

Thermal Bonding of Nonwovens as Simulated by Polypropylene Films: Effect of Time, Temperature, and Molecular Weight

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Received 22 May 2009; accepted 27 July 2009

DOI 10.1002/app.31220

Published online 6 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Many nonwoven fabrics are made by melt spinning semicrystalline fibers followed by thermal bonding using heated calendar rolls. In this work, we have studied thermal bonding of polypropylene films to simulate bonding of nonwoven fibers. We have tried to relate the thermal bond strengths with the concepts of chain dynamics via interfacial adhesion development at symmetric polymer interfaces. This requires relating the microscopic dynamics of chains with macroscopic interfacial adhesion measurements. It was found that the interfacial bond strength was proportional to the fraction of the crystals melted. This required heating the interfacial region between the polymer layers into the melting

region. Bond strengths were also related to process time as $t^{1/2}$. This dependence is consistent with the literature for reptation, but is also due to the required thermal diffusion to bring the interfacial region to the bonding temperature. Finally, the bond strength is also dependent on the polymer molecular weight as $1/M^{1/2}$, which is consistent with forming the bonds via chain reptation, provided that the bonding time is less than the reptation time. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3322–3330, 2010

Key words: nonwovens; polypropylene; thermal bonding; reptation; molecular weight

INTRODUCTION

Thermal bonding, also known as “calendar,” is one of the most popular methods for bonding nonwoven fabrics. It employs direct contact of the fibers with heat and sufficient pressure to produce localized bonding in nonwovens. Factors that dictate the properties of calendar-bonded nonwoven fabrics can be broadly categorized as process-related, fiber related and polymer related.¹

Previous studies indicate that thermally bonded nonwoven fabric strengths rise to a maximum and then fall as bonding temperature is raised, or as the contact time rises.¹ Rationale for such behavior has been supported in qualitative terms where fundamental understanding of the polymer physics is lacking. An overview of the literature is presented to assist the reader in deriving useful and relevant interrelations between fracture energy, polymer chain reptation and diffusion, entanglements and

bond strengths during thermal bonding of nonwovens.

Bonds formed during the process of thermal bonding in nonwovens can be classified into three types, i.e. under-bonded, over-bonded and well-bonded. Wang and Michielsen² analyzed the changes that occur at the bond periphery in thermally point bonded nonwovens. For under-bonded fabrics, the fabrics fail at low stress since the bonds simply pull apart. Over-bonded fabrics also fail at low stress; however, in over-bonded fabrics the failure occurs at the bond periphery. Although well-bonded fabrics also fail at the bond periphery, their strength is much higher than those which are over-bonded. In their review of bonding in thermally point bonded nonwovens Michielsen et al.¹ suggest that bonding occurs through partial melting of the crystals, diffusion of the released chain ends across the interface, entanglement with the polymer chains on the opposite side of the interface, and recrystallization of the polymer to entrap the polymer chains. To understand the molecular aspects controlling thermal bonding, we examine the effect of the process variables as well as the dynamics of the polymer chains affecting the bonding strengths.

The dynamics of chain motion in a polymer with particular application to the rheological properties of polymer melts was developed by de Gennes³ and Doi and Edwards.⁴ This theory was described as the

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Contract grant sponsor: Nonwovens.

reptation theory and included entangling of random coil chains. Interfacial strength development at a symmetric polymer-polymer interface depends on the structure formed during welding or bonding and is related to the dynamics of the chains that attempt to diffuse across the interface.^{5,6}

Relating pressure and bond strength

Although Warner⁷ has stated that the melting point of isotactic polypropylene is raised by $\sim 15^\circ\text{C}$ at pressures used in thermal bonding of nonwovens, such an effect has not been observed elsewhere in literature. Michielsen et al.¹ have reported that the main effect of pressure is to compact the web for efficient heat transfer via conduction. Beyond this pressure, there appears to be little effect on bond strength. In the work reported in this article, thin polymer films have been used to simulate nonwoven webs, primarily to simplify the data analysis and interpretation. Since there is no web to consolidate, the effect of pressure on bonding will not be discussed further in this article.

Relating nip time and bond strength

Warner also reported that the time, t , taken by a nonwoven web in the nip is:⁷

$$t = [R(C_0 - G)^{1/2}]/S \quad (1)$$

where R is the radius of the calendar roll, S is the surface speed of the roll, C_0 is the initial thickness of the web and G is the nip gap between the surfaces of the rolls. Michielsen et al.¹ found that the time range to compress, heat and bond the web is typically between 6 and 60 ms, depending on the line speed. During the time spent in the nip, the material must heat up and form the bond, which requires that the polymer chains diffuse across the interface.

Wool⁶ related the time dependence of bond strength with reptation theory for two uncrosslinked elastomers as well as glassy polymers.⁵ These experiments were conducted on two pieces of the same amorphous polymer brought into contact above the glass transition temperature (T_g). De Gennes³ reported such experiments led to interdiffusion and mechanical strength development. For welding, the intersecting time interval is usually smaller than the reptation time and has been measured using the time dependence of the fracture energy of the bonded or welded polymers.

Fracture energy has been found to be a direct indication of strength at the polymer interface⁸ and has been used by several authors to relate the bond strength to molecular entanglements at the interface.⁹⁻¹² Fracture tests performed by Wool revealed

that the fracture energy release rate at time t , $G(t)$, saturated after one reptation time, τ_r , and increased at earlier times according to the equation:

$$\begin{aligned} G &= G_{\max}(t/\tau_r)^{1/2} & \text{for } t \leq \tau_r \\ G &= G_{\max} & t > \tau_r \end{aligned} \quad (2)$$

Thus, it appears that reptation leading to entanglements promotes adhesion. Furthermore, Wool⁶ found that the maximum strength of the bond occurs at $t = \tau_r$ for polymer molecular weight $M \leq 8M_c$ where M_c is the critical molecular weight (M_c). However, Wool's analysis applies directly only to noncrystalline polymers and involves molten polymer chains. In thermal bonding of nonwovens, semicrystalline polymers are bonded at temperatures at which the polymer does not completely melt to prevent the polymers from sticking to the rolls; hence modification of Wool's theory is required.

Michielsen et al.¹ reported that for a noncrystalline isotactic polypropylene (iPP) chain having molecular weight $M = 8M_c$, the reptation time is between 2.5 and to 8.8 ms at 132°C . These times are similar to the time that nonwoven webs spend in the nip of a calendar. They claim that a strong bond can form in a partially melted semicrystalline iPP nonwoven web if a sufficient fraction of the iPP chains are melted at the bonding temperature.

Relating molecular weight and bond strength

The reptation time of a molten polymer is proportional to the third power of the molecular weight, $\tau_r \propto M^3$. Thus, the bond strength should depend on the molecular weight. However, Wool found that the molecular weight dependence of the bond strength was more complicated. At very long bonding times ($t \gg \tau_r$):

$$\begin{aligned} G_{\max}(M) &\sim 0 & M < M_c \\ &\propto (1 - [M_c/M]^{1/2})^2 M/M_c & M_c < M < 8M_c \\ &\propto M^0 & M > 8M_c \end{aligned} \quad (3)$$

To understand the relation of reptation time and molecular weight, we note that at a polymer-polymer interface, such as polypropylene-polypropylene, the diffusion of the chains to a distance radius of gyration (R_g) is necessary and sufficient to attain the interpenetrated structure of the original state of the melt.⁶ The time to achieve this level of interpenetration can be denoted as the welding time (t_w) which Wool showed was the same as the reptation time (τ_r). Therefore, when M is greater than M_c , indicating highly entangled polymer melts, the welding time is:

$$t_w = \tau_r \propto M^3 \quad (4)$$

Thus it may be inferred that small differences in molecular weight can have a large effect on the time needed to achieve the optimum weld conditions through reptation. This can be extended to infer that small changes in molecular weight can affect bonding significantly.

Wool⁶ reported that there is a strong analogy between development of adhesive strength at the interface and the molecular weight dependence of the fracture toughness of amorphous polymers. However, in the case of semicrystalline polymers, the presence of the crystalline phase can prohibit the use of linear fracture mechanics. In our work the effect of polymer molecular weight on bonding has been determined keeping in mind the significant influence of polymer chain diffusion and entanglements on bond strengths.

Relating temperature and strength

Experiments performed by Bhat et al.¹³ on thermally bonded polypropylene webs indicated that the web strength increases with bonding temperature up to a maximum and then decreases. They concluded this result was due to a change in the failure mechanism.

It has been observed¹ that at high temperature or low calendar speed the fibers break at the bond edge and are over-bonded. Wang and Michielsen² showed that these fibers have a lower modulus in the vicinity of the bond. Upon stretching, this region deforms more than the remainder of the fiber, which retained its original modulus. These fibers subsequently break at the bond edge. They found that morphology changes in the vicinity of the bond are larger and have steeper gradients at high temperatures. However, at low temperatures or high calendar speeds, the fibers in the nonwovens remained under-bonded; the bonds are not fully formed and hence are pulled apart at low stresses in agreement with Bhat et al.¹³

Relating fracture energy and crystallization temperature

It is known that semicrystalline polymers crystallize when they are processed between their glass transition temperature, T_g , and melting temperature (T_m). This takes place with nucleation and growth of spherulites, which affect and alter the failure mode. The development of crystals with a chain-folded structure reduces the entropy of the polymer near the interface. Hence it may act as a barrier limiting the interdiffusion of polymer chains. The competition between interdiffusion and crystallization makes it difficult to interpret the failure modes for semicrystalline polymers. Lo¹⁴ developed a kinetic model to explain the behavior at semicrystalline polymer

interfaces taking into account the effect of crystallization, miscibility and interdiffusion. The rate of crystallization is based on the Avrami equation and the mutual diffusion coefficient is obtained from fast mode theory.

For symmetric interfaces, the polymers are identical and self-diffusion is responsible for the behavior at the interface. Wool⁶ derived a scaling law for thickness at the interface using the minor chain reptation model. According to De Gennes³ for times less than the reptation time, τ_r , interdiffusion at the interface is obstructed by the neighboring chains. When time $t > \tau_r$, the minor chains are free to move through the interface and in such a case the interfacial width becomes a function of the self-diffusion coefficient.

The primary objective of this research is to understand adhesion development at a semicrystalline polymer interface. Process control of interfacial adhesion is to be obtained by inter-relating the effects of calendar temperature, speed and polymer molecular weight. To accomplish this we discount the fiber morphology related factors by considering polymer films instead of fibers. By subjecting polymer films of several molecular weights to the two prime process-related factors i.e. temperature and time we have endeavored to determine the polymer physics behind the thermal bonding process.

EXPERIMENTAL

The polymers used in this study were obtained from Sigma-Aldrich (St. Louis, MO). They consisted of several molecular weights of polypropylene pellets, ranging from 95,000 g/mol to 580,000 g/mol. The theoretical M_c for polypropylene is 7000 g/mol.¹⁵ These molecular weights were chosen such that their values were higher than $8M_c$. All chemicals were used as received and had minimal or no additives present. This was important, since the presence of additives would alter the results for interfacial strengths developed at the polymer interfaces. These polymer pellets were then converted into polymer films using a single screw extruder (courtesy of Sunoco Chemicals). The processing system used was a Haake Rheocord 9000 with a T type film die. The films formed had an average thickness of 124 microns with a standard deviation of 15 microns.

The polymers were characterized using differential scanning calorimetry (DSC) to determine their melting isotherms, onset of melting and peak melting points. Gel permeation chromatography (GPC) was performed courtesy of Sunoco Chemicals to determine the weight average molecular weight, number average molecular weight and the molecular weight distribution of the polypropylene polymers.

Simulating bonding

The polypropylene films were thermally bonded in a Kannegiesser fusion bonder. The thermal bonds produced were tested using the T-peel test. Strips of the sample iPP film to be bonded were cut to a dimension of 15.2×2.54 cm (6×1 in.). Two strips were placed face-to-face and passed between the rolls of a Kannegiesser fusion bonder. Bonding was done at predetermined temperatures, pressures and calendar speeds. A small piece of nylon film was also placed between the strips at one end to facilitate separation of the ends so that they could be inserted into grips for mechanical testing of bond strengths. To prevent melting and subsequent sticking of the iPP films to the rolls at higher temperatures, they were enveloped within a nylon-6,6 film. This did not affect the interfacial bonding between iPP films, since at these temperatures nylon-6,6 has almost zero adhesion with iPP. The temperature at the interface was measured using temperature sensitive thermo-labels (Paper Thermometer Company). The labels consisted of temperature rows ranging from 99 to 182°C at regular intervals of 6°C each. A particular temperature row on the label turned black when its temperature was equal to the temperature at the interface. A slight variation within $\pm 3^\circ\text{C}$ of the set temperature was observed.

Bond strength measurements

The samples were tested for bond strengths in an Instron[®] mechanical tester. Previously thermally bonded samples were tested in the T-peel configuration for interfacial adhesion development. The ASTM D1876-01 was used as a guide for testing. Depending on the magnitude of the bond strengths expected, ± 100 N and ± 2 kN load cells were used. The film ends from each side of the bonded interface were clamped in the grips of the Instron[®] at a gauge length of 15 mm. The Instron[®] then peeled the specimen apart at a crosshead speed of 6 mm/min. Since the film thickness was in the μm scale, the error that may have been produced due to bending of the films was negligible. The load was observed until the specimen failed or until it peeled to an extension of 100 mm. A plot of load vs. extension was obtained and analyzed for bond strength using SAS 9.1.

Temperature effect

To understand the influence of temperature on interfacial adhesion, the remaining three variables i.e. pressure, speed and molecular weight were held constant. The calendar pressure was maintained at four bars and speed was fixed at 8 m/min. Tests

were conducted on polypropylene of molecular weight 177,000 g/mol. The temperature of the calendar was varied between 110°C and 160°C for intervals of 10°C. A total of 60 samples were tested to determine the effect of temperature on bond strengths.

Speed effect

The influence of speed on interfacial adhesion was analyzed by varying the calendar speed between 4 and 10 m/min. The pressure was maintained at four bars and polypropylene of molecular weight 177,000 g/mol was tested. After obtaining pertinent data from the temperature series, the effect of speed was tested between the temperature range of 145–165°C. The calendar speed was chosen to be 4, 6, 8 or 10 m/min. A total of 55 samples were tested to determine the effect of speed on bond strengths.

Molecular weight effect

After analyzing the effect of calendar temperature and calendar speed on bond strengths, we were able to reduce the range of processing parameters to determine the effect of polymer molecular weight. Initially a custom design approach was employed using the design of experiments feature in JMP 6.0. A design was generated such that the effect of polymer molecular weight on interfacial strengths could be studied with a minimum number of trial runs. For this design temperature, speed (corresponds to time in calendar) and molecular weight were selected as the continuous variables. The temperature range considered was between 145 and 155°C; the speed was 6, 8, and 10 m/min; and the molecular weight range was between 177,000 and 499,000 g/mol. Because of sample restrictions, 12 runs were chosen. A total of 60 samples were tested.

Data obtained from the above experiments helped us narrow our processing parameters for temperature, speed and molecular weight. Hence specific full factorial experiments were designed in JMP 6.0 for the entire range of molecular weights at temperatures of 150 and 152.5 and 155°C and for average speeds of 6, 8, and 10 m/minute. A total of 75 samples were tested under these conditions.

The experimental setup was further modified for each set of trials such that one sample of each molecular weight along with a temperature indicator were all passed through the thermal calendar at the same time. This helped nullify any inaccuracies due to the calendar heaters going on/off during a single bonding process. Further the sample position was rotated for every run to eliminate any errors due to varying temperatures across the calendar width. This setup ensured identical process conditions

throughout the molecular weight series, thus successfully isolating differences in strengths to be a function of molecular weight alone.

RESULTS AND DISCUSSIONS

As discussed earlier, three parameters were studied in this work: bonding temperature, bonding time, and the molecular weight of the polymer being bonded. We begin by describing how the data was analyzed followed by examining each factor in sequence.

Data interpretation

After thermally bonding, samples were tested for bond strengths using the T-peel test, ASTM D1876-01, as a guide. Bond strengths were used to represent the interfacial adhesion and were extracted from the load vs. extension data produced during testing. To obtain bond strengths, the graph of load vs. extension was plotted for each sample and local peak values obtained from the curve were recorded. Although ASTM D1876-01 uses the average load after the first peak as the adhesive strength, we chose to use the average of several peak loads. When we examined the individual specimens, we noticed that the peak load occurred where bonding was most uniform and thus should be a better measure of the true bond strength. However, from Figure 1, it is clear that the trends in the strength will be the same whether we choose the average or the peak loads.

Since experiments were conducted for a range of calendar temperatures, speeds and polymer molecular weights, the number of peaks produced varied considerably depending upon the process conditions. To extract the peak strength values, SAS 9.1 statistical software was used. Several thousand data points were produced having a data acquisition time of 20 ms. For each data set the local peak value was found by scanning the first 200 data points and a provisional local maximum was identified. This value was compared to the 200 points before and after it and this process was continued to find the true local maximum. Once verified, it was designated as the local maximum value and the analysis proceeded to the next 200 data points. As the analysis progressed it was realized that under different process conditions the number of peaks varied. Hence a counter was incorporated in the program that could be varied depending on the number of peaks present in the data. For example, if there were few peaks present and they were close together, the counter was set to a low value of 100. In such a case, the program located a maximum with respect to 100 data points adjacent to it and denoted it as a peak.

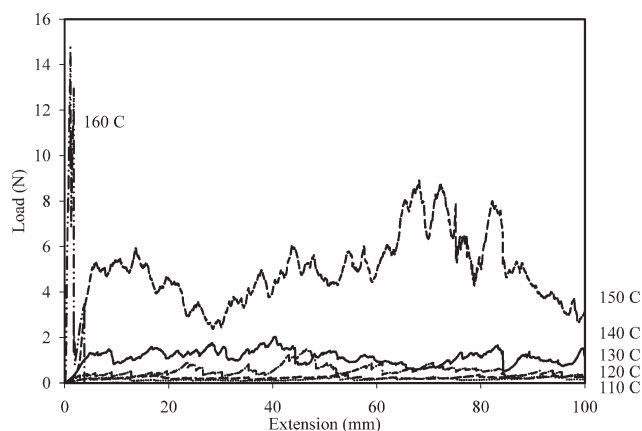


Figure 1 Nature of curves produced for a single set of process conditions to determine the effect of varying temperatures on bond strengths for $M_w = 177,000$ g/mol bonded at a speed of 8 m/min and 4N pressure.

On the contrary, if several peaks were present and they were spaced far apart from one another, then the counter was set to 500 and the peak was assigned to the maxima with respect to 500 adjacent data points. The mean value of the local maxima as well as standard deviation was calculated and used for the bond strength.

Effect of temperature on interfacial bond strengths

To determine the effect of varying calendar temperature on bond strength, the calendar pressure, speed and polymer molecular weight were maintained constant as described in the experimental section. The interfacial adhesion results obtained after the T-Peel test are shown as bond strengths in Figure 1 within the temperature range of 110–160°C.

For lower temperatures, 110–130°C, the strength of the bond was very weak, i.e. below 1 N. At 140°C, the bond strength increased to about 3 N. Further at 150°C, the bond strength increased further to about 4.3 N. For even higher temperatures, i.e. in the vicinity of 160°C, the polymer film exhibited film failure at more than 15 N during the T-peel test. Figure 2 illustrates the interfacial adhesion results for all 60 polypropylene films bonded at temperatures between 120 and 150°C. It is clear that there is a sharp increase in bond strength between 130 and 150°C, which agrees with work done by Michielsen et al.¹ who indicated that thermal bonding requires the interfacial temperature at the midpoint between the films to be equal to or greater than $\sim 132^\circ\text{C}$.

The trend in interfacial strength observed can also be related to DSC data for isotactic polypropylene. The DSC reveals an onset of melting occurring at 130°C with a peak melting point observed at $\sim 160^\circ\text{C}$. Below 130°C the polymer chains remain entrapped in crystals. Once the onset of melting is

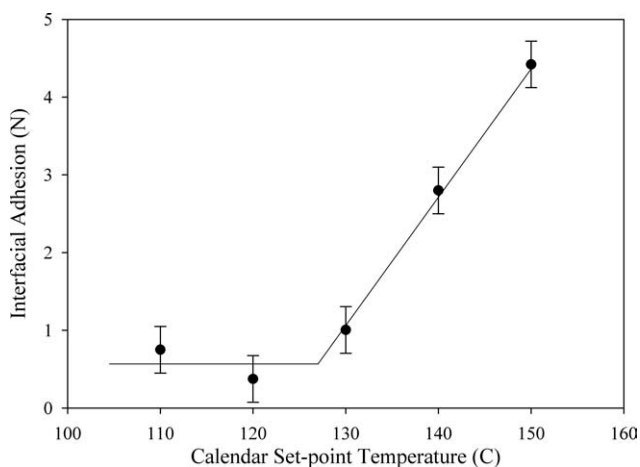


Figure 2 Interfacial adhesion measurements as a function of calendar temperature for iPP of $M_w = 177,000$ g/mol.

reached, the polymer crystals begin to melt and the chains begin to reptate. With an increase in temperature, the crystal fraction melted is greater and the bond strength is higher such that at 160°C the strength of the bond is greater than or equal to the film strength.

Effect of speed on interfacial bond strengths

To determine the influence of bonding time on the bond strength, a series of tests were run at bonder speeds of 6, 8, and 10 m/min and temperatures of 145, 150, and 155°C with a constant compressive load of 4N. For bonding temperatures of 145°C and below, the bond strengths are low and there is no clear trend in the bond strength. At temperatures above 155°C, the films broke during the T-peel test indicating that the bond strengths were as strong as

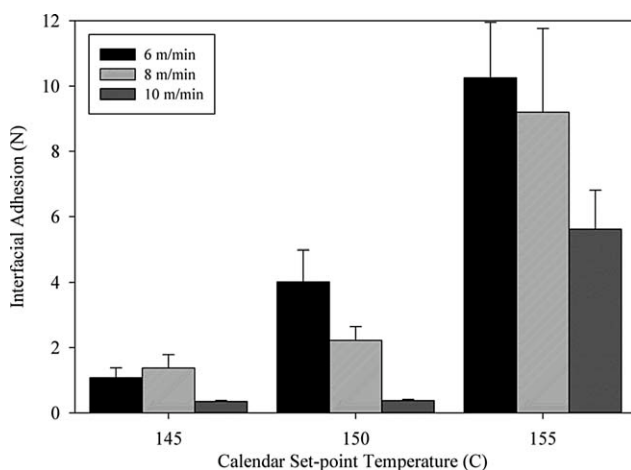


Figure 3 Effect of increase in speed at different temperatures averaged throughout the molecular weight ranging from 177,000 to 499,000 g/mol.

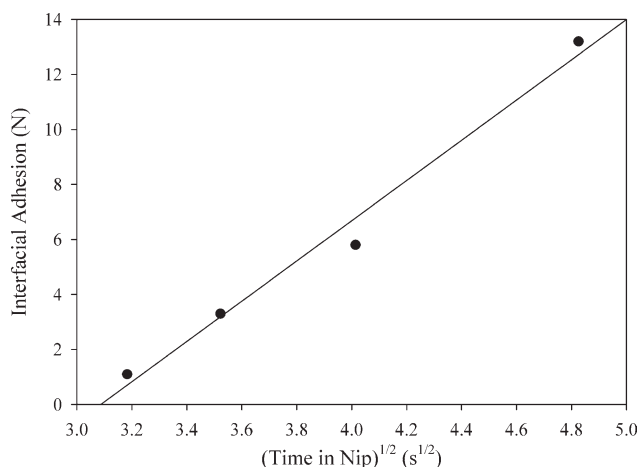


Figure 4 Interfacial adhesion vs. time spent by the polymer in the calendar nip at temperature 150°C for $M_w = 177,000$ g/mol.

the films. However, at 150 and 155°C, the bond strengths varied with speed. The strengths dropped rapidly as the speed increased (see Fig. 3.) The time dependence of bond formation was obtained at constant polymer molecular weight, 177,000 g/mol, and bonding temperature, 150°C. The time spent by the polymer in the heating zone of the calendar was measured with a stop watch. The bond strengths exhibit a good correlation with $t^{1/2}$ as shown in Figure 4. This relationship is exactly what is expected for reptation and for thermal diffusion. Both processes are involved in bond formation.

For bonding to occur, the polymer chain ends must reptate across the interface, entangle and co-crystallize there. From eq. (2), this should depend on $t^{1/2}$. The linear dependence of interfacial adhesion with $t^{1/2}$ in Figure 4 is consistent with previous work done by several authors.¹⁶⁻¹⁹ Guerin et al.¹⁹, Wool,⁶ Boika and Lyngaae-Jorgensen⁸ and Jud et al.²⁰ all observed a linear dependence of adhesive energy with $t^{1/2}$. These behaviors are in agreement with the minor chain diffusion model. Thus our results are consistent with work done by previous studies and suggest that reptation induced by the release of chain segments due to partial melting plays a significant role in interfacial adhesion enhancement. (We note that the reptation time depends on temperature primarily through the bead friction. Since the beads are the same for all molecular weights, the temperature dependence of the reptation time should be nearly independent of molecular weight.)

However, as shown in the temperature dependence section, the temperature of the material being bonded is also an important factor in developing interfacial adhesion. Bonding requires thermal diffusion from the film surface to the interior, which also

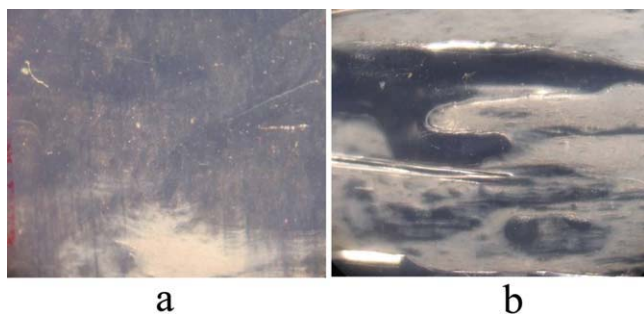


Figure 5 Melted bond area observed at 30 \times magnification for temperature 150 $^{\circ}$ C, speed of (a) 10 m/min and $M_w = 177,000$ g/mol, or (b) 4 m/min and $M_w = 177,000$ g/mol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

depends on $t^{1/2}$. This was illustrated by examination of Figure 5, which shows optical microscope images of the polymer interface at 30 \times magnification taken after interfacial adhesion testing. Figure 5(a) shows the interface near the location where the bond strength was maximum for a specimen bonded at 10 m/min, i.e. when the time spent by the polymer in the nip was 9.4 seconds. Observe that the amount of polymer melted is much less than that shown in Figure 5(b), which spent 24.6 seconds in the nip (bonding speed = 4 m/min). This indicates that more melting and greater bond strengths develop for longer times spent by the polymer in the calendar nip. With more melting, more chains are released from the crystal and are available to cross the interface and form strong thermal bonds. On the contrary, a lower residence time (i.e. 9.4 sec), does not allow sufficient time for sufficient heat to diffuse into the bonding zone to melt the polymer in this region, thus leaving the chains locked in the iPP crystal structure. This leads to lower bond strengths. Note, however, that if too much melting takes place, overbonded conditions result causing the polymer interface to fail via tensile tear, as observed at bonding temperatures of 155 $^{\circ}$ C or higher.

To better understand the roll of time in thermal bonding and to separate the heating effect from the molecular diffusion effect, thermally sensitive labels were placed alongside of the specimens while bonding to determine the interfacial temperature reached during bonding. The temperatures measured by the thermo-labels were used to extract the fraction of the polymer that had melted based on DSC melting curves. From the DSC analysis, the fraction of iPP melted was calculated for each molecular weight. The onset of melting as well as the melting points was found to be similar within the range of molecular weights tested (i.e. 177–499 kg/mol). The temperature for the maximum rate of melting was found to be $\sim 159^{\circ}$ C with an onset of melting $\sim 140^{\circ}$ C and

complete melting at 165 $^{\circ}$ C. By integrating the area under the curve for various temperatures, the fraction of iPP melted was found for each temperature measured by the thermo-labels and the fraction of the polymer that was melted is graphed vs. temperature in Figure 6.

From this, we infer that at $\sim 140^{\circ}$ C, the fraction melted is ~ 0 . For a 5 $^{\circ}$ C increase in temperature from 140 to 145 $^{\circ}$ C, the fraction of iPP melted was only 0.05 or 5%. For a further 5 $^{\circ}$ C increase the melting increases to 0.15 (15%) at 150 $^{\circ}$ C. Beyond 150 $^{\circ}$ C the fraction of iPP melted increased rapidly such that at 155 $^{\circ}$ C, it more than doubles to 0.37 (37%). This can be understood easily by noting that in semicrystalline polymers the motion of the chain is restricted by the crystals. If X_{cr} is the fraction of crystalline material at room temperature, then $1 - X_{cr}$ is the fraction of the free chain segments in the non-crystalline region. As the temperature is raised towards the melting point T_m , the fraction of the free chain segments increases such that at 165 $^{\circ}$ C, the fraction of these segments is ~ 1 . Based on the temperature readings obtained from the thermo-labels, the actual fraction melted for a combination of temperatures and speeds are shown in Table I. These values were graphed with the interfacial adhesion values to obtain Figure 7, which reveals that the strength at the polymer interfaces is clearly a function of the polymer interfacial temperature and not the set calendar temperature. This is because at higher speeds the polymer interface does not reach the set calendar temperature; hence the crystal fraction melted is less than expected, resulting in lower interfacial strengths. Consequently the above result indicates that the $t^{1/2}$ dependence of the interfacial strength in the thermal bonding process described in this work is primarily due to thermal diffusion. However, molecular diffusion via reptation must still play a role.

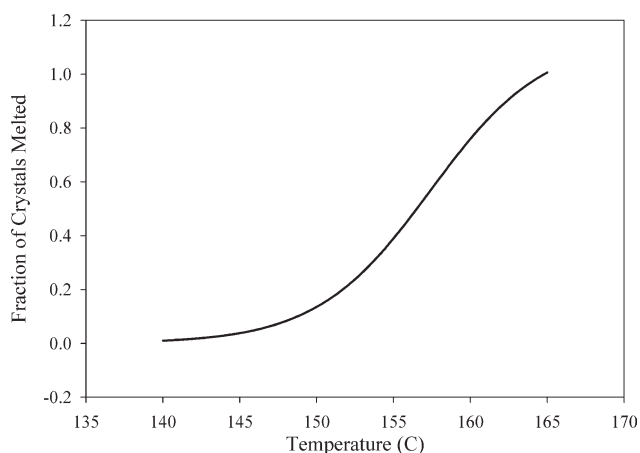


Figure 6 Fraction of iPP melted at each temperature from DSC analysis for M_w 177, 223, 304 and 499 kg/mol.

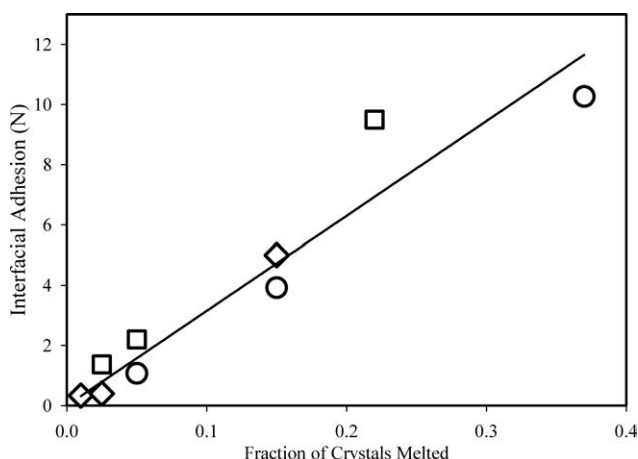


Figure 7 Interfacial adhesion vs. the bonding temperature as measured by the thermolabels. Samples were bonded at 10 (diamonds), 8 (squares), and 6 (circles) m/min.

Effect of polymer molecular weight on interfacial bond strengths

The sections above detail the individual effect of temperature and speed on interfacial adhesion, independent of molecular weight. However, eqs. (2)–(4) indicate that the interfacial adhesion should also be a function of molecular weight. To test this iPP films of molecular weights between 177 and 499 kg/mol were bonded and the bond strengths measured. Size exclusion chromatography was used to obtain the molecular weights and the results are listed in Table II (Courtesy: Sunoco Chemicals). An additional sample with a molecular weight of 95,000 g/mol was bonded and tested for strengths, but the polymer films were very brittle and snapped at the testing grips making it impossible to measure the interfacial strength.

Figure 8 shows the interfacial adhesion for the four molecular weights used for this study. The temperature was kept constant at 150°C and the calendar speed was 8 m/min. For times greater than the reptation time, eq. (3) indicates that the interfacial adhesion should increase with molecular weight if $M_c < M < 8M_c$. If $M > 8M_c$, the interfacial adhesion should be independent of molecular weight. For iPP

TABLE I
Crystal Fraction Melted for Various Calendar Speeds and Temperature

	Speed (m/min)		
	6	8	10
Temperature (C)	Fraction melted		
145	0.05	0.025	0
150	0.15	0.05	0.025
155	0.38	0.22	0.15

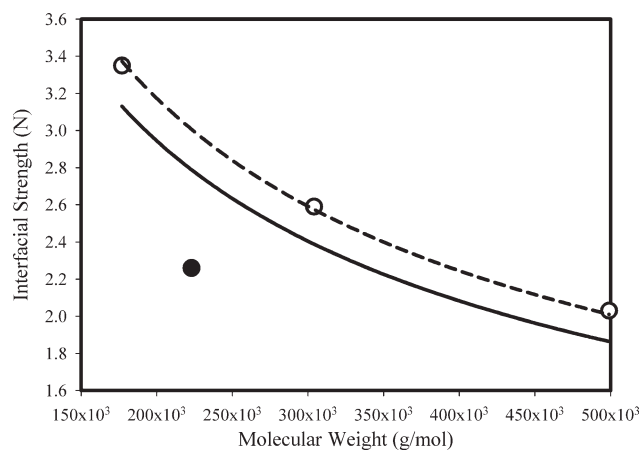


Figure 8 Interfacial strength is shown as a function of the molecular weight. Solid curve is a regression fit to all of the data to the function $G = a/M^{1/2}$. Dashed curve is a regression fit excluding the solid point.

M_c is 7000 g/mol.¹⁵ It is clearly evident that the interfacial strength decreases with increasing molecular weight, so the bonding time must be less than the reptation time. In this case, Wool predicted the interfacial strength should behave according to eq. (2). However, according to eq. (4), the reptation time is a function of molecular weight. Wool²¹ suggested that, for consistency with the reptation model, the fracture energy, G_{IC} , (synonymous to interfacial adhesion) can be expressed as a function of time (t) and molecular weight (M) as:

$$G_{IC} \propto t^{1/2}/M^{1/2} \tag{5}$$

The relationship, $G_{IC} \propto t^{1/2}$, is consistent with our experimental results and is discussed in the previous section. The interfacial adhesion vs. the weight average molecular weight, M_w , is shown in Figure 8 along with the best fit to:

$$G_{IC} = C/M^{1/2} \tag{6}$$

where C is a fitting constant and the bonding time is kept constant (solid line). The dashed curve in Figure 8 is the fit of eq. (6) excluding the filled circle.

TABLE II
Size Exclusion Chromatography Results for iPP (in kg/mol)

Nominal M_w^a	M_n	M_w	M_z	M_{z+1}
177	21.7	95		
250	50.5	177	403	718
340	63.1	223	737	1619
580	119	304	976	2122
		499	1529	2960

^a As provided by Sigma-Aldrich.

Thus our data is consistent with the analysis by Wool and O'Connor if it is assumed that the bonding time is less than the reptation time.

At first glance, the molecular weight dependence observed and the agreement with Wool and O'Connor is surprising since the films in our study are semicrystalline and only 15–40% of the crystals have melted in these experiments. However, according to the DSC results, all of the materials studied had nearly the same melting enthalpy and thus, nearly the same percentage crystallinity. In this case, the length of the free chain ends released from the crystals should be linearly related to the molecular weight used for the film and the reptation times should still scale as $1/M_w^{1/2}$. Further analysis of this data is not warranted at this time.

Thus, it has been shown that the interfacial bond strength is proportional to $t^{1/2}$ and $1/M^{1/2}$. It is also proportional to the fraction of crystals that have melted.

CONCLUSIONS

In this work we have endeavored to determine the individual and inter-related effects of the calendar temperature, time and polymer molecular weight on interfacial strengths. In semicrystalline polymers, the chains are trapped by the crystalline structure, which hinders their motion. With an increase in temperature these crystals partially melt releasing chain segments which are now available to reptate and diffuse across the interface to form entanglements with the polymer chains across the interface. We found that the most important role of temperature in thermal bonding was its effect on the fraction of the polymer that melts, thus releasing the chains from the crystals. Our experiments demonstrated that interfacial bond strengths are a function of the temperature reached by the polymer at the interface between the layers and not the temperature set point of the calendar. To obtain significant bond strengths, the temperature must be in the proximity of the melting point for the polymer. Our experiments with polypropylene indicate that significant adhesion is achieved when the interfacial temperature is between 150°C and 155°C.

Further, the calendar speed must be adjusted such that the polymer spends sufficient time in the calendar nip to allow the interfacial temperature between the films to be high enough to melt a significant fraction of the crystalline phase. The time must be sufficient to partially melt the crystal and induce the release of chain segments. Our experiments revealed bond strengths had $t^{1/2}$ dependence. This depend-

ence is expected for both thermal diffusion for heating the interface and for reptation of chains leading to diffusion across the interface took place to form entanglements. Literature in this area confirms that for times equal to and greater than the reptation time, entanglements are the primary source of adhesion and that diffusion is the mechanism by which the chains cross the interface.

Finally, we found that for iPP, the interfacial adhesion had a $1/M^{1/2}$ on the molecular weight over the range 177,000 to 499,000 g/mol. This is consistent with Wool's reptation model for bonding.

To achieve high interfacial strength during thermal bonding, one should use the lowest molecular weight that gives adequate tensile properties, bonding temperatures that are high enough to melt several percent of the crystalline phase and at speeds low enough such that the interfacial region between the materials being bonded reach the desired temperature.

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