slope of this line could be different. Thus, the fractal dimension could used to characterize the disorder or roughness of a fractal structure in a quantitative way.

Fujii’s group investigated whether or not the fractured surfaces of epoxy adhesives have fractal characteristic by using the box counting method. Fractals were shown to be a useful tool to quantitatively characterize the fractured surfaces of adhesives. Experimental results confirmed that fractured surfaces under both static and fatigue loadings have fractal characteristics. The fractal dimension could be related to the fracture toughness and the fatigue crack growth rate. The energy release rate could be
correlated to a fractal dimension of the fractured surfaces; that is, a larger energy release rate will produce a rougher surface which has a higher value of fractal dimension. Therefore, the fractal dimension could be used to exhibit the complexity of the fractured surfaces. In their further work, a higher fractal dimension was found for fractured surfaces of epoxy adhesives containing rubber modification, whereas it is not affected by the adhesive thickness and the cross-head crack speed. This is attributed to the fact that the fracture tests were performed at room temperature, much lower than the glass transition temperature of their epoxy adhesives.

In a typical Richardson plot, the ideal fractal relationship is a straight line existing between the measured length or area and the measurement scale over the whole scale range. However, in the real world, it is possible that a fractal object contains a mixing of two or more discrete fractals because many surfaces are not uniform and isotropic. In this case, it is common that the observed data may depart from the ideal fractal relationship. This intertwining of the two or more fractals represents a more complicated

Figure 2.15. Schematic Diagram of a Richardson Plot. (Adapted from Figure 6, Russ, Fractal Surfaces, 1994, pp. 29)
behavior and interpretation. One of the operational definitions of mixed fractal behavior is strikingly illustrated by the work of Brian Kaye\textsuperscript{55-57}. In his research on the formation of particle agglomerates, the Richardson plots were described by two straight line segments instead of just one straight line over the whole measurement scale. Kaye used the terms of “structural” and “textual” for these two different regions, as illustrated in Figure 2.16. In this Figure, a “textural” dimension given by the slope of the line at the smaller measurement scales and described one physical process that controlled the surface roughness. But at larger scales, the “structural” characteristics of the object emerge. If this interpretation is right, the transition between these two behaviors might contain important information about the object. The dimension at which the transition from textural to structural behavior occurred would be significant and possibly is related to some underlying physical processes in the formation of the boundary or surface, or to the size of the subunits making up the structure. It is the latter option that was used by Kaye to explain the two fractal dimensions and the transition for the particle agglomerates.

Mixed fractals could also occur spatially. The fractured surfaces obtained in autohesion of branched polyethylenes do not consist of 100% amorphous structure nor of a single homogeneous crystal. There are either two or more distinct phases with different crystal structure and composition, or many grains with essentially random orientation. It is reasonable to suppose that these differences, which affect mechanical and physical properties, might change the fractal characteristics and consequently the local fractal dimension. This information from fractal analysis in return will help the understanding of the structure-property relationships of these materials.
2.4 Molecular Scale of Interfaces

Wool et al\textsuperscript{58-60} proposed a theory of crack healing in polymers that introduce the five stages of crack healing, namely, (a) surface rearrangement, (b) surface approach, (c) wetting, (d) diffusion, and (e) randomization. A schematic diagram of processes is shown in Figure 2.17 which displays two random coil chains on opposite crack surfaces during the five-stage crack healing phenomena. The surface arrangement stage affects the diffusion initiation time and topological features of the interfaces. The surface approach stage controls the mode of healing, that is, point or line mode. The wetting stage controls the wetting distribution function. The diffusion stage is the most important and controls the development of mechanical properties in a crack healing process. The randomization stage results in complete loss of memory of the previous crack interface. The mechanical properties recovery ratio \( R \) for a crack healing process with time can be determined as a convolution product,
\[ R = R_h(t) \times \phi(t) \]  

(2.1)

where \( R_h(t) \) is an intrinsic healing function, and \( \phi(t) \) is a wetting distribution function for the crack interface or plane in the material.

The reptation model for a chain diffusing in a tube is found to be excellent in providing a molecular basis for the time dependence of the intrinsic healing function, \( R_h(t) \) via \( \chi \propto t^{1/4} \), where \( \chi \) is the diffusion distance at time \( t \). The wetting distribution function \( \phi(t) \) was formulated by a phenomenological approach in parallel with the Avrami analysis of crystallization such that nucleation and propagation of wetted areas in the crack interface was considered. The resulting expression for \( R_h(t) \times \phi(t) \) provided a wide range of possible time dependences for healing based on the choice of \( \phi(t) \) and the diffusion initiation function \( \varphi(t) \) in \( R_h(t) \).

**Table 2.1** Summary of theoretical relationships (Adapted from Table II, Wool and O’Connor, *J.Appl.Phys.*1983, 52, 5963)

<table>
<thead>
<tr>
<th>Relationship</th>
<th>Form</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma, \varepsilon, K_{1C}, \sim t^{1/4} + c )</td>
<td>( t \leq t_\infty )</td>
<td></td>
</tr>
<tr>
<td>( E, G_{1C}, \sim t^{1/2} + c )</td>
<td>( t \leq t_\infty )</td>
<td></td>
</tr>
<tr>
<td>( \sigma, \varepsilon, K_{1C}, \sim M^{1/2} + c )</td>
<td>( t \geq t_\infty )</td>
<td></td>
</tr>
<tr>
<td>( E, G_{1C}, \sim M + c )</td>
<td>( t \geq t_\infty )</td>
<td></td>
</tr>
<tr>
<td>( \sigma, \varepsilon, K_{1C}, \sim M^{-1/4} )</td>
<td>( \text{const. } t \leq t_\infty )</td>
<td></td>
</tr>
<tr>
<td>( E, G_{1C}, \sim M^{-1/2} )</td>
<td>( \text{const. } t \leq t_\infty )</td>
<td></td>
</tr>
<tr>
<td>( t_\infty \sim M^3 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( t_\infty \sim \exp P )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( t_\infty \sim \exp l/T )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In the exploration of the healing between the chain segments of two identical polymer A/A, de Gennes\textsuperscript{67-69} concluded that the chains ends played a crucial role based on experimental observations and discussions by Kausch and coworkers\textsuperscript{70,71}. Thus, any attraction between a chain end and the free surface of one segment of polymer A will react significantly on the A/A mechanical properties after bonding. This type of attraction was related to the surface tension of the polymer, that is, the chain ends were attracted to the surface to reduce the interfacial energy. An attractive space is created normal to the
surfaces due to this type of interaction where the distribution of chain ends on the surface 
(\phi_s) is

\[ \phi_s \propto N^{-1/2} \]  \hspace{1cm} (2.2)

and \( N \) is the degree of polymerization, assumed to be much larger than the critical number for entanglement. Under this case, “hairpin” processes in adhesion were negligible, as shown in Figure 2.18. Then, at long enough times when the diffusion distance is greater than the diameter of the polymer tube in the reptation model, all the interdigitation was due to the motion of chain ends; thus, an end would start from some initial position, and may cross the interface several times. Thus the total number \( \nu \) of monomers D going through the interface is proportional to \( N^{-1/2} \). These concepts can be used to obtain the following relationships regarding the bonding time \( (t) \) and fracture energy \( (G) \).

\[ \phi_s \propto t^{1/4} \quad \text{and} \quad G \propto t^{1/2} \]  \hspace{1cm} (2.3)

Another crack healing mechanism for certain polymers is the cocrystallization process\(^{18,19}\). It is typically useful in describing the very high molecular weight polymers which are too viscous to be processed in the melt and also can crystallize. Solution cast films of ultrahigh-molecular-weight polyethylene for example consist of thin lamellae with a thickness of 107 Å, which are regularly stacked, probably due to the combined action of gravity and shrinking forces upon removal of the solvent. When annealing these films close to, but lower than, the melting temperature, the lamellar thickness changes from 107 to 209 Å, almost doubled. It was also found that the thickening occurred through sliding diffusion of the chain segments in the direction of the chain axis. That is,
not through melting and subsequent recrystallization. The doubling of the lamellae below the melting temperature offered a unique way to introduce a well-defined amount of cocrystallization across the interface. Cocrystallization was reported to enhance the peel energy to such a level that the bonded films could not be separated. This is quite different from the cases discussed before, because this cocrystallization process is independent of formation of entanglements created the large-scale chain diffusion. However, the cocrystallization can result in high level of fracture energy in a relatively short welding time.

\[ t = 0 \]

\[ l(0) \]

\[ l(t) \]

**Figure 2.18.** “Hairpin” processes in adhesion. (Adapted from Figure 39, de Gennes, *Soft Interfaces*, 1997, pp. 86)
Chapter 3

EXPERIMENTAL APPROACHES

3.1 Materials

The four polyethylene samples used in this study include an HDPE (DOWEO-1) and three ethylene/1-octene copolymers (DOWEO-2, DOWEO-3 and DOWEO-4) provided by DOW® Chemical Company. The 1-octene contents are 0.00, 4.30, 7.80, and 13.15 wt%. Gel permeation chromatography (GPC) results show that their molecular weights and molecular weight distributions are quite similar. Other research in Differential scanning calorimetry (DSC) shows that the crystallinity decreases with increasing the branching degree. The available molecular characteristics of these samples are listed in Table 3.1.

<table>
<thead>
<tr>
<th>PE Sample</th>
<th>DOWEO-1</th>
<th>DOWEO-2</th>
<th>DOWEO-3</th>
<th>DOWEO-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-octene wt%</td>
<td>0.00</td>
<td>4.30</td>
<td>7.80</td>
<td>13.15</td>
</tr>
<tr>
<td>1-octene mol%</td>
<td>0.00</td>
<td>1.11</td>
<td>2.07</td>
<td>3.65</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>0.952</td>
<td>0.935</td>
<td>0.927</td>
<td>0.917</td>
</tr>
<tr>
<td>Melt Index (I₂)</td>
<td>3.81</td>
<td>2.55</td>
<td>1.95</td>
<td>2.32</td>
</tr>
<tr>
<td>Mₙ (GPC)</td>
<td>22200</td>
<td>23700</td>
<td>24400</td>
<td>23900</td>
</tr>
<tr>
<td>PDI (Mₙ/Mₘ)</td>
<td>3.65</td>
<td>3.90</td>
<td>3.93</td>
<td>3.99</td>
</tr>
<tr>
<td>Mₙ (GPC)</td>
<td>229600</td>
<td>274200</td>
<td>283700</td>
<td>283500</td>
</tr>
<tr>
<td>Degree of Branching/1000C</td>
<td>0.00</td>
<td>5.38</td>
<td>9.75</td>
<td>16.44</td>
</tr>
<tr>
<td>Crystallinity, %</td>
<td>73</td>
<td>62</td>
<td>58</td>
<td>52</td>
</tr>
</tbody>
</table>
3.2 Methodology

3.2.1 Molding Films

Molding of the HDPE and other three ethylene/1-octene copolymer films was done by “melt-pressing” between two Kapton® (500 µm) films covered by two stainless steel sheets at 193 °C and 182 °C respectively for 8 minutes using a pressure about 3.36 MPa and degassing by 3 time bump cycles. The films were then cooled to room temperature at 10 °C/min.

3.2.2 Bonding Films

The molded films were cut into strips with dimension of 0.5 mm in thickness, 20 mm in width and 120 mm in length. Two of these strips of the same polymer were welded at a number of bonding temperatures (T_b) by applying a pressure at about 1.13 MPa for several bonding times. The bonded strips were then cooled down to room temperature at a controlled cooling rate 10 °C/min. In the study on effects of bonding temperature, the bonding temperatures were chosen at 120 °C, 130 °C, 140 °C, and 150 °C for 1 hour of bonding time. The variation in the bonding temperatures were monitored by an Omega® 20 µm-thick copper-constantan type-T thermocouple probe with precision of ± 0.5 °C. The thermocouple was inserted into the two molded films using an extra pair of strips to avoid interference to the specimens for further testing. This experimental setup for strip bonding is shown in Figure 3.1. In the study of effects of the bonding time, two temperatures were selected for each sample. The bonding times are selected from 1 second to 60 minutes for the higher temperature conditions and 1 to 60 minutes for the lower temperature conditions. The experimental selections for the bonding time effect
tests are shown in Table 3.2. $T_c$ refers to the characteristic temperature, which was determined from DSC measurements with different heating rates. The details on methodology for finding the characteristic temperature will be described in Chapter 4. The $\Delta T$ reveals the difference in the bonding temperature and the characteristic temperature.

![Scheme of bonding process](image)

**Figure 3.1** Scheme of bonding process

### 3.2.3 Differential Scanning Calorimetry (DSC)

The thermal behavior of each molded ethylene/1-octene copolymer films was characterized using a differential scanning calorimeter (TA MDSC 2902). Experiments were performed at different scanning rates ranging from 5 to 20 °C/min. A temperature calibration of the DSC during heating was accomplished by recording the onset of the melting transition of an indium standard sandwiched between two molded branched
polyethylene films. A temperature calibration during cooling was achieved by recording the isotropic-to-nematic transition of p-azoxyanisole (T_{1N} = 136 °C). The results of temperature calibration are shown in Figures 3.2 – 3.5.

**Table 3.2** Experimental set-up for the influences of bonding time tests

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>T_{b,0}°C (Hot Press)</th>
<th>T_{eq,0}°C</th>
<th>ΔT,°C</th>
<th>Bonding Time (t), s</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOWEO-1</td>
<td>140.0</td>
<td>128.4</td>
<td>11.6</td>
<td>1, 10, 30, 60, 300, 600, 900, 1800, 2700, and 3600</td>
</tr>
<tr>
<td></td>
<td>130.0</td>
<td></td>
<td>1.6</td>
<td>60, 420, 600, 900, 1800, 2700, and 3600</td>
</tr>
<tr>
<td>DOWEO-2</td>
<td>137.0</td>
<td>123.4</td>
<td>13.6</td>
<td>1, 10, 30, 60, 300, 600, 900, 1800, 2700, and 3600</td>
</tr>
<tr>
<td></td>
<td>125.0</td>
<td></td>
<td>1.6</td>
<td>60, 420, 600, 900, 1800, 2700, and 3600</td>
</tr>
<tr>
<td>DOWEO-3</td>
<td>135.0</td>
<td>122.0</td>
<td>13.0</td>
<td>1, 10, 30, 60, 300, 600, 900, 1800, 2700, and 3600</td>
</tr>
<tr>
<td></td>
<td>123.5</td>
<td></td>
<td>1.5</td>
<td>60, 420, 600, 900, 1800, 2700, and 3600</td>
</tr>
<tr>
<td>DOWEO-4</td>
<td>130.0</td>
<td>118.1</td>
<td>11.9</td>
<td>1, 10, 30, 60, 300, 600, 900, 1800, 2700, and 3600</td>
</tr>
<tr>
<td></td>
<td>120.0</td>
<td></td>
<td>1.9</td>
<td>60, 420, 600, 900, 1800, 2700, and 3600</td>
</tr>
</tbody>
</table>

The crystalline and the amorphous fractions of these ethylene/1-octene (EO) copolymers at a given temperature were calculated using the method of Mathot and Pijpers. In this method, the heat of fusion ∆h(T) is calculated from the area between the melting peak curve and the baseline, which is extrapolated from the heat flux above the melting temperature. Then the percent crystallinity was obtained with dividing the ∆h(T) by a reference value for the heat fusion ∆h^0(T) of a 100% crystalline polyethylene at the
same temperature. This reference value is calculated from the equation suggested by Mathot and Pijpers:

\[ \Delta h^0(T) = 293 - 0.3092 \times 10^{-5} \cdot (414.6 - T)^2 \cdot (414.6 + 2T) \] [J/g] \hspace{1cm} (3.1)

The crystallinity at \( T, f_{\text{crys}}(T) \) is calculated from the total crystallinity \((\Delta h(T_{mf})/\Delta h^0(T_{mf}))\) of the original sample minus the melted fraction \((\Delta h(T)/\Delta h^0(T))\).

The amorphous fraction \( f_{\text{am}}(T) \) is then obtained from the following equation:

\[
f_{\text{am}}(T) = 1 - f_{\text{crys}}(T) = 1 - \left[ \frac{\Delta h(T_{mf})}{\Delta h^0(T_{mf})} - \frac{\Delta h(T)}{\Delta h^0(T)} \right]
\] \hspace{1cm} (3.2)

where \( \Delta h^0(T) \) is the heat of fusion for a 100% PE crystal at \( T \);

\( \Delta h(T) \) is the heat of fusion for EO sample calculated from DSC thermograph, the area under the melting curve and the baseline at \( T \);

\( \Delta h(T_{mf}) \) is the total heat of fusion for EO sample calculated from DSC thermograph, the total area under the melting curve and above the base line at fully melted temperature \( T_{mf} \), which is different from the peak melting temperature \( T_m \); and

\( \Delta h^0(T_{mf}) \) is the heat of fusion for a 100 % PE crystal at \( T_{mf} \).

The results of calculation will be further discussed in Chapter 4.

### 3.2.4 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical properties of the polymer samples were tested using the single cantilever mode of a Netzsche DMA 242 dynamic mechanical analyzer. Rectangular samples of about 25mm × 8mm × 1mm were cut from compression molded sheets. The samples were analyzed by a dynamic strain amplitude of 1.0 % in the
temperature range of –150 °C to +150 °C with the testing frequencies of 0.1 Hz, 1 Hz, 10 Hz, and 50 Hz. The results of the DMA will be discussed in Chapter 4.

**Figure 3.2** Calibration curves of DSC in heating cycles

**Figure 3.3** Calibration results for determining the melting points in DSC measurements
**Figure 3.4** Calibration curves of DSC in the cooling cycles

**Figure 3.5** Calibration results for determining the crystallization temperature in DSC measurements
3.2.5 Rheology Measurements

A TA Instruments ARES-LS\textsuperscript{®} Strain-Controlled Rheometer was used to determine the melt rheology of the polyethylenes. Polymer pellets were molded into 25-mm diameter disks and placed within the parallel plate fixture of the rheometer. The sample was then tested using a Frequency/Temperature Sweep mode under a fixed strain rate (2 \%) with varying frequency from 0.1 to 500 Hz and with a fixture gap of 1 mm. Four or more isothermal temperatures above the melting temperature were selected. Following data reduction using time-temperature superposition (tTS), average values and statistics for non-linear regression fits of the “Cross-Model” equation parameters (reference temperature, flow activation energy, zero-shear viscosity, Cross Model relaxation time, and Cross Model exponent) were estimated. The activation energy was also calculated from the shifting factor versus temperature plots. These parameters will be used for heat sealing simulation, which will be discussed in Chapter 5. The rheological properties will be presented in Chapter 4.

3.2.6 Tensile Testing

Young’s moduli and yield stresses of these molded samples were determined by uniaxial tension tests according to the ASTM standard method D882-02\textsuperscript{73}. An Instron 5500 tensile testing instrument was used to record the applied force as a function of displacement. Molded polyethylene described above strips of width 20 mm and thicknesses 0.5 mm were elongated at an extension rate at 25.4 mm/min at room temperature. The modulus was then calculated from the initial slope of the stress – strain engineering values curve. The moduli each sample were calculated from the average
values of at least five repeated measurements. The tensile properties will also be presented in Chapter 4.

### 3.2.7 T-peel Fracture Testing

The peel energy ($G_{1c}$) of the symmetrically bonded polyethylene films were determined by the T-peel fracture tests according to ASTM standard method D1876-01\textsuperscript{74}. The T-peel test is the method for determination of the adhesive fracture strength and fracture energy. In steady state, at a constant peel rate, a bonded sample with two laminates of width $b$, and a thickness $h$ are peeled at constant peel force, $F$, as shown in Figure 3.6. At a peeling displacement, $\ell$, the crack has advanced over a distance, $a$. The elongation in the arms is always small; therefore, $\ell = 2a$. In this study, the peel energy, $G_{1c}$, is defined as to describe the energy to separate the bonded sample per unit area

$$G_{1c} = \frac{1}{ab} \int_0^\ell F \text{d}\ell = \frac{2F}{b}$$

(3.3)

And the peel strength, $P$, according to ASTM D1876-01, as defined as

$$P = \frac{F}{b}$$

(3.4)

Note that the units for peel energy and peel strength do not fit the classical definition here. The Instron 5500 tensile testing instrument was used to record the applied force as a function of displacement and time. All the T-peel tests were performed at room temperature. The peel rate was preset at three different values: 2, 20 and 200 mm/min. All $G_{1c}$ values that will be discussed in this work are the average values of at least three repeated measurements. The results of T-peel tests were shown in Chapter 5.
3.2.8 X-ray photoelectron Spectrometer (XPS) Measurements

Oxidation on the surfaces of the molded films during the molding process was analyzed using a Perkin Elmer 5400 X-photoelectron spectrometer with Mg Kα and X-ray source (1253.6 eV), which was operated at 300W and 14 keV with an emission current of 24 mA. Average atomic concentrations were determined from the C1s, O1s, and Si2p photo peaks, which have been collected from three different spots on the surfaces of the film. The binding energies were referenced to the hydrocarbon binding energy at 285.0 eV. An electron take off at an angle of 15° was used in the experiments. The results of XPS measurements will be discussed together with the other surface analysis results in Chapter 6.
3.2.9 Atomic Force Microscopy (AFM) Characterization of Surfaces

The surface morphology and topology study of polymer films before bonding and also after T-peel fracture tests was carried out using a Digital Instrument Dimension 3000 atomic force microscope. The AFM was operated in tapping mode at room temperature using nanosensor TESP (tapping etched silicon probes) type single beam cantilevers. The amplitudes of the drive signal used to the cantilever oscillation were in the range between 2.8 and 4.2 V. The scan rate ranges from 0.8 to 1 Hz. The images were processed only by flattening to remove background shapes. Images were collected in both the height and phase modes.

Fractal analyses of the AFM results were performed using the software Nanoscope IIIa provided by Digital Instrument Co.. Fractal analysis superimposes a three-dimensional array of cubes on the height images so that these cubes completely encompass the image. In this scheme, the size of these cubes was progressively reduced smaller and the total surface area of the image intersected by these cubes was recorded for each cube. The total surface area is then plotted against the cell area in a log-log scale. For a 3-dimension fractal analysis, the fractal dimensions \( D_s \) of these fractured surfaces were obtained from the slope of this curve by \( D_s = 2 - \text{slope} \). The root-mean-square roughness of the surfaces was also calculated from these AFM height images. The AFM images and the results of fractals will be described in Chapter 6 in detail.

3.2.10 Transmission Electron Microscopy (TEM)

The interfacial thickness and the morphology of the symmetric bonded samples before T-peel facture tests were studied using a Philips 420T Transmission Electron
Microscope operated at 100kV. Samples were cryotomed on a Reichert-Jung Ultracut-4E Ultramicrotome with an FC-4D cryoattachment at –100 °C. The cryosectioned face was then stained in the vapors of RuO₄ for about 7 hours or until the color of the staining solution changed from black to red. The staining solution was made by adding 1 mL of 10 (w/v)% sodium hypochlorite solution to 0.02 g of RuCl₃·3H₂O in a 10 mL glass vial. The stained samples were microtomed to get a 70nm thick section from the stained face at ambient temperature. The TEM micrograph results will be presented in Chapter 6 together with the surface analysis results.
Chapter 4

CHARACTERIZATION OF ETHYLENE/1-OCTENE COPOLYMERS

4.1 Introduction

The simplest form of a polyethylene linear chain is that a long backbone of methylene groups and two chain ends terminated by methyl groups\textsuperscript{76}. However, there are many other types of polyethylenes available as commercial resins. The major variation arises from branches that modify the architecture of the polymer chains. The chemical structure of the branches varies from simple alkyl groups to acid and ester functionalities. Long- and short-chain branches can be formed during the polymerization process due to the chain transfer mechanism. The branch length, branch density and branch spacing cannot be controlled in this case. On the other hand, there also may be some defects obtained in the polymer backbone due to side reactions in polymerization such as vinyl groups associated with the chain ends. However, the more controlled branching is the short-chain branching that is formed from copolymerization of ethylene and short chain alpha-olefins, such as 1-butene, 1-hexene and 1-octene. In case of ethylene/1-octene copolymers, the composition may be considered as a linear polyethylene backbone to which hexyl groups are attached at random intervals. The hexyl groups behave as short branches and function to hinder the crystallization and reduce density to some extent in the solid state\textsuperscript{77}. These materials are produced by the coordination polymerization (Ziegler-Natta catalysts or metallocene catalysts) of ethylene with 1-octene.
In practice, ethylene/alpha-olefin copolymers contribute one of the four main classes of polyethylene that of linear low density polyethylene (LLDPE). One key to the variety of linear low density polyethylenes attributed to its “tunable” two-phase morphology, which can be controlled by manipulating both molecular and processing variables. For example, the toughness, clarity and other physical characteristics of LLDPE can be regulated by altering average molecular weight, comonomer type and comonomer content. A major application of the films of LLDPE is in the packaging market, including grocery sacks, fresh produce packages, stretch-wrap, domestic trash can liners and scientific balloons. Four ethylene/1-octene copolymers provided by DOW Company were selected for this thesis work because they were commercialized and represent a wide range of behaviors suitable for scientific investigation of adhesion. The bulk properties of these four ethylene/1-octene copolymers were characterized via thermal, mechanical and rheological experiments, which are important for further autohesion theory development and critical for simulation of the heat sealing process in semicrystalline polymers.

4.2 Results and Data Analyses

4.2.1 DSC Results

The melting points and the crystallization temperatures of these Ziegler-Natta EO copolymers at a heating rate 10 °C/min were determined and are shown in Figures 4.1 and 4.2. There is only a single narrow melting peak detected in the DSC result for DOWEO-1. The peak temperature is found to be 130.9 °C. The peak melting point of DOWEO-2 sample is 123.9 °C and the melting peak is broader than that of DOWEO-1
sample. The melting peak of DOWEO-3 sample is found to be even broader and the peak temperature is at 122.9 °C. The DSC measurement showed that the DOWEO-4 sample has three melting peaks at 123.0, 119.8 and 106.8 °C. In Figure 4.2, the crystallization temperatures obtained by cooling DOWEO-1, DOWEO-2, DOWEO-3, and DOWEO-4 are illustrated to be at 114.3, 110.9, 105.9, and 103.3 °C, respectively. There is only one observed crystallization temperature for the DOWEO-4 sample but this exothermic peak has a broad shoulder on the left. From a comparison of these four samples, increasing branch content has not only lowered the melting/crystallization temperatures but also resulted in lowering the crystallinity as shown in Table 3.1. In addition, multiple melting transitions were observed for the highest 1-octene content polymer indicating that multiple sizes of crystals have been introduced into the polymer morphology as opposed to its having a homogeneous crystal structure.

The relationship of the amorphous phase weight fraction to the temperature of these PE samples is shown in Figure 4.3. The initial amorphous fraction of DOWEO-1 is about 27%, which changes only a little up to 120 °C. Then the majority of the crystals begin to melt and the polymer amorphous reach 100% (melt) at about 139 °C. With increasing branch contents, the initial amorphous phase fraction of DOWEO-2 is at 38%, DOWEO-3 is at 42% and DOWEO-4 is at 49%. For these three samples, the melting of crystals gradually increases with temperature, of course, is 100% complete beyond the T_m. The characteristic temperatures were determined by extrapolating the melting temperature versus heating rate curves to zero heating rate as shown in Figure 4.4. For all the samples, the variation of the melting temperature is almost linear with heating rate; therefore, a linear fit was used for extrapolation. The interceptions of the linear fit with
The characteristic temperatures were found to be 128.4 °C for DOWEO-1, 123.4 °C for DOWEO-2, 122.0 °C for DOWEO-3, and 118.1 °C for DOWEO-4. Since there are three melting peaks detected for DOWEO-4 sample, the middle melting temperature was chosen for this correlation because most of the crystals are melted (92% amorphous fraction) and most importantly, the highest melting peak showed almost no changes with changing the heating rate. The results from this analysis showed that the characteristic temperature decreases with an increase in the branch content.

**Figure 4.1** Heating curve of DSC thermogram
Figure 4.2 Cooling curve of DSC thermogram

Figure 4.3 Fraction of amorphous phase versus temperature
Melting points obtained from DSC

\[ y = 0.068x + 122.01 \quad R^2 = 0.9636 \]

\[ y = 0.1923x + 123.37 \quad R^2 = 0.9823 \]

\[ y = 0.3092x + 128.41 \quad R^2 = 0.9709 \]

\[ y = 0.1979x + 118.1 \quad R^2 = 0.9891 \]

Figure 4.4 Variation of melting temperature versus heating rate

4.2.2 DMA Results

Dynamic mechanical properties measured using the cantilever bending mode of these copolymers are shown in Figure 4.5. The storage moduli are shown at more than 1000 MPa at -150 °C and drop by two orders of magnitude above 100 °C. The relaxation dispersions were observed from the variation in the storage modulus and more easily from response of Tan Delta.

In the literature, three distinct low frequency relaxation processes were reported from dynamic mechanical measurements on polyethylenes, isochronally referred to as \( \gamma \), \( \beta \) and \( \alpha \) relaxations in the temperature interval between liquid nitrogen temperatures and the melting point. In Figure 4.5, the \( \gamma \) relaxation is shown to be around -110 °C and the \( \beta \) relaxation is about 0 °C. A great number of investigations have been undertaken to characterize these relaxation processes and to elucidate and describe the
molecular motions underlying them. It has been well established that the β relaxation in such polymers is dominated by an amorphous relaxation and is associated with the glass-rubbery relaxation and does not occur in a completely crystalline polymer. DOWEO-3 and DOWEO-4 samples of present work the exhibited a well-resolved β relaxation; whereas, the less branched of the four samples (DOWEO-1 and DOWEO-2) showed no obvious β peak. Moreover, the β relaxation peak for the DOWEO-4 is better defined than that of DOWEO-3 which has about 5% less hexyl branching groups. In this present study, the linear polyethylene and DOWEO-2 samples which have very few hexyl branches did not exhibit β relaxation response.

![Figure 4.5 DMA results of DOW samples at frequency 1 Hz](image)

**Figure 4.5** DMA results of DOW samples at frequency 1 Hz
4.2.3 Rheology Results

Time-temperature superposition of the rheological behavior was accomplished by using the Cross Model and a reference temperature was chosen at 190 °C. This model may be described as:

\[
\eta = \frac{\eta_0}{1 + (\lambda \gamma)^{1-n}} 
\]

(4.1)

where \( \eta_0 \) is the zero shear viscosity and \( \lambda \) and \( n \) are the fitted parameters. This model is used to predict Newtonian behavior at relatively low shear rates, shear-thinning behavior of a power law form at higher shear rates, and also for intermediate behavior characterized between these rates limits\(^{84,85} \). The parameters of the Cross Model and an activation energy \( E_a \) calculated from the shifting factor versus temperature are summarized in Table 4.1. The results of the rheology tests and the tTs master curves are shown in Figure 4.6-4.16. The zero-shear viscosity (\( \eta_0 \)), relaxation time (\( \lambda \)) and power law index (\( n \)) did not show any apparent dependence on the branching content of these polymers. However, this result may be affected by the differences in the molecular weight and molecular weight distribution among this series even though these differences are not large.

Table 4.1 Parameters of the Cross Model in rheology test, \( T_{ref} = 190 \degree C \)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DOWEO-1</th>
<th>DOWEO-2</th>
<th>DOWEO-3</th>
<th>DOWEO-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_0 ) (Pa)</td>
<td>5.93×10⁴</td>
<td>3.89×10⁴</td>
<td>7.23×10⁴</td>
<td>4.61×10⁴</td>
</tr>
<tr>
<td>( \lambda ) (s)</td>
<td>0.18</td>
<td>0.03</td>
<td>0.11</td>
<td>0.04</td>
</tr>
<tr>
<td>( n )</td>
<td>0.48</td>
<td>0.35</td>
<td>0.42</td>
<td>0.35</td>
</tr>
<tr>
<td>( E_a ) (kJ/mol)</td>
<td>31.23</td>
<td>29.78</td>
<td>32.17</td>
<td>31.32</td>
</tr>
</tbody>
</table>
Figure 4.6 Frequency sweeps at temperatures (160, 170, 190, 210 and 230°C) for DOWEO-1 samples to yield storage modulus ($G'$), loss modulus ($G''$) and complex viscosity ($\eta^*$).

Figure 4.7 tTs master curve of storage modulus ($G'$), loss modulus ($G''$) and complex viscosity ($\eta^*$) for DOWEO-1 samples ($T_{ref} = 190^\circ C$)
Figure 4.8 $tT$s shift factors of DOWEO-1 samples in rheology tests

Figure 4.9 Frequency sweeps at temperatures (170, 190, 210 and 230°C) for DOWEO-2 samples to yield storage modulus ($G'$), loss modulus ($G''$) and complex viscosity ($\eta^*$)
Figure 4.10 tTs master curve of storage modulus ($G'$), loss modulus ($G''$) and complex viscosity ($\eta^*$) for DOWEO-2 samples ($T_{ref} = 190^\circ C$)

Figure 4.11 tTs shift factors of DOWEO-2 samples in rheology tests
Figure 4.12 Frequency sweeps at temperatures (150, 170, 190 and 210°C) for DOWEO-3 samples to yield storage modulus ($G'$), loss modulus ($G''$) and complex viscosity ($\eta^*$).

Figure 4.13 tTs master curve of storage modulus ($G'$), loss modulus ($G''$) and complex viscosity ($\eta^*$) for DOWEO-3 samples ($T_{\text{ref}} = 190\degree\text{C}$).
Figure 4.14 tTs shift factors of DOWEO-3 samples in rheology tests

DOWEO-4

Figure 4.15 Frequency sweeps at temperatures (150, 170, 190 and 210°C) for DOWEO-4 samples to yield storage modulus ($G'$), loss modulus ($G''$) and complex viscosity ($\eta^*$)
Figure 4.16 tT's master curve of storage modulus \((G')\), loss modulus \((G'')\) and complex viscosity \((\eta^*)\) for DOWEO-4 samples \((T_{ref} = 190^\circ C)\)

Figure 4.17 tT's shift factors of DOWEO-4 samples in rheology tests
4.2.4 Tensile Properties

The tensile properties of the investigated ethylene/1-octene copolymers are shown in Figure 4.18. The average Young’s modulus is 0.57 GPa for DOWEO-1, 0.33 GPa for DOWEO-2, 0.26 GPa for DOWEO-3, and 0.23 GPa for DOWEO-4. The moduli of these copolymers distinctly drop with increasing branch content. It indicates that adding more hexyl branches into the chain topology led to more flexible materials.

The bulk DOWEO-1 samples appeared to fracture in a plastic and ductile manner. In this stress-strain response, the polymers showed an elastic deformation first, then a yield point induced by the stress, the material was observed to be necking at this moment, then followed by the plastic deformation. Referring to Figure 4.18, the yield stress of the DOWEO-1 samples is about 21 MPa, which is the maximum stress. Meanwhile, the bulk DOWEO-2 and DOWEO-3 samples which have higher 1-octene content than DOWEO-4 samples displayed a similar deformation behavior, but with much lower yield stresses and broader yield peaks. In contrast, a distinct yield point was not observed for DOWEO-4 samples. There is no apparent maximum stress in this latter curve, and the response merely changed from a higher plastic plateau to a lower stage. The phenomenon of yield in a tensile test involves considerable disruption of the crystal structure for these semi-crystalline polymers. There are at least two possible types of deformation for a crystal: 1) sliding between the crystalline lamellae and 2) fracture within the individual lamellar by a process comparable to a glide in monatomic crystals\textsuperscript{86}. The second type of deformation is dominant which could lead to molecular orientation along the tension direction and resist further extension. Then the lamellae and spherulites increasingly lose their identity.
and a new fibrillar structure is formed during the plastic deformation. The existence of large crystalline regions could stiffen these materials and raise the yield stress.

It is noticeable that the shape of yield peak observed in these plots became broader and the yield strength was lower with increasing branch content. The hexyl groups attached to the linear backbone will hinder the crystallization and reduce the density to some extent in the solid state. It is also possible for this branching to produce more defects inside the crystal structure. As discussed above, in the DSC measurements, the results demonstrate that the higher branch content not only lowers the crystallinity, but also result in the broader distribution of crystal sizes. Thus, the results from DSC measurements may be correlated to the results of the tensile tests.

![DOW Tensile](image)

**Figure 4.18** Stress-strain curves of DOWEO samples in tensile tests
5.1 Introduction

Strength development at polymer-polymer interfaces is a macroscopic characteristic associated with random coil chain mobility during the bonding process. This is because the interfacial structure is determined by the molecular dynamics of the polymer chains as well as thermodynamics. When two pieces of molten polymer films are brought into contact, surface arrangements first occur which is followed by wetting and interdiffusion of chain segments across the boundary. The mechanical energy ($G$) that is required to separate these contacting two pieces of polymer films is known to be a function of the bonding time, $t_b$, interfacial temperature, $T$, contact pressure, $P$, and molecular weight, $M$ of the polymers. In general, the chain mobility of a polymer could be enhanced by either heat or solvents, two of the common processes used to introduce bonding strength. In case of semicrystalline polymers, crystallinity will also play a very important role in the bonding development. This chapter focuses on the interfacial mechanical properties exhibited due to autohesion of the four ethylene/1-octene copolymers discussed above. Two identical polymer strips are brought together with pressure, temperature and time being regulated in a hydraulic hot press. A T-peel geometry was applied to generate fracture energies of these symmetric interfaces after welding. The peel strength and peel energy were investigated among these four
copolymers as a function of bonding temperature and bonding time. The influences of peel rate on the peel energy were also studied. The correlation of the mechanical properties of symmetric interfaces and branch content with the autohesion will also be discussed.

5.2 Results and Data Analyses

The ethylene/1-octene (EO) copolymers used in this study are discussed in previous chapters and have different 1-octene content. The characteristic temperatures \( T_c \) of these EO copolymers were determined from the extrapolation of the plots of the melting point as a function of heating rate, as shown in Figure 4.4 in Chapter 4. These characteristic temperatures are to be used as reference temperatures in the autohesion study, and are 128.4, 123.4, 122.0, and 118.1 °C for DOWEO-1, DOWEO-2, DOWEO-3, and DOWEO-4 respectively. The characteristic temperatures were used to determine the bonding temperatures which were chosen at 120, 130, 140, and 150 °C for the investigation of the bonding temperature effects. Each EO copolymer sample actually was partially or completely melted at these bonding temperatures. In the study of the bonding time effects, two bonding temperatures (i.e. one is very close to \( T_c \) and the other is much higher than \( T_c \)) were chosen for each sample and at various bonding times.

When a fracture test is carried out on a bonded sample using the T-peel geometry, a pre-crack was usually initiated and this crack would propagate along the contact line of the two films at a relatively constant load under a certain peel rate. If the bonded sample formed a “weak” adhesion, the T-peel fracture test would lead to interfacial failure. A typical plot of T-peel energy versus displacement which resulted in interfacial failure is
shown in Figure 5.1. The peel energy is calculated from the plateau peel strength value at which a crack is initiated and propagating under steady state conditions. On the other hand, if the bonded sample formed a strong seal, the peel arms might start to neck and tear resulting in cohesive failure.

5.2.1 Effects of Bonding Temperature on Peel Strength

The effects of bonding temperature on the apparent peel strength are shown in Figure 5.2. At 120 °C, adhesion of the DOWEO-1 films for up to 1 hour of contact time could not be obtained so that the T-peel fracture test was not performed. In contrast, all the DOWEO-4 films were bonded so efficiently that cohesive failures were observed during T-peel tests and the apparent peel strength are about 4.86 ± 0.09 N/mm at a low peel rate of 2 mm/min. Interfacial failures were observed for the welded films of DOWEO-2 and DOWEO-3 samples at 120 °C. At the lowest peel rate tested, 2mm/min, the apparent peel strength are about 0.11 ± 0.02 and 0.25 ± 0.02 N/mm for DOWEO-2 and DOWEO-3 samples, respectively. As the bonding temperature increased to 130 °C, interfacial failure was observed for DOWEO-1 sample and cohesive failure for all the other three samples. Their apparent peel strengths are 1, 2, 3, and 4 N/mm for DOWEO-1, DOWEO-2, DOWEO-3, and DOWEO-4 samples. When the bonding temperature increased to 140 and 150 °C, all the welded films showed cohesive failures.

The effect of branch content on the peel strength is shown in Figure 5.3 at different bonding temperatures. This Figure was created using data from Figure 5.2. A 3-D diagram showing the combined effects of the branch content and bonding temperature on the peel strength is shown in Figure 5.4. At low bonding temperatures, the peel strength increase with branch content; while the peel strength decrease with branch
content at higher bonding temperatures; which, however, results from cohesive failures. These results show that at 1 hour of bonding time, the peel strength obtained for samples bonded below the $T_c$ show weak bonding, while the samples bonded above the $T_c$ show strong bonding.

![T-Peel](image)

**Figure 5.1** Variation of the peel strength versus displacement during a T-peel fracture test of DOWEO-2 films bonded at 120 °C for 1 hour, in which interfacial failures were observed. The peel rate is 20 mm/min. At least three specimens were used to repeat for each sample and the average is used for later comparison.
Figure 5.2 The effects of bonding temperature on peel strength for bonded samples at 1 hour. The peel rate is 2 mm/min.
Figure 5.3 The effects of branch content on peel strength for bonded samples at 1 hour. The peel rate is 2 mm/min.
3.647
2.071
1.111
0
2
4
6
8
10
Plateau Peel Strength, N/mm
Figure 5.4 3D diagram of peel strength versus bonding temperature and branch content

5.2.2 Effects of Peel Rate on Peel Energy

The peel energies, $G_{IC}$, are shown as a function of the peel rate for DOWEO-2 and DOWEO-3 samples that have been bonded at 120 °C for 60 minutes in Figure 5.5. For both samples, $G_{IC}$ increases with increasing peel rate. The fracture energy increased from 0.21 mJ/mm² at 2 mm/min to 0.35 mJ/mm² at 20 mm/min, and to 0.47 mJ/mm² at 200 mm/min for DOWEO-2. Fracture energy went up from 0.51 mJ/mm² at 2 mm/min,
to 0.66 mJ/mm² at 20 mm/min, and to 0.90 mJ/mm² at 200 mm/min for DOWEO-3. The value of the peel energy of DOWEO-3 is found to be roughly two times of that of DOWEO-2 at all three peel rates. It is very interesting that the 1-octene content of the former is also about two times of the 1-octene content of the later. The larger peel energy of DOWEO-3 compared to that of DOWEO-2 could be indirectly due to the higher 1-octene content in DOWEO-3. But it might also be related to the fact that the characteristic temperature of DOWEO-3 is 122 °C compare to 123 °C for DOWEO-2 which is also a result of different branch content.

Interfacial failures were observed for the bonded DOWEO-1 films at 130 °C for one hour. Figure 5.6 shows the peel energy, $G_{IC}$, as a function of displacement at three peel rates, 2, 20 and 200 mm/min. In the bonding experiments at 130 °C, adhesion of the DOWEO-1 films for 1 hour did not achieved a good seal, and resulted in a low apparent peel strength about 0.19 ± 0.04 N/mm at a low peel rate (2 mm/min) in the T-peel tests. The fracture energy calculated from the peel strength increased from 0.35 mJ/mm² at 2 mm/min, to 0.55 mJ/mm² at 20 mm/min, and to 0.80 mJ/mm² at 200 mm/min.

The peel rate dependence of the peel energy has been discussed in literature. In addition to the energy taken to separate the interface, part of the fracture energy may be attributed to the other deformation modes such as extension and bending of the peel arms, which are sensitive to the change of peel rate. The fractured surface morphology generated from these peel experiments will be discussed in Chapter 6 and will provide some information at a microscopic scale in assigning the dissipated energy during T-peel fracture tests.
Figure 5.5 The effects of peel rate on peel energy for DOWEO-2 and DOWEO-3 samples that have been bonded at 120 °C for 1 hour.
Figure 5.6 The effects of peel rate on peel energy for DOWEO-1 that have been bonded at 130 °C for 1 hour.

5.2.3 Effects of Bonding Time

The effect of the bonding contact time on the peel energy was examined for each copolymer samples at two bonding temperatures, T_c + ~1.7 °C and T_c + ~12.5 °C. The bonding conditions have been shown tabulated in Table 3.2. These DOWEO films were welded at bonding times from 1 to 3600 seconds, longer than the bonding time used in the industry. It will be seen that this approach will help an understanding of the fundamental aspects of autohesion under isothermal conditions. Much longer times are found to be required in order to achieve equilibrium even though very short bonding times are more practically necessary.
The effects of the bonding time on the peel energy for DOWEO-1 sample are shown in Figures 5.7 where the peel energy has been plotted against the square root of the bonding time. The bonding temperatures for DOWEO-1 were chosen at 130.0 °C ($T_c + 1.6$ °C) and 140.0 °C ($T_c + 11.6$ °C). At 140 °C, the development of adhesion is very fast; consequently it takes only about 180 s to reach the full peel energy of about 14 mJ/mm$^2$. However, the growth of adhesion fracture energy is actually slowly developing at 130 °C. It is observed that the peel energy reaches 0.35 mJ/mm$^2$ after 1 hour bonding at 130 °C. The peel energy never reaches the full peel strength within the selected bonding times at this lower temperature even the bonding temperature is above the characteristic temperature.

In the bonding time research on DOWEO-2 samples, the two bonding temperatures were selected at 125.0 ($T_c + 1.6$) °C and 137.0 ($T_c + 13.6$) °C. The development of adhesion fracture energy at the higher temperature was also very fast, as shown in Figure 5.8. It took about only 30 seconds to obtain the full peel energy of 11 mJ/mm$^2$. Similar to what was found for DOWEO-1, the growth of adhesion fracture energy is slower at the lower temperature. The peel energy after 1 hour of bonding is only about 0.42 mJ/mm$^2$, which are two orders of magnitude lower than the full peel energy. Figure 5.9 shows the bonding time effect on the peel energy for DOWEO-3 sample at bonding temperatures 123.5 ($T_c + 1.5$) °C and 135 ($T_c + 13.0$) °C. It is very similar to that of DOWEO-2 sample except that the peel energy after 1 hour of bonding at the lower temperature is 0.81 mJ/mm$^2$.

Figure 5.10 illustrates the results of the bonding time variation for the DOWEO-4 sample. The lower bonding temperature is chosen as at 120 °C which is about 1.9 °C
higher than the $T_c$, while the higher bonding temperature was about 11.9 °C higher than $T_c$. Again the development of adhesion fracture energy at the higher temperature was very fast and took less 30 s to form a complete bonding. Different from the other three samples in this case, the bonding at lower temperature shows fairly fast bonding strength development. In fact, the bonded samples after 1 hour at the lower temperature displayed a peel energy value that is very close to the full peel energy.

A strong bonding temperature dependence of the sealing rate can be concluded from the above cited experiments. There is a big transition on the sealing rate between the bonding at the high temperature and at the low temperature. The only exception is for the bonding of DOWEO-4 sample at long bonding times which showed that a strong seal could be obtained given enough time. As discussed in Chapter 4 and shown in Figure 4.3, the amorphous fractions of polymer at the lower bonding temperatures are about 85%, 95%, 98%, and 93% for DOWEO-1, DOWEO-2, DOWEO-3, and DOWEO-4 samples. The small fraction of residue crystals in the materials and the lower chain mobility at lower temperature accounts for the big difference between the bonding at two temperatures. These results suggest that the development of autohesion not only depends on the the external conditions such as time and temperature, but also depends on the topological type of melted chains. Introducing more short-chain branches into the backbone will lead to a lower degree of crystallinity and more defects in the crystalline phases; the mobility of chains will be higher and also their ability to diffuse across the interface to form a good seal.

As discussed in Chapter 2, the bonding time dependence of the peel energy has been accurately described using the one-half power law. This assumes that a bridge
formed at the interface is capable of transferring stress leading to a requirement that a
chain segment needs to cross the interface several times to be adhesively effective. This
situation may be modified for a semicrystalline polymer, in which a chain can create a
bridge by diffusing across the interface in the melt and crystallizing into crystalline
anchors on either side of the interface on cooling, thus becoming a tie molecule. Figures
5.7-5.10 showed the peel energy versus $t^{1/2}$ with a linear regression for bonding at both
temperatures. But at the higher bonding temperature, the one-half power law was only
valid for the shorter times before a complete seal was obtained. Figure 5.11 shows the
normalized peel strength versus the square root of bonding time at the lower bonding
temperature. The peel strength was normalized against the full peel strength of each
sample. The bonding at higher temperature is shown in Figure 5.12 for only the linear
part (up to 180 seconds). The development of peel strength is found to be faster for
higher contents of short-chain branches at either the high temperature or the low
temperature bonding.

In summary, the effects of bonding temperature and bonding time on the peel
strength/energy suggest that the autohesion of ethylene/1-octene copolymers are strongly
associated with the topological and morphological variation of the melted chains. The
chain composition of these DOWEO copolymers reported in this thesis is highly
heterogeneous with the branches concentrated in the lower molecular weight portion$^{17,75}$. These short branches usually lead to the observed broader melting peaks and lower
melting points. Also, long linear chain segments could form large, well-ordered crystals
that provide strong anchors for tie molecules in autohesion and hence determine the
density of intercrystalline links. Short-chain branches on lower molecular weight species
could act as protrusions along the contour length to hamper chain disentanglement and restrict a chain in unfolding from a crystal. Due to these reasons, these short chains with branches would contribute much less than the long linear chains to the final peel strength. Therefore, the higher branch content sample might generate a lower maximum peel strength. However, for these samples with fewer branches, stronger peel strength could be obtained only at higher temperatures at which the long linear chains begin to melt and diffuse across the interface. On the other hand, if the higher branch content samples have lower crystallinity and can obtain higher chain mobility at lower bonding temperatures and with same bonding time, then peel energy should increase. It has been observed that ethylene/1-octene copolymers with the higher branch content resulted in better bonding performance at lower bonding temperatures. It is thus easier to regulate the bonding strength in order to obtain a “medium strength”, which may find many applications.

Overall, the fracture of the interface formed between two semicrystalline polymer films is an irreversible process and involves substantial energy dissipation. The results from T-peel mechanical tests provided a value for this energy; and, the correlation between this value and the bonding temperature, bonding time and peel rate indicated that this energy dissipation is the result of a complicated process involving interplay between the ability of the interface to transfer stress and its plastic and viscoelastic deformation properties. However, further information on the morphology of the fractured surfaces is needed to better interpret such energy dissipation processes. Therefore, to create a link between the fracture process and the bonding process, the morphology of the fractured surfaces will be discussed in next chapter.
Figure 5.7 The change of peel energy with bonding time for DOWEO-1 samples
Figure 5.8 The change of peel energy with bonding time for DOWEO-2 samples
Figure 5.9 The change of peel energy with bonding time for DOWEO-3 samples
Figure 5.10 The change of peel energy with bonding time for DOWEO-4 samples.

The equation for bonding at 120.0°C is: \[ y = 3.4384x - 2.3539 \]

The equation for bonding at 130.0°C is: \[ y = 0.1841x - 1.9783 \]
Figure 5.11 The effects of branch content on normalized peel strength ($\Delta T \sim 1.7 \, ^\circ\text{C}$)
Figure 5.12 The effects of branch content on normalized peel strength ($\Delta T \sim 12.5 \, ^\circ C$)
Chapter 6

AUTOHESION OF ETHYLENE/1-OCTENE COPOLYMERS
--- INTERFACIAL INTERPRETATION

6.1 Introduction

Research involving the mechanical properties of polymer-polymer interfaces often incorporates the fractured surfaces to characterize the adhesion mechanism. It is believed that such fractured surfaces have intrinsic properties in response to the deformation process of these interfaces leading to failure. Atomic force microscopy (AFM) is a powerful tool to distinguish these fractured surface features in the mesoscopic and microscopic scales by mapping the topography of these surfaces. It is also very useful to extract quantitative information from the AFM images in three dimensions in order to correlate with the macroscopic scale parameters, such as fracture toughness. Root-mean-square roughness ($R_q$) is the most reported parameter obtained to compile the various moments of the height distribution of an AFM image. However, it is insufficient to provide the information on the surface orientation or dimensionality\textsuperscript{94}. Power spectral density (PSD) is a better method to characterize the surface roughness, it transforms the AFM spatial elements into an array of time-dependent constructs (sine waves) using fast Fourier transformation. It is used to determine the most probable underlying wavelength, which may reflect the dominant physical features on the surface’s topography\textsuperscript{95}. However, a PSD limitation is that the PSD only reveals the periodic surface features since this approach characterizes by a series of fixed wavelengths or frequencies. Therefore, PSD is
much more useful in analyzing a uniform, flat or regular patterned surface rather than complex geometry such as fractured surfaces.

Many real fractured surfaces cannot be simply described with conventional Euclidean geometry such as straight lines and circular arcs. Since the pioneering work of Richardson\textsuperscript{50}, the concept of fractal analysis became available and has been introduced in a previous chapter to give a clear and graphic meaning to non-integer dimensions. One of the particular advantages of fractal analysis is that this approach makes it possible to build up the roughness of a fractured surface using compact and simple mathematical relationships\textsuperscript{48}. These simple relationships may be furthermore related to physical processes that created the real surfaces. This is, because fractals treat the disorder of a surface as an intrinsic property rather than a perturbative phenomenon and this analytical scheme is very valuable. Fractal dimension, $D$, calculated from fractal geometry, can represent the height irregularity of the examined surfaces quantitatively. Therefore, the quantitative comparisons between complex surfaces become much easier and more precise. The fractal dimension can be directly related to the roughness of a surface. Some previous investigations have shown that a higher fractal dimensions correlates to a rougher surface\textsuperscript{54}.

In this chapter, fractal analysis of the surface topography of ethylene/1-octene copolymers both before bonding and after T-peel fracture testing is discussed. The fractal analysis uses a continuum model to compute the dimensionality of these surfaces. Ideally, a fractal surface was mathematically defined as having a statistical self-similarity at any dimension scale. However, many real fractured surfaces were only observed to have fractal features over a limited range of scale. The cell sizes in the cube-counting method
described previously at which the fractal characteristics emerge, or fractal dimension changes, are defined as the characteristic sizes. The characteristic sizes may also describe the fractals quantitatively because it accounts for the scale at which the self-similarity appears, or the dominant pattern changes. In the present study, the fractal dimensions and the characteristic sizes were associated with of values assigned to the fractured surfaces of ethylene/1-octene copolymers whose interfacial histories and properties are different. This section will only focus on the fractal analysis of these surfaces; note the mechanical properties from the T-peel fracture tests have been already presented in Chapter 5.

Found in this chapter, in addition, the interfacial structures after bonding were investigated by using Transmission Electronic Microscope (TEM). TEM has been successfully applied to describe the bonding structures of semicrystalline polymers. However, it is difficult at present to examine the interfacial structure resulting from autohesion when two films have achieved a complete heal or a strong bonding is obtained. This limit may be due to the crystals on two sides of the interface usually being identical to one other; limiting contrast, with careful sample preparation and imaging techniques, the thickness of interfaces might be observed when an amorphous interface has been formed when the adhesion strength is relatively weak.

6.2 Results and Data Analyses

6.2.1 X-ray photoelectron Spectroscopy (XPS)

The chemical compositions of the upper surface of the molded films have been obtained from X-ray photoelectron Spectroscopy (XPS) and are shown in Table 6.1, 6.2, 6.3, and 6.4 for DOWEO-1, DOWEO-2, DOWEO-3, and DOWEO-4, respectively.
Oxygen and silicon were identified in addition to carbon atoms. Oxygen is generated by oxidation on the surface while the PEs are molded at elevated temperatures. But the silicon contamination may arise from the releasing agent found on the surface of the Kapton release film, or from the XPS equipment. The results demonstrate that oxidation and contamination during the current molding procedure are present to a very low extent. Therefore, the surfaces of all the present molded films were considered as clean and appropriate for further mechanical testing and microscopic studies as well as the autohesion experiments.

<table>
<thead>
<tr>
<th>Element Name</th>
<th>Concentration (1st spot),%</th>
<th>Concentration (2nd spot),%</th>
<th>Concentration (3rd spot),%</th>
<th>Average Concentration,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1s</td>
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<td>98.75</td>
<td>98.64</td>
<td>98.61±0.15</td>
</tr>
<tr>
<td>O-1s</td>
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<td>1.37±0.13</td>
</tr>
<tr>
<td>Si-2p</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01±0.02</td>
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<table>
<thead>
<tr>
<th>Element Name</th>
<th>Concentration (1st spot),%</th>
<th>Concentration (2nd spot),%</th>
<th>Concentration (3rd spot),%</th>
<th>Average Concentration,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1s</td>
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<td>96.56</td>
<td>96.23±0.55</td>
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<td>O-1s</td>
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<td>3.14</td>
<td>3.46±0.61</td>
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<tr>
<td>Si-2p</td>
<td>0.25</td>
<td>0.39</td>
<td>0.29</td>
<td>0.31±0.07</td>
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<table>
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<th>Element Name</th>
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<th>Concentration (2nd spot),%</th>
<th>Concentration (3rd spot),%</th>
<th>Average Concentration,%</th>
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<td>99.83</td>
<td>99.94±0.10</td>
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<td>0.17</td>
<td>0.06±0.10</td>
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<tr>
<td>Si-2p</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00±0.00</td>
</tr>
<tr>
<td>Element Name</td>
<td>Concentration (1st spot),%</td>
<td>Concentration (2nd spot),%</td>
<td>Concentration (3rd spot),%</td>
<td>Average Concentration,%</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>C-1s</td>
<td>98.27</td>
<td>98.51</td>
<td>98.61</td>
<td>98.46±0.17</td>
</tr>
<tr>
<td>O-1s</td>
<td>1.62</td>
<td>1.49</td>
<td>1.39</td>
<td>1.50±0.12</td>
</tr>
<tr>
<td>Si-2p</td>
<td>0.11</td>
<td>0.00</td>
<td>0.00</td>
<td>0.04±0.06</td>
</tr>
</tbody>
</table>

**Figure 6.1** TEM representative micrographs of DOWEO samples bonded at 130 °C for 1hr
Changes in the microscopic structure of the welded samples prepared with different bonding temperature were analogous to those observed in the T-peel fracture test. TEM images were obtained with a Philips 420T Transmission Electron Microscopy operated at 100 kV. Two series of representative images at 130 and 150 °C, were obtained from the bonding samples of DOWEO-1, DOWEO-2, DOWEO-3 and DOWEO-4. These are shown in Figures 6.1 & 6.2. Contrast is created by differing degrees of absorption of the RuO$_4$ by the crystalline and amorphous regions. The crystalline phases almost completely exclude the heavy metal stain and appear light in these images, while the amorphous phases may absorb some RuO$_4$, thus appear darker.

For example, TEM micrograph of DOWEO-1 samples bonded at 130 °C (Figure 6.1a) clearly contains a heavily stained band, about 50 nm wide, indicating an amorphous phase exists at the interface. In contrast, this amorphous interface could not be observed for the sample bonded at 150 °C (Figure 6.1b). The boundaries of interfaces were also found not uniform which could be produced by the irregularity of the hot press plateau.

At both bonding temperatures (130 °C and 150 °C), each of the TEM micrographs of DOWEO-2, DOWEO-3 and DOWEO-4 samples were observed to have very similar microscopic structures. The information obtained from these images was consistent with the results from the T-peel fracture test, in which substantial knitting was achieved at 150 °C whereas a weak bonding was found at 130 °C for the DOWEO-1 sample. In contrast, completely healing was obtained from the other three samples at both temperatures; and, the maximum bonding fracture strength was achieved. These results suggest that the interfacial structures of the autohesion of ethylene/1-octene copolymers are strongly
associated with the topological and morphological types of the melted chains with respect to external conditions as discussed in Chapter 5.

Figure 6.2 TEM representative micrographs of DOWEO samples bonded at 150 °C for 1 hr
6.2.3 Atomic Force Microscopy (AFM)

In order to make comparisons with the morphology and topology of the T-peel fractured surfaces, the surface features of molded films of these four ethylene/1-octene copolymers before bonding were examined by AFM, the results are shown in the Figure 6.3. The lamellar structures are apparent on the surfaces. Lamellar structures become more orderly and better defined for the sample with higher 1-octene content. In spite of this difference, the root-mean-square roughnesses (RMS) of these original (unbonded) films remain about 4 nm regardless of the scanning surface area, as shown in Figure 6.4. The value of RMS roughness for each sample is quite similar.

Representative AFM 3D images and phase images of the original molded film and of the final fractured surfaces of DOWEO-1 samples after the T-peel tests at 2, 20 and 200 mm/min peel rates are shown in Figures 6.5 & 6.6. These films were bonded at 130 °C for one hour. Compared to the surfaces of the original films, much rougher surfaces were observed after welding and the subsequent T-peel fracture tests. At the lowest peel rate (2 mm/min), discrete rupture points were observed to have developed on the surfaces. With increasing the peel rate to 20 and 200 mm/min, these rupture points developed into larger, higher fracture surfaces and became more complex. They thus appear more like a network from the phase images. However, it is difficult to identify any further differences of these images only by visual inspection.

Similarly, the representative AFM 3D images of the original and the fractured surfaces after the T-peel tests are shown in Figures 6.7 & 6.8 for DOWEO-2 sample. Figures 6.9 & 6.10 show the AFM images for DOWEO-3 sample. These films were bonded at 120 °C for one hour. DOWEO-2 displayed very similar features to those of
DOWEO-1. However, the DOWEO-3 shows some structures with larger size and it is less complicated. Further analysis using fractals has been performed on these images in order to provide a systematic and quantitative comparison and is discussed in the following section.

Figure 6.3 AFM phase images (5 × 5 µm²) of DOWEO samples before bonding
Figure 6.4 RMS roughnesses of DOWEO samples before bonding
Figure 6.5 AFM images in 3D of fractured surfaces of DOWEO-1. (A) Prebonding; (B) 2 mm/min; (C) 20 mm/min; (D) 200 mm/min
Figure 6.6 AFM phase images (5 × 5 µm²) of fractured surfaces of DOWEO-1. (A) Prebonding; (B) 2 mm/min; (C) 20 mm/min; (D) 200 mm/min
Figure 6.7 AFM images in 3D of fractured surfaces of DOWEO-2. (A) Prebonding; (B) 2 mm/min; (C) 20 mm/min; (D) 200 mm/min
Figure 6.8 AFM phase images of fractured surfaces of DOWEO-2. (A) Prebonding; (B) 2 mm/min; (C) 20 mm/min; (D) 200 mm/min
Figure 6.9 AFM images in 3D of fractured surfaces of DOWEO-3. (A) Prebonding; (B) 2 mm/min; (C) 20 mm/min; (D) 200 mm/min
Figure 6.10 AFM phase images of fractured surfaces of DOWEO-3. (A) Prebonding; (B) 2 mm/min; (C) 20 mm/min; (D) 200 mm/min
6.2.4 Fractal Analyses on the AFM Images

Generally, when an AFM image of a fractured surface was analyzed by fractal techniques, the upper scale limit typically corresponds to maximum size of the images, while the lower limit is set by the available image magnification. In the current work, the fractal analyses of all of the AFM images were performed in the scale range from 5 µm × 5 µm to 10 nm × 10 nm. Then the calculation was executed by using the Nanoscope IIIa software provided by Digital Instruments. The fractal dimension of the 3D fractured surface was calculated as \( D = 2 - m \) for these two ethylene/1-octene copolymers, where \( m \) is the slope of a straight line previous described obtained by fitting the box counting through the data points on a log-log scale.

Figure 6.11 shows a comparison of the fractal analysis results of the surfaces of the original films before autohesion for DOWEO-1, DOWEO-2, DOWEO-3, and DOWEO-4. In these curves, the total surface area is plotted against the counting cell area. For all the films, the linear line fit through data points could be divided into two distinct regimes, where the slopes are different. The slopes in the first regime are -0.018, -0.094, -0.081, and -0.022 for DOWEO-1, DOWEO-2, DOWEO-3, and DOWEO-4 films respectively. In the second regime which range from ca. 10^{-2} \( \mu \text{m}^2 \) to the maximum image size at 25 \( \mu \text{m}^2 \), the slope of lines nearly equal to zero, indicating a “flat” surface at this measurement scales. The cell size that separates these two regimes is defined as the characteristic size of that particular film. Thus, the characteristic size of DOWEO-1, DOWEO-2, DOWEO-3, and DOWEO-4 films were found to be 0.009, 0.016, 0.013, and 0.025 \( \mu \text{m}^2 \), respectively. From a length scale point of view, these characteristic sizes are
in the range of 90 to 160 nm, which is about the spacing distance between lamellae as can be seen from both AFM and TEM images shown in previous sections.

A construction to explain the characteristic size and the schematic surface structures of the molded, pre-bonding films were generated and shown in Figure 6.12. The crystal structures are usually randomly distributed on such molded surfaces. There are some short chains from the lattice excluded on the surfaces because they cannot crystallize. Typically, the amorphous regions and the crystalline regions appear as different heights under the AFM tip because of their hardness differences. Therefore, when the box counting size from fractal detection is much larger than the size of these crystals, the irregularities inside the crystals and the excluded chains on the surface are insignificant, corresponding to a fractal dimension of very close to 2. However, when the box counting size is quite close to the crystal size, which is of the order of $10^{-2} \mu m^2$, a change in the fractal dimension is observed. In the analysis graphs the surfaces reveal self-similar on the scale from $0.9 \times 10^{-2} \mu m^2$ to $1 \times 10^{-4}$ for DOWEO-1, $1.6 \times 10^{-2} \mu m^2$ to $1 \times 10^{-4} \mu m^2$ for DOWEO-2, $1.3 \times 10^{-2} \mu m^2$ to $1 \times 10^{-4} \mu m^2$ for DOWEO-3, and $2.5 \times 10^{-2} \mu m^2$ to $1 \times 10^{-4} \mu m^2$ for DOWEO-4. Basically, this is because the local differences between a lamellar and an amorphous layer inside one crystal may dramatically increase the irregularity of these surfaces at the smaller counting scale. At even smaller scales, the excluded chains on the surface would become significant as well.

The fractal dimensions of DOWEO-1, DOWEO-2 and DOWEO-3 samples after T-peel fracture tests are also found in Figures 6.13, 6.14 & 6.15. As pointed out earlier, the DOWEO-4 sample showed completely heal and cohesive failure so that no fractured surfaces were available for fractal analysis. Comparing the same regimes of line
segments between the original surfaces and fractured surfaces, the slopes of lines in the first regime are noted to have been almost unaffected, or perhaps slightly increased. However, it is noted that the fractal dimension in the second regime have remarkably increased. The changes in fractal dimensions and the characteristic cell sizes are tabulated in Table 6.5, 6.6 and 6.7. These results indicate that the surfaces become much more complex textured after the T-peel fracture tests. As discussed in Chapter 5, the interfacial failures resulted from weak adhesion strength of the symmetric bonded joints for these three LLDPEs. The small changes in fractal dimensions in the first regime suggest that these weak strengths (low available strain energies) are not large enough to deform the underlying lamellar structures. For, example, the possibilities for fracture are: 1) the entire crystal structure could be either pulled out as an entity; or 2) the crystal structures could be distorted or tilted to some extent due to the interactions between the crystal region and amorphous region; or 3) there might be the influence of the movement of the short chains on the surfaces; 4) chain scission leaves a crystal region unchanged. The small changes in fractal dimensions also indicate that no co-crystallization has occurred between different layers during the adhesion process. In other words, only a small portion of the amorphous region and excluded short chains on the surfaces are thought to have inter-diffused with joining process. Thus, this type of adhesion could be described as a “stitch-welding”, as depicted in Figure 6.16. It is consistent with an amorphous interface that was observed using Transmission Electron Microscopy in Figure 6.1. These described, smaller fractal scale events are not major contributions to autohesion.
Table 6.5 Surface fractal analysis of DOWEO-1

<table>
<thead>
<tr>
<th>Peel Rate, mm/min</th>
<th>$D$ in Regime I</th>
<th>$\Delta D$ in Regime I</th>
<th>$D$ in Regime II</th>
<th>$\Delta D$ in Regime II</th>
<th>Characteristic cell size, $\mu m^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original film</td>
<td>2.018</td>
<td>0.00</td>
<td>2.001</td>
<td>0.00</td>
<td>0.009</td>
</tr>
<tr>
<td>2</td>
<td>2.097</td>
<td>0.079</td>
<td>2.223</td>
<td>0.222</td>
<td>0.857</td>
</tr>
<tr>
<td>20</td>
<td>2.123</td>
<td>0.105</td>
<td>2.307</td>
<td>0.306</td>
<td>1.259</td>
</tr>
<tr>
<td>200</td>
<td>2.118</td>
<td>0.100</td>
<td>2.269</td>
<td>0.268</td>
<td>1.361</td>
</tr>
</tbody>
</table>

Table 6.6 Surface fractal analysis of DOWEO-2

<table>
<thead>
<tr>
<th>Peel Rate, mm/min</th>
<th>$D$ in Regime I</th>
<th>$\Delta D$ in Regime I</th>
<th>$D$ in Regime II</th>
<th>$\Delta D$ in Regime II</th>
<th>Characteristic cell size, $\mu m^2$</th>
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<tr>
<td>Original film</td>
<td>2.094</td>
<td>0.00</td>
<td>2.003</td>
<td>0.00</td>
<td>0.016</td>
</tr>
<tr>
<td>2</td>
<td>2.122</td>
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<td>0.098</td>
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<td>20</td>
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<td>2.146</td>
<td>0.052</td>
<td>2.116</td>
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<td>1.585</td>
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Table 6.7 Surface fractal analysis of DOWEO-3

<table>
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<th>Peel Rate, mm/min</th>
<th>$D$ in Regime I</th>
<th>$\Delta D$ in Regime I</th>
<th>$D$ in Regime II</th>
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<th>Characteristic cell size, $\mu m^2$</th>
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<td>2.003</td>
<td>0.00</td>
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<tr>
<td>2</td>
<td>2.161</td>
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<td>20</td>
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<td>2.108</td>
<td>0.105</td>
<td>19.95</td>
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</table>

Even though the fractal dimensions, $D$s, were found not to change with increasing T-peel rate, as indicated from Figures 6.13, 6.14 and 6.15 and also from Table 6.5, 6.6 and 6.7, the characteristic size monotonically did increase with an increase of peel rate. As mentioned in Chapter 5, higher peel energies, $G_{1c}$ are usually required at higher peel rates due to viscoelasticity. These results indicate that the formation of fractals at the larger scale also corresponds to a larger fracture energy. This may be rationalized as the
strain energy taken to pull out bigger structures from one side or the other of the bonded interface of autohesion. The correlation between the characteristic fracture size and the peel energy as a function of peel rate also suggests that chain motions inside these interfaces are sensitive to the peel velocity during the fracture process. These may be due to the high chain mobility of these amorphous interfaces attained when the fracture temperature becomes much higher than the glass transition temperatures of these LLDPEs. Chain entanglements of such amorphous interfaces would thus be dominant and lead to the higher fracture energy at the higher peel rate. Overall, the larger scale textures created reflect the viscoelastic energy dissipation during interfacial failure for these autohesion bonded ethylene/1-octene copolymers.

The variations in the fractal dimensions of fractured surfaces among DOWEO-1, DOWEO-2 and DOWEO-3 samples could also be associated to the difference of the properties of original bulk materials, and in the bonding conditions. DOWEO-1 had the highest crystallinity and density, and was bonded at a higher temperature; these factors made the fractal dimension and characteristic size of original films and the fractured surfaces different from those of the DOWEO-2 and DOWEO-3 samples.

Chain architecture could be another factor contributing to the differences observed in the fractal characteristic size between the DOWEO-1, DOWEO-2 and DOWEO-3 samples. The autohesion process for ethylene/1-octene copolymers has been discussed previously as partially controlled by the chain architectures and the strong effects of the bonding temperatures. Note that in the present study, the 1-octene content of the DOWEO-3 sample is almost twice as large as that of the DOWEO-2 sample; this lowered the melting point of the DOWEO-3 sample more than in the DOWEO-2 case.
Further, note the effect of bonding temperature on autoadhesion which was also considered by investigating the effect of heating rate on the melting temperature of these two ethylene/1-octene copolymers using DSC. The melting temperature under isothermal condition was found to be 123.4 °C for the DOWEO-2 sample and 122.0 °C for the DOWEO-3 sample. The experimental bonding temperature was about 120±0.5 °C and that is below the melting temperature for both samples. This lower bonding temperature probably produces a lower degree of inter-diffusion across the interface because the crystals on the surfaces are almost unmelted, or melted at such a low rate so as to strongly restrict the chain mobility for the inter-diffusion process. Consequently, the weak adhesion strengths were obtained during these T-peel fracture tests. Moreover, the isothermal melting point of DOWEO-2 is about 1.4 °C lower than that of DOWEO-3. Thus, the chain motion of DOWEO-2 will be more confined and consequently result in the lower peel energy and smaller fractal characteristic size under the same fracture process.

As discussed above, the characteristic sizes are shown to depend on the peel rate and the chain architecture. The characteristic sizes were also correlated to the fracture energies of ethylene/1-octene copolymers under different peel rates. Fractal dimensions and characteristic sizes determined from fractal analysis suggest that the fractal characteristics depend on the properties and history of the interfaces.
Figure 6.11 Comparison of the fractal analysis (Total surface area versus counting cell area) of the original DOWEO-1, DOWEO-2, DOWEO-3, and DOWEO-4 films
Figure 6.12 Diagram of surfaces features of original films of ethylene/1-octene copolymers
Figure 6.13 Surface fractal diagram of DOWEO-1 before bonding and after T-peel fracture
Figure 6.14 Surface fractal diagram of DOWEO-2 before bonding and after T-peel fracture
Figure 6.15 Surface fractal diagram of DOWEO-3 before bonding and after T-peel fracture
Figure 6.16 Diagram of autohesion process – Stitch Welding
Chapter 7

CONCLUSIONS AND RECOMMENDATIONS ---

AUTOHESION

7.1 Conclusions

The goal of this thesis work is to understand the autohesion of ethylene/1-octene (EO) copolymers in order to correlate the macroscopic mechanical joint fracture properties with the microscopic interfacial structure and the chain parameters. The hexyl groups from the 1-octene comonomers provide short branches and can significantly alter the thermal, rheological and mechanical properties. Four copolymers were selected to examine and model the short chain branching effects on the autohesion.

Symmetric interfaces were formed by bonding two identical EO copolymer films together for selected period of time with various temperature and pressure conditions. The adhesion fracture strength/energy of these interfaces was examined by T-peel fracture tests. The results of these T-peel testing indicated that there were strong effects of bonding temperature \(T_b\) and bonding time \(t_b\) on the final apparent peel strength/energy. In the evaluation of the effects of bonding temperature on the peel strength, it was concluded that when bonding at temperatures much higher than \(T_c\) of each DOWEO copolymer achieved a very strong bond. The bonding time was set at 60 minutes. In fact, the T-peel geometry resulted in a cohesive failure mode, in the films, indicating they have been completely sealed. The observed peel strength increased with decreasing 1-octene content. The peel strength of each DOWEO copolymer
approximately exhibited a constant value irrespective of the bonding temperature, provided this was much higher than its characteristic temperature. However, when the bonding temperature was close to the characteristic temperature, the peel strength of each DOWEO copolymer would dramatically decrease by about two orders of magnitude. It was observed that the interfacial failure occurred in the T-peel tests for such samples. It was noticeable that there is an exception, the DOWEO-4 sample, which contains the highest 1-octene content. In this case, the effective bonding was obtained over the entire experimental temperature range.

In the evaluation of the effects of bonding time on the peel strength, samples were welded at two bonding temperatures, \( T_c + \sim 1.7 \, ^\circ C \) and \( T_c + \sim 12.5 \, ^\circ C \). The bonding time dependence of the measurable peel energies was approximately proportional to \( t_b^{1/2} \) at both temperatures. The strong influences of bonding temperature and branch content on the sealing rate were also obtained for these copolymers. The development of higher peel strength was faster for samples with higher content of the hexyl branches and at the higher bonding temperature.

There was a strong influence of peel rate on the fracture energies for the interfacial failure that was also obtained in the T-peel tests. The “adhesive quality” could be determined as very weak if samples were peeled slowly; however, it became much stronger if they were peeled rapidly. Although it is possible that a potion of the increase of the fracture energy may be partially attributed to the other deformation modes in the specimens such as tension and bending in the arms especially at the very high peel rate. The fractured surface morphologies clearly showed that the surfaces became rougher and more complex with higher deformation speeds, and result in the different visualization of
images. These conclusions reflected strong viscoelastic energy dissipation in the interfacial failures for these DOWEO copolymers.

The results obtained with respect to temperature and time also indicate that the autohesion of ethylene/1-octene copolymers are strongly associated with the types of melted chains. The chain composition of these DOWEO copolymers investigated is known to be highly heterogeneous, with the branches concentrated in the lower molecular weight portion. Long linear chain segments are expected to form large, well-ordered crystals that provide strong anchors for the tie molecules and hence determine the density of intercrystalline links. Short chains with branches are proposed to obstruct chain disentanglement due to the protrusions and to limit a chain in sliding from the crystal structure. Due to these reasons, these short chains with branches would contribute much less than the long linear chains in term of the final peel strength. Therefore, the higher branch content sample would generate the lower peel strength. However, it was found that the larger peel strength could be obtained only at the higher bonding temperatures at which the long, linear chains begin to melt and diffuse across the interface. On the other hand, the higher branch content samples have a lower crystallinity. They obtain a higher chain mobility at a lower bonding temperature and with shorter bonding time. It has been observed that the higher branch content resulted in better bonding performance at lower bonding temperatures. Thus, it is easier to regulate the bonding to obtain a “medium strength”, which may be important for applications of heat-sealing.

Transmission electron micrographs (TEM) of the bonded assemblies showed that the interfacial/interphase structure changed from amorphous to crystalline with an increase in $T_b$. The fractured surfaces of ethylene/1-octene copolymers were
characterized using a cube counting method from fractal analysis on AFM images. Self-similar fractal features were displayed for different finite area scales for all the fractured surfaces. In the fractal analysis of each sample, two distinct regions showing fractal features can be observed at two scale regimes. Fractal features at the smaller length scale (regime I) were observed at certain conditions for the fractured surfaces and also for the original films. A conclusion is that the fractal features at this smaller featured regime are controlled by the heterogeneous morphology in the surface for these ethylene/1-octene copolymers. There was no fractal features observed for the unbonded films at the larger scales (Regime II), only for the fractured surfaces. The fractal dimensions determined in Regime II were computed by using a larger box counting size that yielded a fractal plot comparing the fractured surfaces and the surfaces of original films. It indicated that the characteristic structures of crystals have not been deformed during the T-peel tests. The crystal structures were either moved as an entity or untouched. A “stitch-welding” model was used to describe the autohesion mechanism; this accounts for weak adhesion energies. The fractal dimensions were noted to slightly change with increasing peel rate. The characteristic size at which the fractal features begin to appear increased with peel rate indicating the deformation volume during this fracture test were on a larger scale at the higher peel rate. This observation also provides evidence for the phenomenon of higher peel energy at higher peel rate.

7.2 Recommendations

Due to the limitations on the time and equipment in this thesis work, only the reported representative studies were completed. A more thorough systematic study of this series of copolymers can be achieved with the following noted improvements. It would
also help to obtain a better understanding of the relationship of the morphology at microscopic scale and the mechanical properties at the macroscopic scale.

The four random short-chain branching polyethylene copolymers used in this work were synthesized using Ziegler-Natta catalysts and they are commercial products. Copolymers with different branch type, length, or synthesized using different catalysts (such as a metallocene) catalyst could be used to examine the short chain length effect on the mechanical properties and interfacial structures. This research should not be limited to commercially available resins, available in large quantity, but very limited chain architectures. In order to conduct the adhesion experiments on smaller quantities of samples that are synthesized in laboratory, a sandwiched structure geometry can be used. A thin film made of the lab-synthesized sample can be sandwiched in-between two polymer strips made of a commercial product with similar molecular architectures.

The bonding process, T-peel fracture tests and microscopic experiments in this work were very time consuming. An automatic heat-sealer equipped with T-peel testing features which can conduct the bonding and fracture testing in a single experiment cycle may be used for the future works. This type of equipment would need samples in the thin film form. However, solution cast films from small amount of samples can be used for this kind of equipment directly.

Autohesion of ethylene/1-octene copolymers is a very complicated interplay between the ability of interface to transfer stress and the plastic and viscoelastic properties of polyethylenes. The commonly used peel test generates irreversible phenomena that reflect the bonding process in a somewhat chaotic fashion. Therefore a computational model that considers all the factors during both the bonding and fracture
processes, and which incorporates the fractured surface morphology, would provide a better understanding of the whole process. In the study of the mechanical properties of the autohesion process for polyethylenes, a mathematical model and computer program can be created to simulate the development of adhesion strength with respect to the bonding temperature and bonding time. Some work has been done by which applies the finite analysis model to predict the mechanical properties of interfaces; however, those models did not consider the phase changes in the semicrystalline polymers with heat transfer. A computational program constructed by Moffitt97 simulates some of the mechanical properties obtained from the present studies in term of phenomenological parameters (e.g. rheology). This Moffitt model had been previously used successfully to compute the time dependence of interface strength development of autohesion process for linear polyethylenes. This model described the development of adhesion strength in term of crystalline melting and amorphous interfacial contact, interfacial wetting, chain interdiffusion, and entanglement. The model assumed that the interfacial wetting and subsequent chain diffusion and entanglement only occur when the probability of forming an amorphous-amorphous contact at the bonding interface is non-zero. The model equations used to describe the evolution of the adhesion energy as function of the amorphous contact, interfacial wetting kinetics and chain interdiffusion via reptation at the bonding interface. These parameters might be quantitatively related to chain architecture, bonding temperature and bonding time when applied to the autohesion studies of ethylene/1-octene copolymers. The results to be obtained from modeling can provide better understanding of the correlations among the properties of three length scales.
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Adhesion Studies of Polymers:

Part (II)

Method Development and Adhesive Characterization of Pressure Sensitive Adhesive in Paper Laminates for Postage Stamps
Chapter 8
METHOD DEVELOPMENT AND ADHESIVE
CHARACTERIZATION OF PRESSURE SENSITIVE
ADHESIVE IN PAPER LAMINATES FOR
POSTAGE STAMPS

8.1 INTRODUCTION

Since their commercialization about a half century ago\(^1\), pressure-sensitive adhesives have been successfully applied in many applications closely related to our life. They are used in self-adhesive tapes, labels, protective thin films and coatings, dermal dosage systems for pharmaceutical applications, the assembly of automotive parts, toys, electronic circuits, and keyboards. In order to understand the needs and means of viscoelastic behavior, one firstly needs to identify the most important material properties specifically related to PSAs. For example, adhesives in a bond behave like a fluid or a solid. Fluids are characterized by their viscosity which influences their mobility, whereas solids are characterized by their modulus which determines their deformability\(^2\). Pressure-sensitive adhesives are viscoelastic materials with the flow properties playing a key role in the wetting and bond forming and the elasticity plays a key role in the storage of energy that will generate resists to the debonding process. The balance between these properties governs their time dependent responses and their adhesion strength. The
adhesion and other end-use properties of PSAs require a viscoelastic, non-Newtonian flow behavior, which is basically the nature of macromolecules³.

In general, PSA products are used as thin layers; therefore their flow is limited by the interactions with the solid components of the laminate (liner and face) materials⁴. On the other hand the solid components of the laminate are commonly flexible, and/or elastic layers, allowing a relatively broad and non-uniform distribution of the applied stresses. Thus the properties of the bonded adhesive (adhesion strength) may differ from those of the bulk (unbonded) adhesive materials. It remains difficult to merely introduce the properties of bulk PSAs as valid information for the end-users and manufactures in the form of thin layers coated on backing materials. Pressure-sensitive adhesives are seldom used as thick layers between motionless rigid surfaces (i.e., as fluids)⁵. Instead, as known from industrial experiences³, the nature of the face stock material or of the substrate used, and their characteristics and dimensions may significantly influence the properties of the PSA laminate.

The manufacture of PSA laminates includes the manufacture of the raw materials and their formulations⁶. The manufacture of the raw materials refers to manufacturing the components of a PSA recipe, which can be natural materials or synthetic polymeric materials. PSA formulations contain the polymers, tackifiers (plasticizers), fillers, stabilizer, and carrier agents (solvent or water). This constitutes a base formulation, where all the components (except the carrier agent) also contribute to the end-use adhesive properties⁷.

Adhesive performance of pressure sensitive adhesives could be described in term of bonding or debonding because the applications require multiple bonding and
debonding processes during the lifetime of the products\textsuperscript{8}. Therefore, the test methods have been developed to characterize the bonding properties, such as tack testing, as well as the debonding properties, such as peeling or shearing. In the study of dynamical mechanical properties of PSA in the form of paper laminates that used for postage stamp application, the lap-shear geometry has been used for the shearing tests. Lap-shear tests determine the shear strength of adhesives. The test method is primarily a comparative method for determining the adhesive strengths, the surface preparation parameters and the environmental durability of the adhesive\textsuperscript{9}. This method provides a good basis for evaluating adhesives in the form of laminates, but some modifications or additional tests are required when testing materials for specific applications in order to obtain more meaningful results.

The objectives of this project is, first, to develop a reliable testing method to characterize the dynamic mechanical properties of pressure sensitive adhesives in paper laminates for postage stamp applications; second, to evaluate the temperature and frequency responses of these PSAs; and third, to predict the long term performances using the time-temperature superposition of the temperature/frequency sweep results generated from DMA tests. This project also investigated the influence of the thickness (number of layers in the paper-PSA laminate specimen) on the dynamical mechanical properties of these PSA products to determine the optimal geometry that enhances the DMA results.
8.1.1 Physical Bases of Viscoelastic Behavior on PSA Performances

8.1.1.1 Rheology on PSA Laminates

In producing the pressure sensitive adhesive laminates, the pure or unbonded pressure-sensitive adhesives undergo a film-forming and a bonding process. The elastomeric film material, which combines a high degree of tack with an ability to quickly wet the surface to which it is applied, is subjected to a low to moderate pressure to provide instant bonding as a result of its flow characteristics. On the other hand, PSAs possess sufficient cohesion and elasticity, therefore despite their aggressive tackiness they can be handled without much difficulty and can be removed from smooth surfaces without leaving any residue. So fundamentally PSAs require a delicate balance between their viscous and elastic properties. In general, most thermoplastic polymers can be used as PSA at certain conditions. However, under ambient conditions, PSAs need satisfy these contradictory requirements under different shear rates, that is, at low shear rates they must flow (bonding) and at high peeling rates they have to respond elastically (debonding).

Based on the above discussions, PSAs do not perform as Newtonian systems: they do not obey Newton's law, their viscosity is not a material constant, but depends on the stress value or shear rate:

\[ \eta(\tau) = \frac{\tau}{\dot{\gamma}} \]

that is

\[ \tau = \eta_\infty \times \dot{\gamma}^n \]  

(2.1)

where \( \eta_\infty \) is the apparent viscosity, and \( n \) denotes the flow index. For non-Newtonian systems the exponent \( n \) does not equal to one, which implies that the viscosity depends on the shear rate. Pure pressure-sensitive adhesives are polymers containing long-chain
entangled molecules with intra- and intermolecular mobility. At low strain rates, the polymer chains have enough time to respond to the motion and as a result the resistance to debonding forces is low. This viscous flow dissipates the debonding energy. On the other hand, the molecules have less time to disentangle, and slide past one another at higher strain rates. In this case, the viscous flow is reduced, but the elastic modulus or stiffness of the polymer increases. This motion results in additional stored energy, and the debonding resistance intensifies accordingly.

Pressure-sensitive adhesives are mostly used in a coated, bonded state enclosed within a laminate. Generally the adhesive acts as a liquid elastomeric intermediate layer between face stock and release liner, or finally, between face stock and substrate. The rheology of the bonded PSAs will be strongly influenced by the components, structure, and manufacture of the laminate. First, this is because the flow properties of the relatively small thickness of the adhesive layer are strongly influenced by the properties of the delimiting solid surfaces. At least one component of the laminate (the face stock), but mostly both (face stock and release liner or substrate) are flexible. These soft materials usually allow non-uniform distribution of the applied force or strain, and undergo a pronounced deformation during converting and end-use of the PSA laminates. Second, the flow properties of the adhesive film are strongly influenced by the adhesive/surface interactions. The adhesive/face stock, adhesive/release liner, and adhesive/substrate interactions depend on the nature of the adhesive and also depend on the characteristics of these solid components. Finally, the rheology of the adhesive also depends on the thickness of the PSA film, the continuous/discontinuous nature of the laminate components, and the lamination in manufacturing process. It is relatively easy to
determine the rheological properties of the adhesive or of the materials used as face stock or release liner separately, but there is no means for direct measurement of the rheology of the pressure-sensitive adhesive in the laminate form. Practically one can investigate the bulk adhesive properties, converting and end-use properties of the coated (bonded) PSAs, and thus indirectly evaluate the rheology of the bonded PSAs\textsuperscript{16}.

8.1.2 Role of Glass Transition Temperature and Modulus in Characterizing PSAs

It was shown earlier that PSAs are required to bond rapidly to a variety of substrates under conditions of low contact pressure and short contact time, which is a characteristic feature of PSAs, tack. Tack is a characteristic feature of any amorphous polymers above the glass transition temperature $T_g$ only. In terms of physical properties, $T_g$ represents the temperature range through which the polymer changes from a hard, glassy state into a liquid, rubber-like state\textsuperscript{17}. In general PSAs with low viscosity (low $T_g$) will be able to wet a substrate surface and establish intimate contact with the adherent. An increase in $T_g$ will lead to a stiffer polymer, decreased wettability and most likely a decline in tack properties. Therefore, $T_g$ is one of the most important parameters in order to determine the minimum usage temperature for polymeric materials as a PSA. Several methods are used to determine the glass transition of a polymer material; the most commonly used ones are mechanical/rheological, calorimetric, dilatometric, and dielectric methods.

The glass transition temperatures of PSA polymers could be altered when pressure-sensitive adhesives are in a coated, bonded state enclosed within a laminate\textsuperscript{18}. It
is because the pure polymer will be blended with different macro- or small molecular compounds such as tackifiers and fillers, during the formulation procedure. The purpose of formulating is to enhance or adjust viscoelastic, surface-active, and chemically stabilizing properties. These components have strong influences on the intra- and intermolecular interactions of the polymer chains. Thus, $T_g$ of final PSA product may be different from the pure PSA polymer and in some cases it may be deceived in some testings. In addition, there are possible further chemical reactions occurring when the carrier agent (water or solvent) is used in the lamination.

Although $T_g$ is a good predictor of the properties of PSAs, the $T_g$ alone cannot provide a whole image of the adhesive performance. The modulus of PSAs is another important parameter in characterizing the adhesive flow and mechanical responses. Generally the modulus is a material characteristic, for materials in a composite structure it may depend on the structure and component characteristics of the composite. Therefore, the modulus of the final PSA product could be modified or improved during the formulation and lamination procedures. Alike the $T_g$, there are several factors having the influences on the modulus, such as the chemical composition and functionality, molecular weight, molecular weight distribution, tackifiers, and fillers etc. The interdependence between the creep compliance and the tack has been demonstrated by Dahlquist.

### 8.1.3 Time-Temperature Superposition of PSA

In predicting the long term performance, time-temperature superposition (TTS) can provide this type of information from the mechanical rheological testing in dynamic mode at different temperatures and frequencies. Williams-Landel-Ferry (WLF) equation
is a useful tool to generate time-temperature superposition curves for PSAs\textsuperscript{23, 24}. The WLF equation considered the equivalency of time and temperature in the context of free volume theory for an activated flow process in viscoelastic materials such as the PSAs. The WLF equation yields an equivalent frequency for a given temperature relative to a reference temperature and experimental frequency:

$$\ln a_T = \frac{-C_1(T - T_o)}{C_2 + (T - T_o)}$$  \hspace{1cm} (2.2)

where $a_T$ is the shifting factor at $T$, $C_1$ and $C_2$ are constants for a given polymer, and $T_0$ is the reference temperature. The activation energy ($E_a$) can be calculated from the Arrhenius relationship of the shifting factor with temperature from the following equation:

$$\ln a_T = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$  \hspace{1cm} (2.3)

with $R$ being the gas constant and $E_a$ is a constant number for PSA polymers.

\textbf{8.1.4 Lap-Shear Geometry}

The lap-shear test method is one of the most common, maligned and studied test methods for the evaluation of adhesive bonds. This standard test method for evaluating the shear strength of adhesive bonds is described in ASTM D1002. The specimen specified in ASTM D1002 is shown in Figure 8.1. The adhesive is usually applied to the region to be lapped. It is certainly reasonable to think that the bending of specimen and the real stress applied to the adhesive depends on the distance from the loading point to the lap region\textsuperscript{25}. The lap shear specimen can be prepared in a number of ways including the single specimen and multiple specimen methods. The advantages of the multiple
specimen method are the elimination of adhesive flash over the finger specimen and the higher reproducibility of the lap shear strength\textsuperscript{26}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{lap_shear_geometry.png}
\caption{The construction of conventional lap-shear geometry}
\end{figure}

In the adhesive bond analysis of lap-shear test proposed by Goland and Reissner\textsuperscript{27}, an assumption was made that the deformation of the adherends is due completely to the longitudinal stress of shearing in the adherend. As a result of this assumption, the adhesive then basically acted as a Hooke’s law solid between the two adherends. The mathematics in their discussion was very complicated and led the expressions that can not be easily interpreted. The major conclusion obtained is that at the center of the bond, the shear stress is less than the average shear stress of bond; while at the edge of the bond, the shear stress is much larger than the average shear stress of the bond.

The lap shear test, when applied logically and realistically, could be used as a reasonable and easy comparison of the strength of adhesives. It could also be used as a quality control method when testing for consistency of adhesive bond strength.
8.2 EXPERIMENTAL APPROACHES

8.2.1 Materials

The testing sample of PSA stamp was constructed by laminating a water-based polyacrylic PSA to the face paper. The face paper contains a water-soluble primer coating that could be able to water soak and remove the stamp from a bonded substrate. All individual components as well as the lamination construction have met the criteria in the USPS stamp specification, USPS-P-1238F. This kind of construction is called the unprinted laminate. There are four PSA stamp samples (called 65004, 65007, 65010 and 65013) testing in this work, which were manufactured by four different polyacrylic polymers and lamination processes.

For each of PSA-paper layer, the paper backing is about 0.005" (0.127 mm) thick, the water soluble primer is about 0.0001" (0.0025 mm) thick, and the PSA layer is about 0.001" (0.025 mm) thick. The dimension of one PSA-primer-paper layer is shown in Figure 8.2. In the calculation of the shear moduli in DMA tests, the thickness of the water-soluble primer was neglected because this layer is much thinner than the PSA layer and paper backing.

![Diagram of PSA in face paper laminate](image_url)

**Figure 8.2** Dimensions of PSA in face paper laminate
8.2.2 Thermal Analysis

A thermogravimetric analyzer (TGA, TA Instruments model: Hi-Res TGA 2950), a differential scanning calorimeter (DSC, TA Instruments model: MDSC 2920), and a dynamical mechanical analyzer (DMA, TA Instruments model: DMA 2980) in the Chemistry Department at Virginia Tech were used for the majority of this project. A TA Instrument Q800 DMA at Advanced and Applied Polymer Processing Institute (AAPPI), Institute for Advanced Learning and Research was also used to conduct some experiments when the DMA 2980 was under maintenance. Subambient conditions were used for the DSC and DMA measurements.

For the TGA and DSC experiments, the PSA coatings were peeled off from the backing paper, by soaking in water for 10 minutes. The PSA layers were dried at room temperature for overnight before carrying out the TGA and DSC measurements. This was done because no differences were observed from the calorimetric thermograph of the unpeeled PSA and that of the pure backing paper.

8.2.3 DMA Test Geometry (Multiple Layers of Lap-Shear Geometry)

The geometry shown in Figure 8.3 has been used to perform the DMA tests. The size of overlap area is about 20mm (length) \( \times \) 10mm (width) \( \times \) 0.85 (thickness) for an 8-layers sample. For such an 8-layer structure, there are only 7 layers of PSA coating being sheared and tested. The mechanical properties were recorded as tensile properties because the tensile test mode was used for DMA measurement. Therefore, the tensile moduli measured were converted to shear moduli by the following relationships, and it is also schematically described in Figure 8.4.
\[ \Delta = \frac{P}{(w \cdot t)} \times \ell \div E \] 
(3.1)

\[ \Delta = \gamma \times (N - 1) \times h \] 
(3.2)

\[ \gamma = \frac{\tau}{G} = \left( \frac{Ph}{w \cdot \ell} \right) / G = \frac{\Delta}{(N - 1)h} \] 
(3.3)

so

\[ \Delta = \frac{P}{(w \cdot t)} \times \ell = \left( \frac{Ph}{w \cdot \ell} \right) / G \] 
(3.4)

finally,

\[ G = (N - 1) \frac{t \cdot h}{\ell^2} \div E \] 
(3.5)

where \( P \) is the tensile force applied on the 8-layer sample during the shearing deformation;

\( \ell \) is the overlapped length of the 8-layer PSA-paper sample;

\( w \) is the width of the 8-layer PSA-paper sample;

\( t \) is the overlapped thickness of the 8-layer PSA-paper sample;

\( \Delta \) is the displacement of the 8-layer PSA-paper sample during the shearing deformation;

\( E \) is the Young’s modulus when measured using the tensile mode in DMA for the 8-layer PSA-paper sample;

\( G \) is the shear modulus of the 8-layer PSA-paper sample after converted;

\( h \) is the thickness of a single pressure sensitive adhesive;

\( N \) is the total number of layers of sample;

\( \gamma \) is the shear strain of deformation; and
\( \tau \) is the shear stress of deformation,

There are also three pictures taken to display the experimental set-up of the DMA test, as shown in Figure 8.5-7. In Figure 8.5, the sample of multiple layers of lap-shear geometry is shown mounted on the tension clamp of TA 2980 Dynamic Mechanical Analyzer (DMA). In Figure 8.6, the picture is showing the top-view and side-view of the sample of multiple layers of lap-shear geometry. Figure 8.7 gives the view of the whole experimental set-up. The TA DMA 2980 was hooked up to a 100 L TA liquid nitrogen tank and a Dell computer that does the controlling and data acquisition works. All the experimental control and data analysis was accomplished by using the TA software.

There are two type of tests carried out using DMA. The first type of test is the frequency sweep / isothermal temperature test, in which the data was obtained by controlling the temperature at the room temperature and the frequency is changed at 100 Hz, 10 Hz, 1 Hz and 0.1 Hz, in order. The second type is the frequency sweep / temperature step test, in which the data was recorded by sweeping the frequency at 100 Hz, 10 Hz, 1 Hz and 0.1 Hz at temperatures from -50 °C to 60 °C at 5 °C increments. At each step, the sample was equilibrated for 5 minutes before the test starts in order to have thermal homogeneity.
Figure 8.3 Test Geometry for multi-layer of lap-shear DMA test

8 Layers of PSA and backing, but only 7 layers are tested.
**Figure 8.4** Scheme of PSA deformation in paper lamination
Figure 8.5 Set-up of PSA sample on DMA

Figure 8.6 Face view and side view of 8-layers PSA samples
8.3 RESULTS AND DATA ANALYSES

8.3.1 Thermogravimetric Analysis (TGA)

TGA tests were conducted in a temperature ramp mode from room temperature (RT) to 800 °C at 10 °C/min. The results are shown in Figure 8.8. These curves show the weight loss as temperature is increased in a nitrogen inert atmosphere. It is noted that a total of 5 % of weight loss of these four polymers were observed at 295.5 °C, 199.9 °C, 103.0 °C, and 209.8 °C for PSA65004, 65007, 65010, and 65013, respectively. It is observed that the residue amounts at 450 °C are 9.1, 6.8, 8.0, and 4.3 % for 65004, 65007, 65010, and 65013, respectively.
8.3.2 Differential Scanning Calorimetry (DSC)

The thermal behaviors of the polyacrylic PSAs were characterized using the differential scanning calorimeter. Experiments were performed at a scan rate 10 °C/min heated from -50 °C to 60 °C. Temperature calibration of the DSC during heating was accomplished by recording the onset of the melting transition of an indium standard sandwiched between two molded branched polyethylene films. Results are shown in Figure 8.9-8.12.

There is no distinct thermal transition observed in these samples in the temperature range studied. However, a peak observed at about 0 °C for the 65007 sample.
Also, this transition might be the melting transition of water that was not removed completely after soaking and drying during sample preparation. This result could attribute to two possible reasons: first, the formulation of PSAs could alter the thermal properties of the pure acrylic-based polymers. This is because the final PSA product contains not only the polymer but also many other components to achieve best results for end-use, such as tackifier and filler etc. The blend of these components really makes the change of enthalpy quite different than that of a pure polymer in a DSC measurement. Another possible reason is that there may be further chemical reactions occurring due to the carrier agent (water or solvent) is used during the lamination. However, this information in detail is still confidential with the manufacturers at this moment; future work may be carried out after the manufactures release their recipe.

**Figure 8.9** DSC heating scan of Sample PSA 65004
Figure 8.10 DSC heating scan of Sample PSA 65007

Figure 8.11 DSC heating scan of Sample PSA 65010
8.3.3 Dynamic Mechanical Test (DMA)

8.3.3.1 Effects of PSA Thickness on Dynamic Mechanic Properties

As shown above, the multi-layer structure enhances the shearing deformation properties of the PSA coating layer. But the details of interpreting this geometry need to be fine-tuned to get the optimal responses from the dynamical mechanical tests. Therefore, different layers of PSA-paper structure (2, 4, 6, 8, and 10 layers) were tested using the frequency sweep / temperature step over the same frequency and temperature ranges. The 2-layer structure is actually the conventional lap-shear geometry. The sample preparation and testing procedures are also the same as discussed earlier. The Tan Delta versus temperature curves at 4 different frequencies of these structures for 65004 are shown in Figure 8.13-17. One notices that the values of tan delta are sensitive to the
thickness of layers of lap-shearing geometry. For the conventional lap-shear geometry which has no extra layers between two arms, the tensile strength of the backing paper, which behaves as an elastic material contributes significantly to the total strength obtained from the mechanical tests, especially at very high frequency. Consequently, one observes that the value of tan delta at 100 Hz is notably higher than those obtained at lower frequencies. The advantage of the multi-layer geometry is that the addition of the extra layers into the shearing arms promotes the shearing motion between the inter-layers and reduces the tensile deformation of the two arms. Therefore, it could decrease part of the work dissipated which is caused by tensile and bending deformations of the backing papers. There is no Tan delta jump obtained at 100 Hz in Figure 8.14, in which the sample contains two extra layers. If the number of extra layers was increased, the value of tan delta also distinctly increased, as shown in the third plot in which the sample contains four extra layers. This suggests that the shearing motion on each layer is eventually enhanced by adding more layers. When adding more layers, the value of tan delta was slightly increased. This result may suggest that the lap-shearing geometry with overall 6-8 layers (extra 4 or 6 layers) is an optimum condition for testing these postage stamp PSAs.

The relationship of the peak value of Tan delta at 1 Hz and the average shearing strain of each layer versus the total number of layers of samples is described in Figure 8.18. The shearing strain was calculated from Equation (3). It is clear that when the average shear strain of each layer decrease, the peak value of Tan delta increases with increase in the total number of PSA-paper layers. This curve shows that a PSA-paper structure with 5-10 layers is appropriate for conducting these tests.
Figure 8.13 The plot of shear tan delta versus temperature of 2-layers 65004 sample

Figure 8.14 The plot of shear tan delta versus temperature of 4-layers 65004 sample
Figure 8.15 The plot of shear tan delta versus temperature of 6-layers 65004 sample

Figure 8.16 The plot of shear tan delta versus temperature of 8-layers 65004 sample
Figure 8.17 The plot of shear tan delta versus temperature of 10-layers 65004 sample

Figure 8.18 The relationship of Tan delta and strain versus number of PSA-paper layers
8.3.3.2 Sample 65004

8.3.3.2.1 Frequency Sweep / Isothermal Temperature

The shear properties from the frequency sweep/ isothermal temperature tests of the 8-layer PSA-paper sample and the tensile properties of a single bare paper backing sample of 65004 are shown in Figure 8.19 and 20 at nine different frequencies from 0.01 to 100 Hz at room temperature. These data are the average numbers of a number of repeated tests. In Figure 8.19, one can observe the storage modulus and loss modulus increased with increasing frequency. The storage modulus ranges from 0.01 to 0.1 MPa, which is 1 order magnitude higher than the loss modulus at each frequency. Tan delta was found to be fairly flat in the range from 0.4 to 0.46 but with a transition at around 2 Hz. However, the properties of single bare paper backing sample were quite different from that of the 8-layer PSA-paper sample as shown in Figure 8.20. Comparatively, the storage modulus and loss modulus of a single bare paper backing did not have a distinct change with the frequency sweep. These values are about 5 orders of magnitude higher than that of 8-layer PSA-paper samples. The value of Tan delta was in the range of 0.03 to 0.05, which is 1 order of magnitude lower than that of the 8-layer PSA-paper samples and is a typical value of an elastic material.

8.3.3.2.2 Temperature Step/Frequency Sweep

The results of frequency sweep / temperature step tests for the 8-layer PSA-paper sample of 65004 are shown in Figure 8.21-23 for the storage modulus, loss modulus and tan delta at 4 different frequencies over the temperature range from -50 to 60 °C. On each plot, there are three distinct responses which are the glassy, transition and flow regions. From the Loss Modulus versus temperature curves, the glass transition temperatures \( T_g \)
were observed to be -15.04 °C at 0.1 Hz, -4.92°C at 1 Hz, 4.97 °C at 10 Hz, and 15.06°C at 100 Hz. The shape of the curves at different frequencies is very similar to each other. But the curves are shifted to higher temperatures at higher frequency, as expected for a viscoelastic polymer. It is because the material could behave “stiffer” at higher frequency “softer” at lower frequency. The shear storage moduli decreased from around 1 MPa in the glassy region to about 0.1 MPa in the flow region. The moduli obtained in the flow region were consistent with Dahlquist’s criteria for pressure sensitive adhesives. The glass transition temperatures from the peaks in the tan delta versus temperature curves are slightly different from those from the loss modulus curves. The tan delta value increased from less than 0.1 in the glassy region to about 0.6 in the transition region and decreased to 0.3-0.5 in the flow region depending on the frequency.

8.3.3.2.3 Time-Temperature Superposition (tTs) Curves of 65004

The master curves of time-temperature superposition (tTs) of the 8-layer PSA-paper geometry of 65004 were generated from the tTs shifting of the curves in Figure 8.21-23 and they are shown in Figure 8.24-26 for the storage modulus, loss modulus and tan delta, respectively. They are constructed in the frequency space and correspond to room temperature by using a computer program based on Williams-Landel-Ferry (WLF) equation. The frequency of the master curves of the 65004 ranges from 1E+12 to 1E-4 Hz and the activation energy was about 36 kcal/mol. These master curves could be used to predict the adhesion performance of 65004 samples in a very large frequency range, especially at some extremely low and high frequencies that cannot be obtained via traditional experiments.
Figure 8.19 PSA 65004 Lap-shear Test

Figure 8.20 PSA 65004 Paper Tensile Test
Figure 8.21 The plot of shear storage modulus versus temperature of 65004

Figure 8.22 The plot of shear loss modulus versus temperature of 65004
Figure 8.23 The plot of shear tan delta versus temperature of 65004

Figure 8.24 The tTs master curve of shear storage modulus vs. temperature of 65004

\[ T_{\text{ref}} = 23^\circ C, \Delta E = 36 \text{ kcal/mol} \]
**Figure 8.25** The tTs master curve of shear loss modulus versus temperature of 65004

**Figure 8.26** The tTs master curve of shear tan delta versus temperature of 65004
8.3.3.3 Sample 65007

8.3.3.3.1 Frequency Sweep / Isothermal Temperature

The shear properties from the frequency sweep/ isothermal temperature tests of the 8-layer PSA-paper sample and the tensile properties of a single bare paper backing sample of 65007 are shown in Figure 8.27 and 28 at nine different frequencies from 0.01 to 100 Hz at room temperature. These data are the average numbers of a number of repeated tests. In Figure 8.27, one can observe the storage modulus and loss modulus increase with increasing frequency. The storage modulus ranges from 0.01 to 0.15 MPa and the loss modulus ranges from 0.01 to 0.04 MPa. Tan Delta decreases with an increase of the frequency, ranging from 0.35 to 0.60 without the transition as shown for 65004. The properties of single bare paper backing sample were quite similar to that of the 65004 sample. But the difference between the lap-shear structure and the bare paper is quite distinct as shown in Figure 8.28.

8.3.3.3.2 Temperature Step / Frequency Sweep

The results of frequency sweep / temperature step tests for the 8-layer PSA-paper sample of 65007 are shown in Figure 8.29-31 for the storage modulus, loss modulus and tan delta at 4 different frequencies over the temperature range from -50 to 60 °C. On each plot, there are three distinct responses representing the glassy, transition and flow regions. From the Loss Modulus versus temperature curves, the glass transition temperatures (T_g) were observed to be -5.08 °C at 0.1 Hz, 5.13°C at 1 Hz, 15.06 °C at 10 Hz and 24.95°C at 100 Hz. The shape of the curves at different frequencies was very similar to each other. Note the curves are shifted to higher temperatures at higher frequency, as in the case with 65004. The shear storage moduli decreased from around 1 MPa in the glassy region to
about 0.1 MPa in the flow region. The moduli obtained in the flow region are consistent with Dahlquist’s criteria for pressure sensitive adhesives. The glass transition temperatures from the peaks in the tan delta versus temperature curves are slightly different from those from the loss modulus curves. The tan delta value increased from less than 0.1 in the glassy region to about 0.6 in the transition region and decreased to about 0.5 in the flow region depending on the frequency.

8.3.3.3 Time-Temperature Superposition (tTs) Curves of 65007

The master curves of time-temperature superposition (tTs) of the 8-layer PSA-paper geometry of 65007 were generated from the tTs shifting of the curves in Figure 8.29-31 and they are shown in Figure 8.32-34 for the storage modulus, loss modulus and tan delta, respectively. They are constructed in the frequency space and correspond to room temperature reference, by using a computer program based on Williams-Landel-Ferry (WLF) equation. The frequency of the master curves of 65007 ranges from 1E+16 to 1E-5 Hz and the activation energy is about 48 kcal/mol. These master curves could be used to predict the adhesion performance of 65007 samples and to compare to other adhesives in a very large frequency range, especially at some extremely low and high frequencies.
Figure 8.27 PSA 65007 8-Layer Lap-Shear Test

Figure 8.28 PSA 65007 Paper Tensile Test
Figure 8.29 The plot of shear storage modulus versus temperature of 65007

Figure 8.30 The plot of shear loss modulus versus temperature of 65007
Figure 8.31 The plot of shear tan delta versus temperature of 65007

Figure 8.32 The tTs master curve of shear storage modulus vs. temperature of 65007

\[ T_{\text{ref}} = 23^\circ C, \Delta E = 48 \text{ kcal/mol} \]
**Figure 8.33** The tT's master curve of shear loss modulus versus temperature of 65007

**Figure 8.34** The tT's master curve of shear tan delta versus temperature of 65007
8.3.3.4 Sample 65010

8.3.3.4.1 Frequency Sweep / Isothermal Temperature

The shear properties from the frequency sweep/ isothermal temperature tests of the 8-layer PSA-paper sample and the tensile properties of a single bare paper backing sample of 65010 are shown in Figure 8.35 and 36 at nine different frequencies from 0.01 to 100 Hz at room temperature. These data are the average numbers of a number of repeated tests. In Figure 8.35, one can observe the storage modulus and loss modulus increase with increasing frequency. The storage modulus ranges from 0.01 to 0.1 MPa and the loss modulus ranges from 0.003 to 0.02 MPa. Tan Delta decreases with the increase of the frequency, ranging from 0.3 to 0.4 with a transition around 5 Hz. The properties of single bare paper backing sample were quite similar to that of the 65004 and 65007 samples. But the difference between the lap-shear structure and the bare paper is also quite distinct as shown in Figure 8.36. The value of Tan Delta is about 0.04, which is 1 order of magnitude lower than 8-layer PSA-paper samples and typical of an elastic material.

8.3.3.4.2 Temperature Step / Frequency Sweep

The results of frequency sweep / temperature step tests for the 8-layer PSA-paper sample of 65010 are shown in Figure 8.37-39 for the storage modulus, loss modulus and tan delta at the same frequencies and in the same the temperature range as that of the 65004 and 65007 samples. Three distinct responses representing the glassy, transition and flow regions are again identified for only the storage modulus curve. The temperatures at which the regions are divided are similar to the 65004 and 65007 samples, but shifted a little to the lower temperatures. From the Loss Modulus versus temperature curves, the
glass transition temperatures ($T_g$) showing as peaks were observed to be -17.50 °C at 0.1 Hz, -10.03°C at 1 Hz, -2.45 °C at 10 Hz and 5.11°C at 100 Hz, respectively. The shape of the curves at different frequencies is very similar to each other. But the curves are shifted to higher temperatures at higher frequency, as the case with of 65004 and 65007. The shear storage moduli decreased from around 1 MPa in the glassy region to about 0.1 MPa in the flow region. The moduli obtained in the flow region are consistent with Dahlquist’s criteria for pressure sensitive adhesives. The glass transition temperatures in the tan delta versus temperature curves are slightly different from those from the loss modulus curves. The tan delta value increased from less than 0.1 in the glassy region to about 0.4 in the transition region and decreased to about 0.3 in the flow region depending on the frequency.

8.3.3.4.3 Time-Temperature Superposition (tTs) Curves of 65010

The master curves of time-temperature superposition (tTs) of the 8-layer PSA-paper geometry of 65010 were generated from the tTs shifting of the curves in Figure 8.37-39 and they are shown in Figure 8.40-42 for the storage modulus, loss modulus and tan delta, respectively. They are constructed in the frequency space that corresponds to room temperature reference, by using a computer program based on Williams-Landel-Ferry (WLF) equation. The frequency of the master curves of 65010 ranges from 1E+16 to 1E-5 Hz and the activation energy is about 48 kcal/mol. These master curves could be used to predict the adhesion performance of 65010 samples and to compare to other adhesives in a very large frequency range, especially at some extremely low and high frequencies.
Figure 8.35 PSA 65010 8 layer Lap-Shear Test

Figure 8.36 PSA 65010 Paper Tensile Test
Figure 8.37 The plot of shear storage modulus versus temperature of 65010

Figure 8.38 The plot of shear loss modulus versus temperature of 65010
Figure 8.39 The plot of shear tan delta versus temperature of 65010

Figure 8.40 The tTs master curve of shear storage modulus vs. temperature of 65010
Figure 8.41 The tTs master curve of shear loss modulus versus temperature of 65010

Figure 8.42 The tTs master curve of shear tan delta versus temperature of 65010
8.3.3.5 Sample 65013

8.3.3.5.1 Frequency Sweep / Isothermal Temperature

The shear properties from the frequency sweep/isothermal temperature tests of the 8-layer PSA-paper sample and the tensile properties of a single bare paper backing sample of 65013 are shown in Figure 8.43 and 44 at nine different frequencies from 0.01 to 100 Hz at room temperature. These data are the average numbers of a number of repeated tests. In Figure 8.43, one can observe the storage modulus and loss modulus increase with increasing frequency. The storage modulus ranges from 0.01 to 0.2 MPa and the loss modulus ranges from 0.007 to 0.02 MPa. Tan Delta decreases with an increase of the frequency, ranging from 0.45 to 0.55 with a transition at around 10 Hz. The properties of single bare paper backing sample were quite similar to that of the 65004 sample. But the difference between the lap-shear structure and the bare paper is quite distinct as shown in Figure 8.44. The value of Tan Delta is about 0.04, which is 1 order of magnitude lower than 8-layer PSA-paper samples.

8.3.3.5.2 Temperature Step / Frequency Sweep

The results of frequency sweep/temperature step tests for the 8-layer PSA-paper sample of 65013 are shown in Figure 8.45-47 for the storage modulus, loss modulus and tan delta at 4 different frequencies over the temperature range from -50 to 60 °C. On each plot, there are three distinct responses representing the glassy, transition and flow regions. From the Loss Modulus versus temperature curves, the glass transition temperatures ($T_g$) were observed to be -14.96 °C at 0.1 Hz, -4.98 °C at 1 Hz, 4.96 °C at 10 Hz and 15.00 °C at 100 Hz. The shape of the curves at different frequencies is very similar to each other. Note the curves are shifted to higher temperatures at higher frequency, as in the cases
with other three samples. The shear storage moduli decreased from around 1 MPa in the
glassy region to about 0.1 MPa in the flow region. The moduli obtained in the flow
region are consistent with Dahlquist’s criteria for pressure sensitive adhesives. The glass
transition temperatures in the tan delta versus temperature curves are slightly different
from those from the loss modulus curves. The tan delta value increased from less than 0.1
in the glassy region to about 0.7 in the transition region.

8.3.3.5.3 Time-Temperature Superposition (tTs) Curves of 65013

The master curves of time-temperature superposition (tTs) of the 8-layer PSA-
paper geometry of 65013 were generated from the tTs shifting of the curves in Figure
8.45-47 and they are shown in Figure 8.48-50 for the storage modulus, loss modulus and
tan delta, respectively. They are constructed in the frequency space and correspond to
room temperature by using a computer program based on Williams-Landel-Ferry (WLF)
equation. The frequency of the master curves of 65013 ranges from 1E+15 to 1E-5 Hz
and the activation energy is about 48 kcal/ mol. These master curves could be used to
predict the adhesion performance of 65013 samples and to compare to other adhesives in
a very large frequency range, especially at some extremely low and high frequencies.

In the temperature step/ frequency sweep testing, the glass transitions of these
PSAs were shown to begin from about – 20 °C to about 10 °C and there is a distinct
transition observed for each frequency and each sample. Only the glass transition of
65007 is nearly 10 °C higher than other three samples under the same frequencies. The
peak value of Tan Delta for 65004, 65007 and 65013 are about 0.6, but the peak value for
65010 is only about 0.4. The activation energy as shown besides the tTs curves is around
48 kcal/mol except that of the 65004 samples, which is about 36 kcal/mol. The results
obtained from frequency sweep / isothermal temperature tests display the significant difference between the dynamical mechanical properties of the 8-layer PSA-paper structure and that bare paper backing. This confirmed that these multiple-layers lap-shear geometry work promisingly in that the mechanical properties of the PSA layer is separated from the mechanical properties of the backing paper. The results of DMA testing for these four samples are very similar to each other, it indicates that the adhesion performance of these PSAs for postage stamp applications resemble each other.

Figure 8.43 PSA 65013 8 layer Lap-shear Test
Figure 8.44 PSA 65013 Paper Tensile Test

Figure 8.45 The plot of shear storage modulus versus temperature of 65013
Figure 8.46 The plot of shear loss modulus versus temperature of 65013

Figure 8.47 The plot of shear tan delta versus temperature of 65013
Figure 8.48 The tTs master curve of shear storage modulus versus temperature of 65013

Figure 8.49 The tTs master curve of shear loss modulus versus temperature of 65013
8.4 CONCLUSIONS

The lap-shear geometry with multiple layers is proven as a reliable testing method which utilizes the dynamical mechanical properties of polyacrylic pressure sensitive adhesive (PSA) for characterization. The effect of thickness on dynamical mechanical properties for testing sample has been investigated and the results indicated that the multi-layer geometry with 5-10 layers could be an appropriate structure for DMA tests in order to get enhanced responses. The results of DMA testing indicate the frequency and temperature responses of these PSAs were very similar with one another. Time-temperature superposition curves have been produced at room temperature according to the temperature step/ frequency sweep tests on DMA. Those curves could be used to predict either the short-term or long-term performances of these PSAs when applied in a postage stamp adhesive. This method can be developed to be a standard testing method.

Figure 8.50 The tTs master curve of shear tan delta versus temperature of 65013
on the PSA adhesives in the laminate form. It can also be developed as a general standard method on testing adhesives, polymer melts and other materials replacing the more expensive and more difficult-to-maintain rheometers.
REFERENCES (II):


Vita

The author, Hailing Yang, was born in Sichuan, China on March 29, 1974. Hailing Yang went to Tianjin University in 1992. She was enrolled in the Polymer Chemical Engineering Department to study his favorite major, polymer science. She earned her Bachelor’s degree in June 1996. After that, she attended The National Research Institute of Silicone as a research assistant. In December 1999, she came to United States to reunion with her husband, who enrolled at Chemical Engineering Department at University of Maine as a graduate student in Orono, ME. Shortly after that, they move to Blacksburg, VA.

In the fall of 2001, she enrolled in Virginia Polytechnic Institute and State University with Professor Thomas C. Ward’s group to pursue her Ph.D. study at Department of Chemistry. Here, her research interest is to understand the adhesion phenomena of polymers at different length scales. She will join in Advanced and Applied Polymer Processing Institute at Institute of Advanced Learning and Research in Danville, VA after her graduation.