Melt versus Solvent Coating: Structure and Properties of Block–Copolymer-Based Pressure-Sensitive Adhesives

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ABSTRACT: Pressure-sensitive adhesives (PSAs) composed of a styrene–isoprene–styrene triblock copolymer and a midblock-associating resin were prepared via solvent and hot-melt coating. The formulations and thermal histories up to the point of coating were identical, yet significant differences in the properties were observed as a function of the coating method. The solvent-coated PSA showed superior shear holding power, and the hot-melt-coated PSA performed better in tack and peel tests. Two factors resulting from the processing conditions were responsible for these property differences. The quick cooling process occurring after hot-melt coating led to a poorly defined microstructure and, therefore, less physical crosslinking. Rheological data for melt-pressed and solvent-cast PSA films confirmed these microstructural differences. The increased solubility of the tackifier in the solvent additionally created a composition gradient in the solvent coating. Annealing improved the long-range order of both hot-melt and solvent coatings, producing a body-centered cubic microstructure identified by small-angle X-ray scattering. This microstructure improved the shear strength of both types of adhesive coatings, whereas the peel and tack properties of the solvent coatings remained inferior to those of the hot-melt coatings because of differences in the surface compositions. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3355–3367, 2002

Key words: block copolymers; coatings; rheology

INTRODUCTION

A pressure-sensitive adhesive (PSA) is a material that displays aggressive and permanent tack at room temperature and can be applied with very light pressure.[1] The PSA industry includes many diverse applications: PSAs are used in products ranging from pressure-sensitive tapes and labels to electronic circuits and automotive parts, as well as medical products such as dermal dosage systems. PSAs are composed of an elastomeric polymer, tackifying resins, plasticizers, fillers, and antioxidants in various amounts according to the properties desired.[2–4]

Traditionally, PSAs have been coated out of solutions. However, the demand for reduced-cost and environmentally friendly adhesive products has led to recent growth in the field of hot-melt coating. The elimination of solvents is a significant advantage of hot-melt processing, as this reduces material and energy costs and decreases the production time by eliminating drying steps. In addition, melt processing eliminates emissions, this being an important benefit in the face of increasingly strict solvent-emission reg-

ulations. However, although hot-melt processing leads to a significant savings in cost, a simplification of the process, and an abatement of air pollution, switching processing methods may not lead to the same properties in the final adhesive product, even when the composition remains the same. Solvent coatings have better shear strength than melt coatings, and they are preferred for use in applications requiring durability and exposure to high temperatures.[5,6]

Thermoplastic elastomers such as styrenic block copolymers are widely used in PSAs because of their unique structures, which offer advantages in processing. They flow at high temperatures and physically crosslink at lower temperatures, thereby allowing the use of lower molecular weight materials (compared with traditional natural-rubber PSAs) than would otherwise be necessary for the required physical entanglements to be achieved. Because of their lower viscosity, these elastomers provide the option of melt processing. They are also soluble in a variety of organic solvents, permitting solvent coatings.[2,3]

To better understand the influence of processing on the structure and properties of coatings, we investigated model PSAs based on a triblock copolymer and a tackifying resin. Styrenic block copolymers, selected for their ability to be coated through solvent and melt processes, also allow for the observation of microstructure development because of the incompatibility between the styrenic and elastomeric blocks. Adhesive tapes were made through solvent coating and hot-

melt coating. The adhesives had the same formulation and heat history, differing only in their preparation method. Quantifiable differences in the adhesive properties were observed based only on the coating method used.

EXPERIMENTAL

Materials

A polystyrene–polyisoprene–polystyrene (SIS) triblock copolymer was blended with an equal amount of an aliphatic resin to produce a PSA. The polymer, Kraton D1107 (Kraton Polymers, Houston, TX), was 15% polystyrene by weight, as determined by nuclear magnetic resonance spectroscopy, and 18 % diblock copolymer by weight, as determined by gel permeation chromatography (GPC). GPC was used to estimate the molecular weight of the triblock copolymer fraction to be 160,000 g/mol, based on polystyrene standards; the diblock copolymer had a molecular weight that was half that of the triblock. The tackifying resin, Wingtack 95 (Goodyear, Akron, OH), was a low molecular weight resin with a glass-transition temperature (T_g) around 45°C, as determined by differential scanning calorimetry. This tackifier was a highly branched random copolymer made from a variety of C_5 monomers, including isoprene; it was soluble in the polyisoprene phase of the triblock copolymer.

The polymer and tackifier were mixed in a Haake Rheomix 600 (Madison, WI) with sigma blades at 50 rpm. This batch mixer was operated at 160°C, and the chamber was flushed with nitrogen gas. An antioxidant, Irganox 1010 (Ciba, Tarrytown, NY), was added at a ratio of 3 parts per hundred parts of rubber to reduce oxidative degradation catalyzed by high processing temperatures. Small amounts of the polymer and tackifier were alternately added, and mixing was continued until the torque passed through a phase-inversion-like peak and subsequently reached a constant level, after 15 min of mixing. The PSA was then extracted from the mixer and quenched in liquid nitrogen to prevent degradation during cooling.

Coating

Pressure-sensitive-tape samples were hot-melt-coated with an LH-2 laboratory coater/laminator (Acumeter Laboratories, Inc., Marlborough, MA) operated at 160°C. The hopper of the coater was purged with nitrogen. A gear pump was used to meter the flow from the hopper through the manifold, and the adhesive was delivered through a slot die to a PET substrate (2 mil thick) supported by a silicone-covered roll. Tapes used in this work were hot-melt coated at 3 ft/min (0.015 m/s). The measurements of the coating temperature, made with an infrared pyrometer,

showed the temperature dropping from 160 to 80°C in less than 1 s after application to the web. Therefore, the morphology was frozen in place very rapidly after coating. Additional experiments were performed at H.B. Fuller Co. (Vadnais Heights, MN) on PSAs coated at speeds of up to 110 ft/min (0.56 m/s). However, no differences in properties were observed as a function of coating speed.

A portion of the material that was hot-melt mixed and subsequently remelted in the coater was collected after passing through the coating die but before being applied to the substrate. This material was solidified (via quenching in liquid nitrogen) and then dissolved in toluene for solvent coating. The PSA solution was coated onto the PET substrate with a #60-wire-wound rod and was then dried at room temperature in a dust-free environment for several days. The final film thickness for both the hot-melt and solvent coatings was 1.1 mil (28 μm).

Rheology and small-angle X-ray scattering (SAXS)

Rheological testing was performed on as-mixed samples with an ARES (Rheometric Scientific, Piscataway, NJ) with 25-mm parallel plates. Low-temperature measurements (see Fig. 1) were performed on samples that were heated above the order–disorder transition (ODT), stretched to a gap of about 8 mm and to a sample diameter of approximately 5 mm, and subsequently cooled to the test temperature. This allowed for the measurement of the moduli in the glassy region, in which the stiffness of the sample would have otherwise caused serious compliance errors and transducer resonance. After the completion of low-temperature measurements, the sample was heated above the ODT, and the gap was reduced to 1 mm for the second half of the temperature ramp.

SIS and PSA samples to be used for SAXS and the remaining rheological measurements were formed into 1-mm-thick films with a hydraulic press at temperatures 15°C above their ODTs. These higher temperatures were used to ensure that the material was disordered during the molding process, as no shearing or mixing could occur to facilitate the disordering. After molding in the press, the adhesive samples were quenched in liquid nitrogen at an effective cooling rate of approximately 100°C/s. Portions of these samples were then dissolved in toluene, a relatively neutral solvent for both the polyisoprene and polystyrene phases, at 20% by weight. This solution was poured into a Teflon petri dish and allowed to dry at room temperature for 48 h in the presence of a low vapor pressure of toluene (to prevent the formation of a skin on the surface). This was followed by continued drying in air for 5 days (in an enclosed dust-free environment), after which it was placed in a vacuum oven for 5 days. Mild heat was then applied to soften the
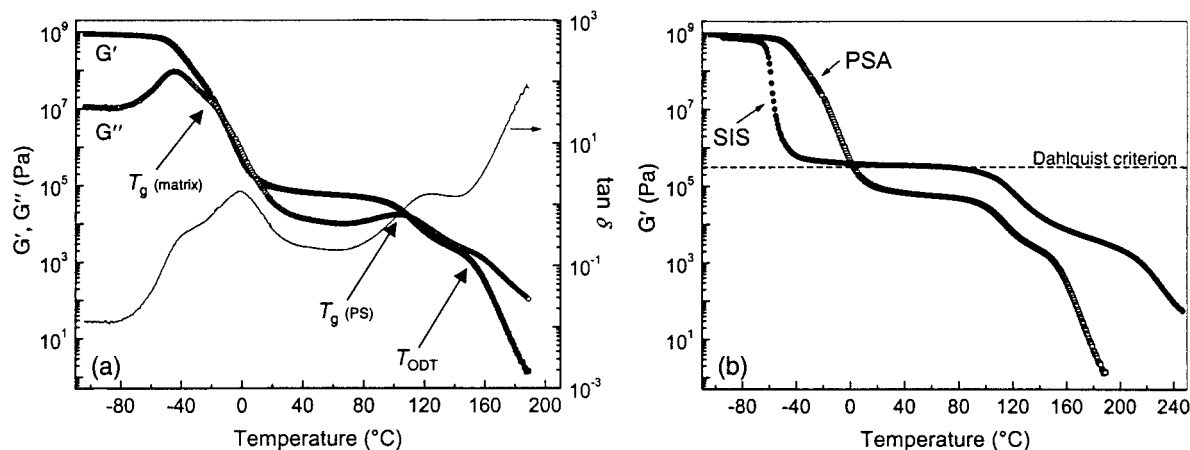
Figure 1 Dynamic moduli as a function of temperature at 1 rad/s and at a ramp rate of 3°C/min for (a) PSA and (b) SIS and PSA.

polymer to allow any residual solvent to escape. The temperature was raised to 50°C and held for 10 min, after which the sample was slowly cooled to room temperature.

Creep measurements were made with 25-mm parallel plates and a 1-mm gap (SR-200, Rheometric Scientific). A capillary rheometer (Goettfert) was used to obtain high-shear-rate viscosity data. A 1-mm-diameter die with a length/diameter ratio of 20 was used, and data were corrected by the single-point method.[7] SAXS measurements were conducted at a sample-to-detector distance of 1.5 m. Cu Kα X-rays were generated by a Rigaku rotating-anode X-ray machine. Two-dimensional images were converted into a one-dimensional format by azimuthal integration to obtain the intensity versus the scattering wavevector.

Adhesion measurements

Pressure-sensitive-tape samples were tested with three types of property tests. The 180° peel test was performed according to Pressure Sensitive Tape Council (PSTC) Test Method 1. In this test, the force was measured as a 1-in.-wide piece of tape was peeled from a stainless steel panel at an angle of 180° and at a rate of 12 in./min. The second test measured the shear holding power of the adhesive tape. A 0.5 in. × 0.5 in. piece of tape was applied to a stainless steel panel, and the free end of the tape was attached to a weight-distributing clamp. After 10 min was allowed for the system to condition in an oven, a 1-kg mass was applied to the clamp. The time required for the tape specimen to completely separate from the panel was recorded. PSTC Method 4 was followed, but the temperature was changed to 50°C; this choice allowed for cohesive failure to occur within a reasonable experimental time but was not so high as to cause the failure to occur too quickly for differentiation between samples. In both tests, toluene was used to remove

any adhesive from the test panel, followed by the recommended PSTC procedure for substrate preparation.[8]

Pressure-sensitive tack was measured with the extension mode of an ARES rheometer. A stainless steel cylindrical probe with a diameter of 5 mm contacted an adhesive coating, was held at a constant force for a specified amount of time, and was then raised from the surface at a fixed rate. The resulting force was recorded during the entire withdrawal event. The reproducibility of the measurements improved as the contact force and time increased and as the withdrawal speed decreased. A high force (350 g) and a long dwell time (30 s) were used to ensure complete contact between the probe and film surface but still allowed for the detection of differences between samples. A withdrawal rate of 0.01 mm/s was chosen for all of the experiments reported here. The probe was cleaned with toluene before each test.

RESULTS AND DISCUSSION

Rheological characterization

The dynamic measurements of a melt-processed PSA and its base triblock copolymer are shown in Figure 1. The dynamic moduli versus temperature reveal the effect of the tackifier on the rheological characteristics of the block copolymer. In both systems, the modulus at low temperatures is high, and the material is glassy. The first drop in the storage modulus (G') corresponds to the glass transition of the rubbery matrix (polyisoprene for the pure block copolymer and a polyisoprene/tackifier blend for the adhesive). In the adhesive, the T_g of the rubbery matrix broadens significantly because of the presence of the tackifier, with the center of the drop in G' at approximately −15°C; the peak in the loss modulus (G'') is shifted from −60 to −45°C. This is necessary for improving the perfor-
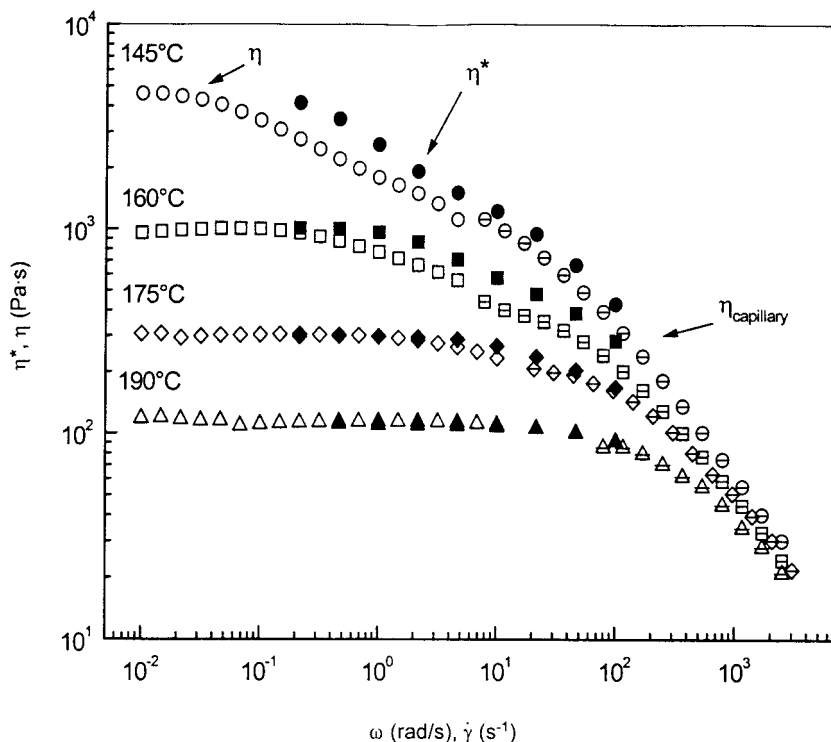
Figure 2 PSA dynamic and steady-shear viscosities. The filled symbols represent dynamic measurements; the open symbols represent steady-shear measurements.

mance of the adhesive at short timescales, such as in peeling. Although time–temperature superposition cannot be quantitatively applied in such a two-phase system, the fundamental concept still holds that low-temperature properties correspond to short-time or high-frequency behavior. A higher modulus in the -40 to $0°C$ range improves the peel strength. The next transition, T_g of the polystyrene phase, is the same in the polymer and PSA, confirming that the tackifier is not incorporated into the minor phase. Finally, at the ODT, there is a terminal drop in modulus, and the material behaves as a typical homopolymer. The ODT temperature (T_{ODT}) is significantly lower in the PSA than in the SIS polymer. Figure 1 reveals that T_{ODT} is 220°C for the SIS polymer. The tackifier lowers T_{ODT} to 160°C for the PSA. This was checked by dynamic frequency sweep measurements that show the low-frequency slopes of G' and G'' reaching 2 and 1, respectively, at 160°C. The onset of these terminal slopes confirms the PSA is at or above the ODT.[9]

The plateau modulus is reduced from 4.1×10^5 to 5.5×10^4 Pa, which is below the Dahlquist criterion[10] for tack ($G' \leq 3 \times 10^5$ Pa). When the shear storage modulus during a 1-s bonding process is below this level, good wetting and contact can occur between the adhesive and substrate. The plateau modulus can also be used to calculate the entanglement molecular weight (M_e). The Guth–Smallwood equation[11] for filled systems has been applied by several groups[12–14]

to calculate M_e for phase-separated triblock-copolymer systems:

$$G_N^0 = \rho RT(1 + 2.5V + 14.1V^2)/M_e$$

where V is the polystyrene volume fraction. The density of the entire rubbery phase is assumed to be

$$\rho = V_1\rho_1 + V_2\rho_2$$

where components 1 and 2 are the resin and elastomer, respectively. Applying this method to the polymer and adhesive in this study indicates an increase in the M_e value of the rubbery matrix from 9.0 kg/mol for the block copolymer to 56 kg/mol for the melt-processed adhesive. This increase in M_e explains the improvement of tack properties and the decrease in cohesive strength due to the addition of the tackifier.

Mixing and coating should be performed above T_{ODT} for sufficiently low viscosity to allow smooth flow and minimize mechanical work on the adhesive. The fact that the tackifier lowers the ODT allows melt processing to occur at a lower temperature than would otherwise be necessary. Figure 2 illustrates the effect of temperature on the viscosity of the adhesive. At 145°C, the dynamic and steady-shear measurements do not follow the Cox–Merz rule; the viscosity curves are in disagreement in the range in which the
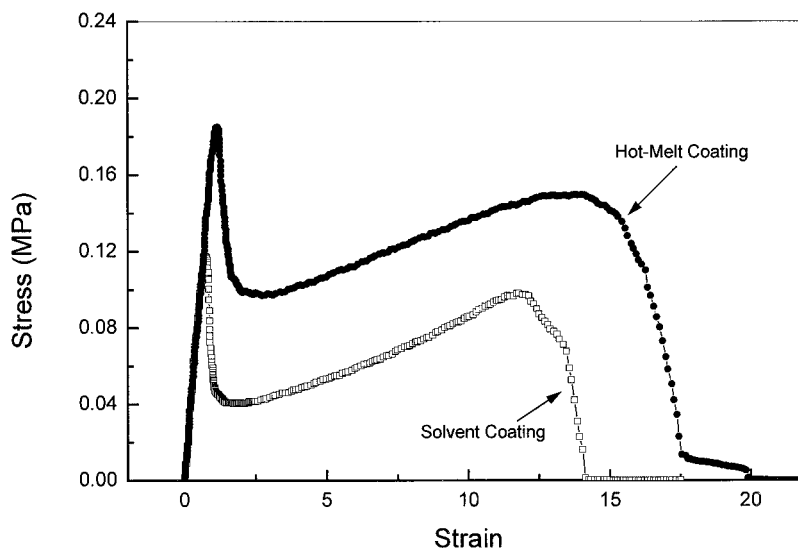
Figure 3 Representative tack-test curves for hot-melt and solvent coatings.

shear rate and frequency values overlap. This is expected for a two-phase system.[15] Large-deformation steady shearing of the adhesive disrupts the network structure that exists at this temperature. More mechanical work would be done on the polymer if it were to be melt-processed at 145°C instead of higher temperatures. As the temperature is increased to the ODT, the unfavorable interactions between polymer blocks are relieved through composition fluctuations.[9,16,17] These fluctuations may exist over some range of temperatures above the ODT, influencing the rheological response and causing some disagreement in dynamic and steady-shear viscosity at 160°C, but these effects disappear as the temperature is increased. Far above the ODT, the adhesive is homogeneous, and the dynamic and steady-shear measurements of viscosity are in agreement. Because increasing the temperature also increases the risk of oxidative degradation, processing at or slightly above the ODT is recommended to minimize mechanical work and oxidative degradation.

Adhesion tests

Representative withdrawal curves of probe tack tests are shown in Figure 3 for hot-melt and solvent coatings. The initial peak corresponds to the initial resistance with the withdrawal of the probe, and it is an indication of how well the adhesive wets the probe surface. This is the value typically reported in a tack test.[18] The hot-melt coating wets the probe surface better than the solvent coating, resulting in a higher initial peak. If the adhesive breaks into fibrils as the probe is raised, a second peak appears, which decays to zero as the fibrils stretch to their maximum elongation. This final distance is a measure of how much the adhesive can be deformed. The total area is a measure of the separation energy under the specific test conditions.[19,20] The hot melt has a larger adhesion energy. It also has a greater separation distance, so the hot-melt adhesive is able to deform and stretch more before detaching from the probe surface. In all of the tack tests, the samples separated cleanly (by visual observation only) from the probe surface.

The average tack, peel, and holding power values are summarized in Table I. The hot-melt-coated tape displays higher peel strengths and lower holding power times than solvent-coated tape with the same composition and heat history. Neither test showed a significant difference between the properties of the hot-melt-coated tapes that had been coated at different speeds. The peel strength is a function of the cohesion of the adhesive and interfacial adhesion or tack. The peel resistance improves as the cohesive strength of the elastomer increases, but an optimum exists past which increasing cohesion will eventually reduce the tack and peel by reducing the ability to wet the sub-

TABLE I
Comparison of Properties of Hot-Melt and Solvent PSA Coatings (Averages for 6–8 Samples of Each Coating)

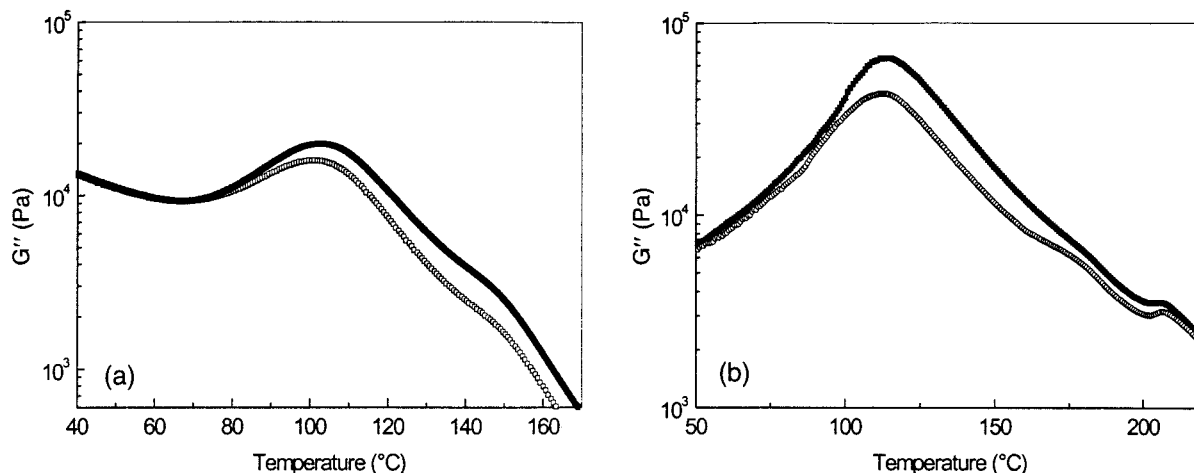| Coating method	Peak Stress* (kPa)	Adhesion Energy* (J/m²)	Final strain*	180°-peel strength (lb/in)	50°C holding time (min)
Hot-Melt	190 ± 21	57.7 ± 7.4	20.1 ± 1.2	5.77 ± 0.41	15.4 ± 1.2
Solvent	120 ± 11	26.5 ± 6.1	14.8 ± 1.7	4.22 ± 0.22	41.8 ± 1.5

Figure 4 Loss moduli at 1 rad/s and at a ramp rate of 1°C/min for melt-pressed and solvent-cast (a) PSA and (b) SIS. The filled symbols represent melt-pressed samples; the open symbols represent solvent-cast samples.

strate.[3,21,22] All of the peel test samples showed adhesive failure, as did the tack tests, so this peel test is a stronger function of the interfacial adhesion. The higher peel strength of the hot melt is, therefore, consistent with the higher tack values. The holding power test is essentially a measurement of the resistance to flow under an applied load. In this test, all samples failed cohesively, within the film rather than at the interface between the adhesive and stainless steel surface. The solvent coating has a much longer holding time than the hot-melt coating. This means that the solvent coating has more cohesive strength and more resistance to creep, and this is also consistent with the tack measurements, which showed a lower final elongation value for the solvent coating.[22,23] Although it is possible that residual toluene remains in the solvent coating, this should not contribute to the property differences. If there were any solvent present, it would act to decrease, rather than increase, the cohesive strength.

Rheological differences in melt-pressed and solvent-cast adhesives

Adhesive properties are known to be dependent on the viscoelastic properties of a material.[24,25] Shear moduli were measured as a function of temperature for both the hot-melt-pressed adhesive and the solvent-cast adhesive. High-temperature data [Fig. 4(a)] show a broader glass transition for the hot melt around T_g of the polystyrene phase. These results indicate that the polystyrene phases of the hot-melt-pressed sample are not as well-defined as those of the solvent-cast sample, with a diffuse interphase region contributing to a broad glass transition. The broad loss modulus also suggests the presence of a broader distribution of polystyrene domain sizes in the melt-pressed sample. The same experiment was performed

on melt-pressed and solvent-cast SIS block copolymer samples undiluted by the presence of a tackifier. As seen in Figure 4(b), T_g is again broader for the melt-pressed sample. These differences in T_g were not measurable by differential scanning calorimetry because of the low concentration of polystyrene in the samples.

The broadening of T_g's has been observed in miscible systems by several groups.[26-30] The broadening of the relaxation spectra in the region of T_g is attributed to a distribution of local compositions resulting from composition fluctuations. This causes a distribution of local interaction parameters and broadening of T_g. Different cooperative volumes are presumed to result from different composition fluctuations, each having its own T_g. The model of Kumar et al.[29] suggests that a large T_g contrast magnifies composition fluctuations, which reveal the nanoheterogeneities suggested previously.

Creep compliance measurements for melt-pressed and solvent-cast adhesives obtained at four different temperatures with an applied stress of 1000 Pa are shown in Figure 5. At 25 and 50°C, the adhesives display only short-term creep, as expected for a crosslinked material.[7] At these temperatures, the polystyrene segments are below their T_g, forming spherical domains that act as physical crosslinks. Both ends of the elastomeric polyisoprene segment are immobilized in the glassy domains, and the adhesive is physically crosslinked. Below 160°C, the creep compliance is greater for the melt-pressed samples. This result is consistent with the holding power test, which is essentially a rough creep test, and indicates a longer holding time, or better creep resistance, for the solvent-cast sample. Although the high stress applied to the film in the holding power test, 60 kPa, was not used in the creep tests (because of edge fracture at higher stresses), it is possible to qualitatively relate the
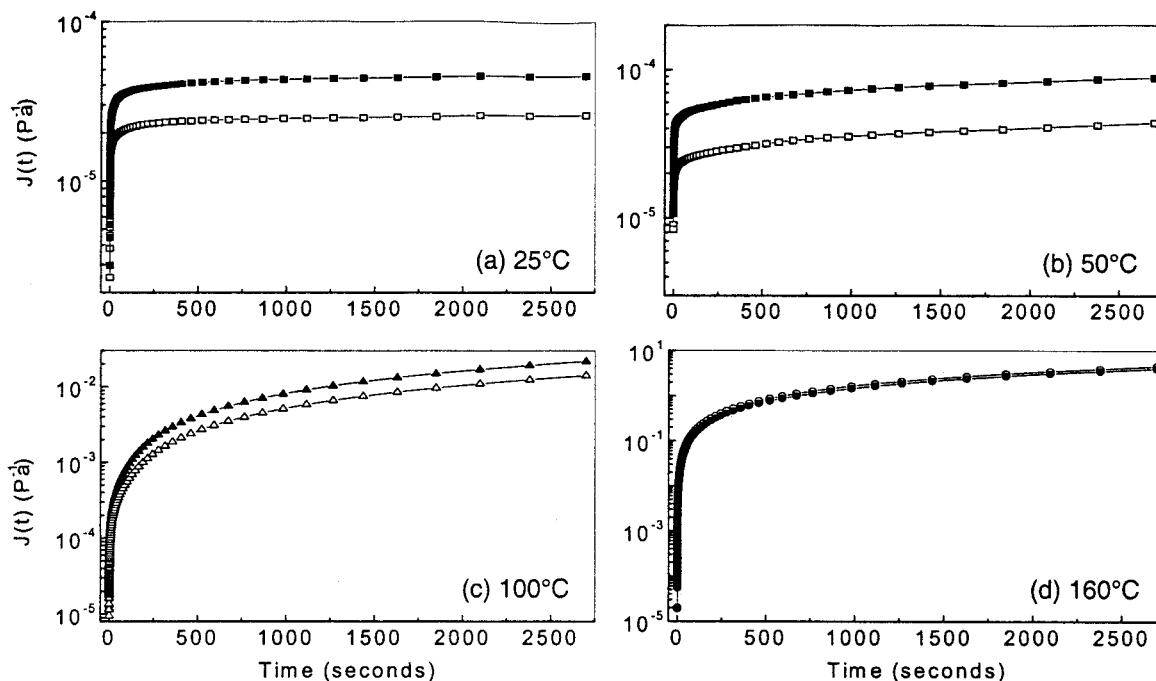
Figure 5 Creep tests (1000 Pa) of melt-pressed PSAs at (a) 25, (b) 50, (c) 100, and (d) 160°C. The filled symbols represent melt-pressed PSA; the open symbols represent solvent-cast PSA.

results of the two tests. The rheological experiment shows a lower creep compliance in the solvent-cast adhesive, which corresponds with creep occurring more slowly in the holding power test and, therefore, a longer holding time. Dahlquist[31] predicted that the holding time is proportional to viscosity, which is a function of the degree of physical crosslinking in the adhesive. The steady-state viscosities estimated from the slopes of the compliance curves at 50°C (the temperature of the holding power test) are 2.4×10^8 and 9.0×10^7 Pa s for the solvent and melt PSAs, respectively.

Ordering kinetics

In a two-phase system, complete phase separation may not be practically possible because of kinetic factors arising from the sample preparation method, thereby affecting the size, shape, and regularity of the minor-phase domains. Often, a film cast quickly has poorly defined morphology.[32] After melt coating, the polystyrene segments may be prohibited from achieving complete phase separation during a short cooling period. The final microstructure achieved will depend on the mobility of the polystyrene chain ends, as they are thermodynamically driven to phase-separate but are also hindered by the covalent bonds linking them to the elastomeric blocks. Similarly, the melt-pressed PSA is kinetically hindered from achieving complete phase separation, leading to less distinction between the polystyrene and polyisoprene phases and a distri-

bution of polystyrene domain sizes. In the solvent-cast sample, more clearly defined polystyrene domains correspond to more physical crosslinking, lower compliance values, and better holding power. The rate of cooling is clearly a key parameter for determining the molecular mobility and coating morphology.

The adhesive materials in this study show an absence of long-range order and possibly the presence of disordered polystyrene spheres trapped in a nonequilibrium state as a result of sample preparation methods. If the sample cools more quickly than the polymer chains can rearrange, the polystyrene chain ends will lose their mobility before they can completely segregate. Although the polystyrene blocks may achieve a considerable degree of phase separation, they do not order onto a lattice. Characteristic relaxation (i.e., reptation) times can be estimated from the rheological behavior of the PSA. The frequency at which G' and G'' cross corresponds to the inverse of the relaxation time of a single chain; it occurs at 0.25 rad/s at 100°C and at 100 rad/s at 160°C. Therefore, the relaxation times are 4 and 0.01 s at 100 and 160°C, respectively. Relaxation is fast at the processing temperature, explaining the lack of evidence for significant chain alignment. In less than 1 s, the coating cools below 100°C; the longer relaxation time of 4 s at 100°C limits the mobility of the polymer chains and prevents the full phase separation of the polystyrene blocks into spherical domains with long-range order.

To create an equilibrium morphology with long-range order, we annealed melt-pressed adhesives at
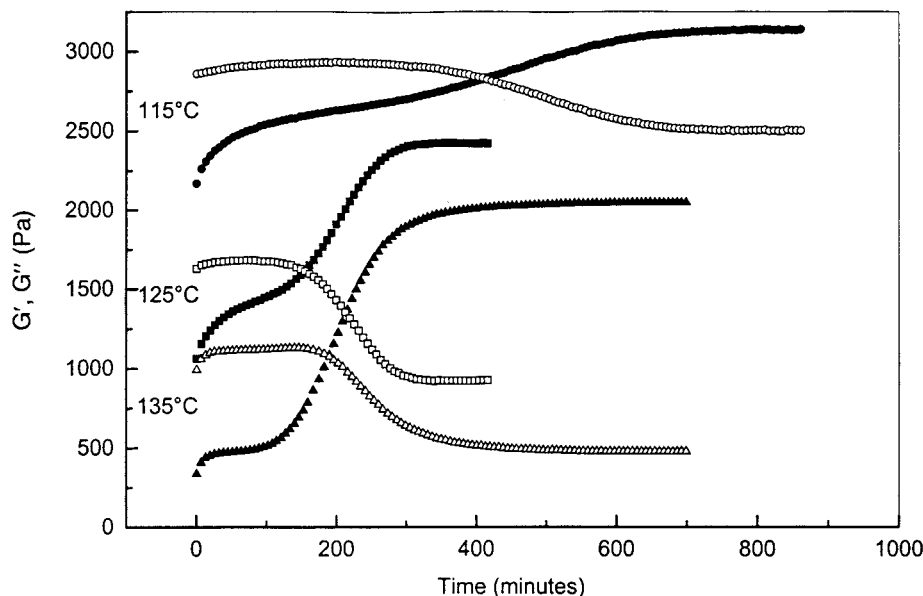
Figure 6 Time evolution of G' and G'' at 0.1 rad/s for three different quench depths. The filled symbols represent G'; the open symbols represent G''.

various temperatures and measured their shear moduli as a function of time. All measurements were performed at a frequency of 0.1 rad/s and at a strain amplitude of 3%. The frequency was selected to be low enough so that the rheology reflected the response of the mesophase structure. The strain was low to prevent the distortion or destruction of any lattice structure. Measurements at higher strain showed no structural development.

Isochronal moduli at 115, 125, and 135°C are shown in Figure 6. The ordering of the polystyrene domains onto a lattice is evidenced by the increase in G' accompanied by a decrease in G''. As the network structure develops, the sample stiffens and loses its ability to dissipate energy. This ordering occurs the quickest at 125°C. The PSA takes twice as long to order at 115°C and never achieves order after 18 h at 105°C (not shown). Similarly, the PSA orders only slightly more slowly at 135°C and does not order after 18 h at 145°C (not shown). The polymer chains need to be sufficiently above the glass transition of the polystyrene to have enough mobility to rearrange yet must be sufficiently below the ODT to have a strong driving force to arrange onto a lattice. Similar observations were made by Adams et al.[33] for styrene–isoprene diblock and triblock copolymers. They reported that triblock copolymers ordered much more slowly than diblocks because of their higher molecular weight. In this work, the addition of the tackifier might be expected to slow the ordering process because of its dilution of the polystyrene phase. However, it also increases the mobility of the polymer chains at lower temperatures. In a pure block-copolymer sample (Kraton D1107), a body-centered cubic (bcc) structure was observed to

develop in less than 2 h at 165°C but was never observed in 18 h of annealing at 125°C. The PSA did reach equilibrium at 125°C after more than 4 h.

The dynamic moduli at 125°C are shown as a function of frequency before, during, and after annealing in Figure 7. At low frequencies before annealing, the slopes of G' and G'' are 1.5 and 0.75, respectively, and G'' is greater in magnitude than G' [Fig. 7(a)]. Therefore, the sample is neither strongly ordered nor completely disordered. During the initial stages of annealing, Figure 6 shows G' quickly reaching the first plateau, presumably after the sample becomes uniformly heated to the test temperature. As the annealing continues, G' begins a second steep rise, whereas G'' decreases. A frequency sweep performed at this point, after 2.5 h of annealing [Fig. 7(b)], shows changes in the low-frequency behavior: G' approaches G'', indicating that some short-range order is developing. The system can be regarded as a composite of ordered and disordered phases.[34] When the time-dependent moduli finally reach the second plateau region, the low-frequency G' in Figure 7(c) becomes constant and is much larger than G''. This is consistent with the behavior of a cubic structure. An elastic plateau is observed in the storage modulus of cubic phases at low frequencies at which the corresponding disordered phase displays terminal behavior. This plateau occurs at frequency values lower than those for the rubbery plateau, G_N^0, which is a function of entanglements. This elastic plateau, termed G_{cubic}^0 by Kossuth et al.,[35] is influenced by the presence of a microstructure, specifically the three-dimensional translational order in cubic phases. Defects in the lattice structure are expected to allow creep that will eventually lead to terminal
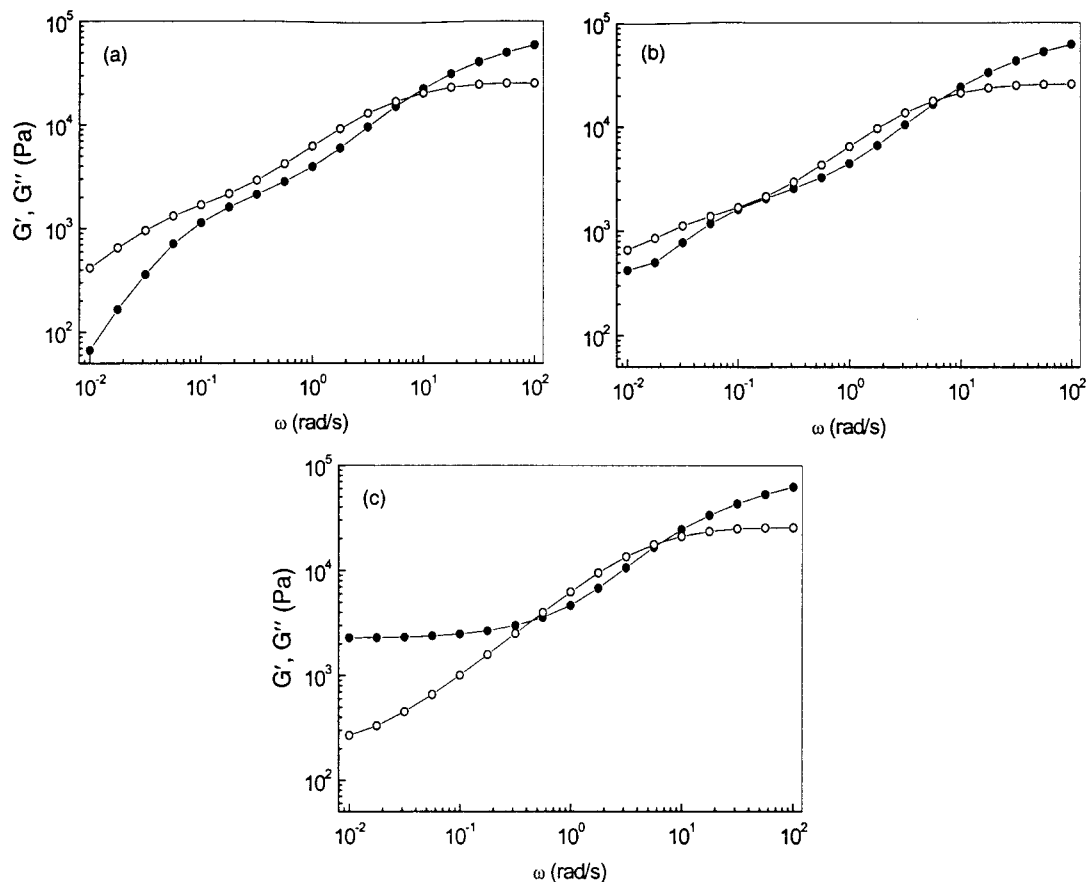
Figure 7 PSA dynamic moduli at 125°C (a) before annealing, (b) after annealing for 2.5 h, and (c) after annealing for 5 h. The filled symbols represent G'; the open symbols represent G''.

behavior at very low frequencies. Kossuth et al. proposed that a perfectly periodic cubic crystal would be expected to exhibit a plateau in G' extending to zero frequency.

SAXS was used to confirm this ordering at 125°C. The development of the structure was monitored via scattering at 15-min intervals throughout the annealing process. The scattering intensity is plotted in Figure 8 as a function of $\mathbf{q}$, the scattering wavevector [$\mathbf{q}$ $= 4\pi(\sin \theta)/\lambda$]. Before annealing, there is a single broad first-order peak and a second-order shoulder (at $\mathbf{q} = 1.035 \text{ Å}^{-1}$). This indicates that the polystyrene and polyisoprene are phase-separated without any long-range order; the polystyrene spheres may instead possess a liquidlike order.[36] The primary peak becomes narrower, and this is followed by the development of the higher order peaks as ordered grains grow at the expense of the disordered spheres. After annealing, three distinct peaks at relative $\mathbf{q}:\mathbf{q}^*$ positions of $1:\sqrt{2}:\sqrt{3}$ develop after approximately the same amount of time required for significant changes to occur in the dynamic moduli. This scattering pattern is indicative of either a bcc or simple cubic structure. However, the simple cubic structure has never been identified in a polymer melt, so the morphology of this

system can be identified as bcc.[35] The domain spacing can be calculated from the position of the primary peak, $\mathbf{q}^*$, according to the following equation: $d = 2\pi/\mathbf{q}^* = 31$ nm.

Structure enhancement in coatings

To test the hypothesis that the solvent coating has a more developed network structure, we have performed two types of experiments. In the first experiment, several samples of pressure-sensitive tape that had been hot-melt coated at various speeds were exposed to a low vapor pressure of toluene for 24 h and subsequently dried for another 24 h. Their peel and shear properties were measured and compared with the properties of the original hot-melt coatings. Figures 9–11 show the effects on peel, shear, and tack properties: the peel strength was lowered, the holding time increased to approximately the same levels as those of the solvent-coated samples, and the tack decreased. The presence of the solvent allowed the polymer chains enough mobility to rearrange and presumably reach the same type of structure found in the solvent coating.
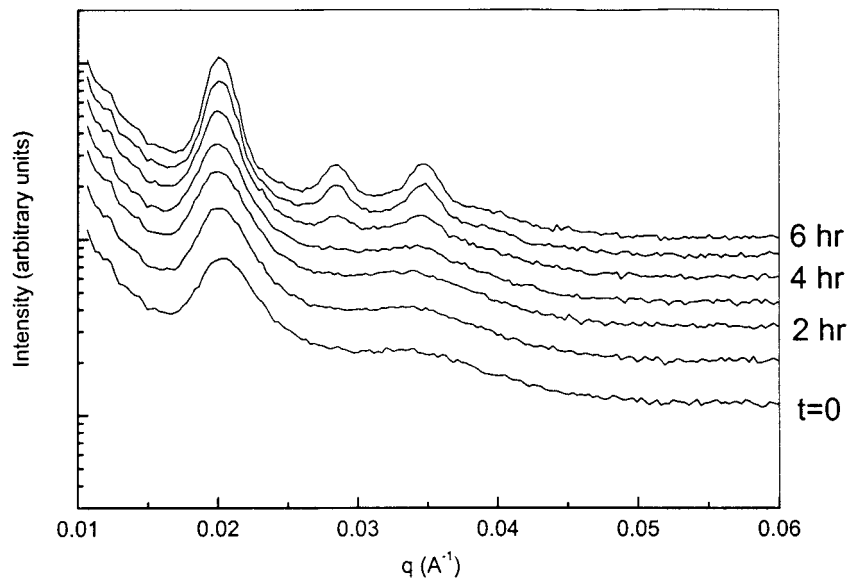
Figure 8 SAXS pattern evolution of PSA during annealing at 125°C.

In the second experiment, hot-melt and solvent coatings were annealed in a vacuum oven. Hot-melt-coated tape was annealed at 125°C for 1 and 5 h. It was expected that both types of coatings would achieve the same final state at equilibrium. After 1 h of annealing, the holding power of the hot-melt coating increased to the level of the solvent coating. After 5 h, the holding power surpassed that of the solvent coating. The peel strengths did not significantly change. For comparison, solvent coatings were also annealed for 5 h at 125°C. The hot-melt and solvent coatings have the same holding time after 5 h of annealing, indicating that they have the same bcc microstructure.

The peel strength of the annealed melt coating is still higher than that of the annealed solvent coating. The tack-test curves of each type of tape also reveal that although both the annealed melt and solvent coatings seem to have the same bcc structure, there are still differences in the properties. Both samples show the development of a sharp shoulder, which indicates an
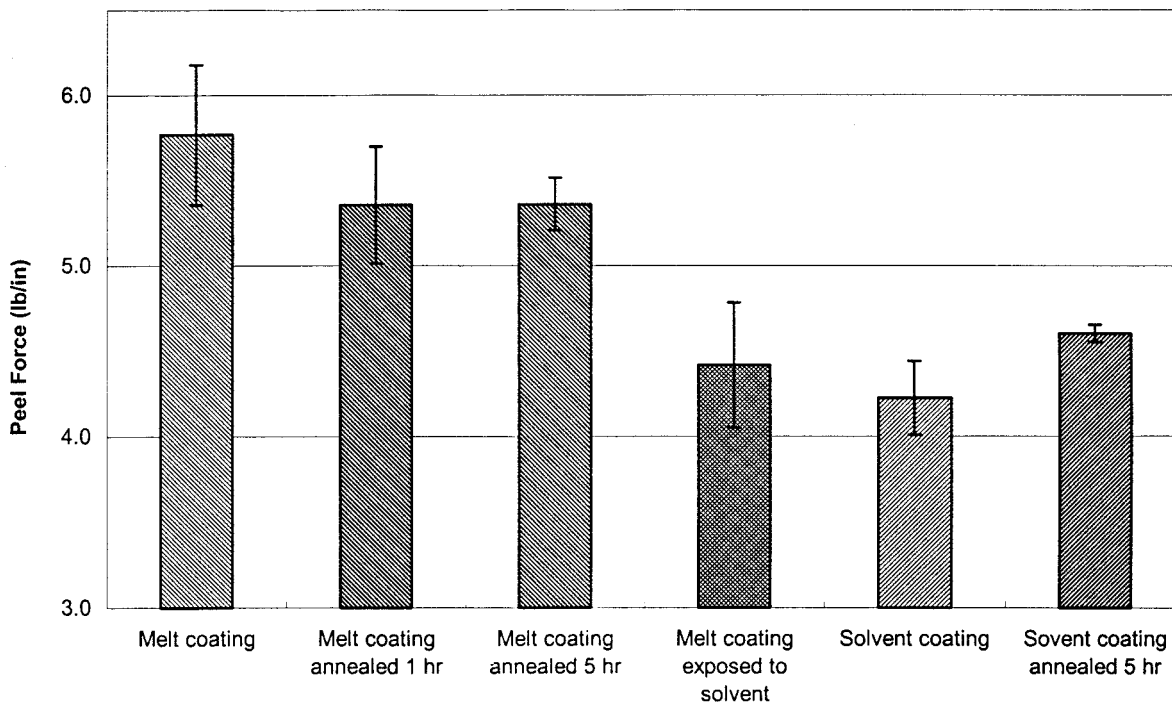

Figure 9 Effect of annealing (125°C) and solvent exposure (toluene) on peel strength.
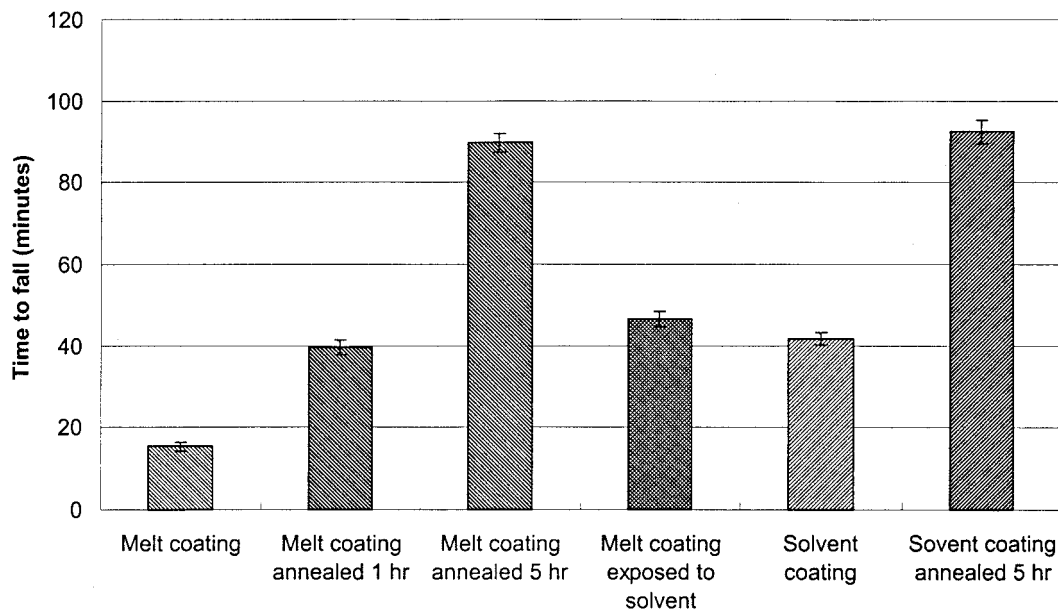
Figure 10 Effect of annealing (125°C) and solvent exposure (toluene) on 50°C holding power.

increase in the cohesive strength of the fibrils. However, the annealed solvent coating has a lower initial peak than the annealed hot-melt coating and a shorter separation distance, as well as a lower total energy of adhesion (the area under the curve). This behavior

Figure 11 Effect of annealing (125°C) and solvent exposure (toluene) on tack properties.

indicates that there is an additional factor causing the differences in properties.

Two key observations can be made by a comparison of this experiment and the previous solvent-exposure experiment. After both types of coatings were annealed for 5 h, their holding power times increased beyond the level of the original solvent coating. This shows that although it might have possessed more physical crosslinks, the solvent coating was not at its equilibrium state initially. Second, the improvement in the physical crosslinking achieved through the annealing of the melt coating does not decrease the peel strength and tack properties to the levels of the original solvent coating. There must be another reason for the lower peel strength of solvent-processed adhesives, such as the composition of the adhesive at the surface.
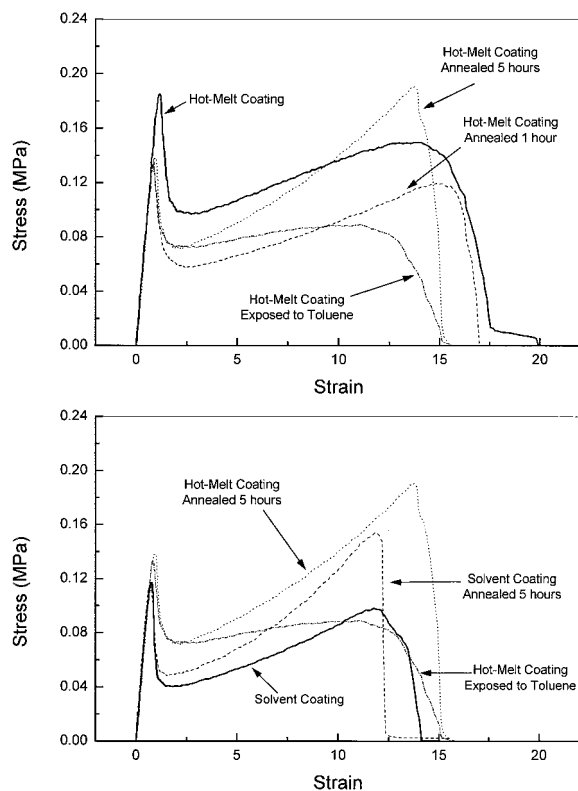
Concentration gradients within coatings

The drying process of a polymer/solvent solution is a complicated process that can result in the appearance of concentration gradients as a function of the drying rate and physicochemical properties of the solution. In the first of two successive stages of drying, the solution is dilute, and there is a significant flux of solvent to the free surface.[37] In the second, the solvent concentration falls in the upper layer, and the drying rate depends on the transport of the liquid to the surface, which can be through diffusion, capillary flow, or other mechanisms.[38] Diffusion is the most common mechanism for drying coatings. During the second drying regime, solvent diffusion becomes slow, pre-

venting the regeneration of the solvent near the interface and creating a large concentration gradient.

The annealed hot-melt and solvent coatings have the same average cohesive strength, as indicated by the equal values for the elevated-temperature holding times. However, the separation distance in the tack test remains longer for the melt-coated PSA, even after annealing. Tack tests are more sensitive to the surface characteristics of a PSA, so this is an indication that the surface compositions are different between the two samples, even though they both possess the same average structure.

We tested this effect by preparing a 1-mm film of PSA cast from toluene and taking thin sections from the top and bottom for analysis by GPC in solutions of tetrahydrofuran. The sampling procedure involved freezing the adhesive film (in liquid nitrogen) and cutting a section from each surface. This was repeated for three PSA films to obtain an average because the sample size was not well controlled. The average relative difference in the tackifier-to-polymer ratio ranged from 6 to 13%, greater for the samples taken from the bottom than for the samples taken from the top. Therefore, the bottom surface of the adhesive is slightly favorable for the tackifier under these mild drying conditions.

In experiments using various amounts of the tackifier, it was found that too much or too little tackifier reduced the peel strength. Decreasing the tackifier content generally leads to a lower initial tack peak and a shorter separation distance.[39] The inferior tack and peel properties and the shorter separation distance of the solvent-coated PSA are consistent with those of a system containing less tackifier. Because both the hot-melt and solvent coatings have the same overall compositions, this indicates that the polymer phase is enriched close to the surface. In the PSAs studied in this work, the tackifier has a low molecular weight and is more soluble than the polymer in toluene. As the toluene evaporates from the solvent coating, the tackifier is carried to the surface by the evaporating solvent. However, after the solvent leaves the surface, the tackifier diffuses back down the concentration gradient to the bottom of the film, where there is more solvent present. Slow drying causes the tackifier to be saturated at the bottom of the film or coating. Similar observations were made by Pan[40] for latex coatings in which the distribution of a soluble binder could be controlled by the drying rate being controlled. He showed that high drying rates or low binder diffusivity caused enrichment of the binder at the surface. Low drying rates or high diffusivity led to a high concentration of binder nearer to the substrate.

CONCLUSIONS

Hot-melt coating is an environmentally responsible alternative to solvent coating for PSAs. Model PSAs composed of equal ratios of SIS polymer and midblock tackifier were prepared through melt mixing followed by hot-melt and solvent coatings. The tackifier served to increase T_g of the rubbery phase while simultaneously increasing M_e and decreasing T_{ODT}. Adhesive properties were measured through probe tack, 180° peel, and holding power tests. Tack tests measured the total adhesion energy of a PSA, and the shapes of the withdrawal curves corresponded well to the peel and shear test results. Materials with the same composition and heat history showed superior tack and peel properties when prepared by hot-melt coating and displayed superior shear holding power when prepared by solvent coating.

Differences in the degree of physical crosslinking and composition gradients within the solvent coatings caused these differences in properties. The hot-melt coating process leads to a microstructure that is further from equilibrium than that found in a solvent coating. Nonequilibrium microstructures are trapped after hot-melt coating when the adhesive film cools below the polystyrene T_g before the chain ends are able to completely separate into spherical domains on an ordered lattice. Solvent-cast adhesives have a more uniform microstructure, revealed by a narrower T_g and lower creep compliance. This improves the physical crosslinking in the coating, which is manifested in longer holding times and a decreased ability to conform to a surface.

Hot-melt coatings have a more uniform composition than solvent coatings. The low molecular weight tackifier is enriched at the bottom of the coating during the solvent-evaporation process. This enrichment does not affect the shear holding power, which is a function of the cohesion of the entire film. Slight differences in the surface composition have a greater effect on the tack and peel strength, contributing to the lower tack and peel properties of the solvent coating.

Annealing adhesive films at a temperature between the glass transition of polystyrene and the ODT of the adhesive improves the distinctness of the polystyrene spheres and their long-range order, as confirmed by rheology and SAXS. This improvement in the microstructure has been shown to enhance shear performance, with a small effect on the tack and peel properties. The cooling rate in a hot-melt-coating process is, therefore, an important variable to control to achieve the optimum balance of tack, peel, and shear properties in the final adhesive product.

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