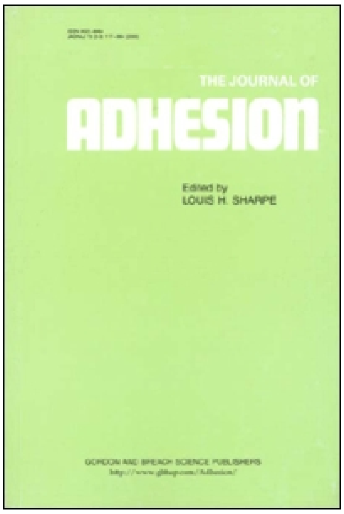
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Block Copolymer Based Pressure Sensitive Adhesives Modified with PPO for Increased Service Temperatures

Rong-Ming Ho[a]; David W. Giles; Christopher W. Macosko[b]; Frank S. Bates[b]
[a] Department of Chemical Engineering, National Chung Hsing University, Taichung, Taiwan, ROC [b] Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, USA

To cite this Article Ho, Rong-Ming , Giles, David W. , Macosko, Christopher W. and Bates, Frank S.(2000) 'Block Copolymer Based Pressure Sensitive Adhesives Modified with PPO for Increased Service Temperatures', The Journal of Adhesion, 73: 1, 65 — 85

To link to this Article: DOI: 10.1080/00218460008029297

URL: http://dx.doi.org/10.1080/00218460008029297

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 2000, Vol. 73, pp. 65–85
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Block Copolymer Based Pressure Sensitive Adhesives Modified with PPO for Increased Service Temperatures

RONG-MING HO[b], DAVID W. GILES[a,*],
CHRISTOPHER W. MACOSKO[a] and FRANK S. BATES[a]

*[a]Department of Chemical Engineering and Materials Science,
University of Minnesota, 421 Washington Ave. S.E., Minneapolis,
MN 55455, USA; [b]Department of Chemical Engineering,
National Chung Hsing University, 250 Kuokuang Road,
Taichung, Taiwan, ROC*

(Received 17 August 1999; In final form 24 March 2000)

Higher service temperature pressure sensitive adhesives were formulated from poly(styrene-*b*-isoprene-*b*-styrene) (SIS) block copolymer blended with low molecular weight midblock and endblock associating resins. The aliphatic midblock resin was WingTack 95® and the aromatic endblock resin was a polyphenylene ether, PPO. In even small amounts ($< 3\%$) the PPO raised the service temperature of the adhesive, as measured by elevated temperature holding power (lap shear) tests. The formulations were also examined with transmission electron microscopy (TEM), small angle X-ray scattering (SAXS), dynamic mechanical analysis (DMA), and 180° peel strength tests. A tentative ternary phase diagram for SIS/WingTack 95®/PPO was constructed and a basic understanding of structure/property relationships for this PSA system was accomplished. The large improvements in the elevated temperature holding power tests correlated with increases in the polystyrene microphase glass transition and order-disorder transition.

Keywords: Poly(styrene-*b*-isoprene-styrene); Triblock copolymers; Tackifier; Polyphenylene ether; Block copolymer phase behavior; Peel strength

---

*Corresponding author. Tel.: 612-625-0880, Fax: 612-626-1686, e-mail: giles@cems.umn.edu

INTRODUCTION

Pressure sensitive adhesives (PSAs) based on triblock copolymer *thermoplastic elastomers* have the advantage that they can be melt processed, avoiding the environmental problems and expense associated with solvent processing [1–4]. Typical are the styrene–isoprene–styrene (SIS) triblock copolymers, where the polystyrene endblocks microphase separate to form glassy, thermoreversible "crosslinks" for the polyisoprene matrix phase. The matrix phase needs to be rubbery in the service temperature range, and hydrogenated or partially-hydrogenated rubbers are also used for the midblock matrix phase. The rubbery plateau modulus of the neat elastomer is usually too high for adequate tack. "Tackifiers" (lower molecular weight resins, miscible in the rubbery matrix phase), are added to lower the shear modulus (G', measured at about 1 Hz) below 3×10^5 Pa, the Dahlquist criterion for tack [5].

The glass transition of polystyrene normally places an upper limit on the service temperature, but it has been recognized that high-softening-point, polystyrene-compatible resin additives could increase the glass transition temperature of the polystyrene domains [6, 7]. Thus, two types of resin additives could be used in formulating PSAs from triblock copolymers: a midblock associating resin that lowers the modulus to an acceptable level allowing tack, and an endblock associating resin with a high softening point to raise the upper service temperature. Polyphenylene ether, also referred to as polyphenylene oxide or PPO, is completely miscible in polystyrene homopolymer [8–10]. It has been disclosed to be a useful endblock associating resin to raise the service temperatures of PSAs [11, 12]. More recently, methods to improve the blending of PPO into the polystyrene domains have been disclosed [13]. The effect of PPO on the phase behavior in styrenic triblock copolymers has also been studied at temperatures below the order-disorder transition [14].

This study uses a model PSA three-component blend system consisting of block copolymer, midblock associating resin, and endblock associating resin. The adhesive is formulated to achieve good properties in tack and peel strength from the midblock associating resin, and improved holding power at elevated temperature from the endblock associating resin. Compositions with midblock and endblock associating resins were prepared by solution blending with SIS triblock copolymer and examined by transmission electron microscopy (TEM), small angle X-ray scattering (SAXS), and dynamic mechanical analysis (DMA). Two property tests were also conducted: the 180° peel strength test, and the lap shear holding power test at elevated temperature. The objectives of this work are to illuminate the composition, microstructure, property relationships of triblock-copolymer-based PSAs modified with midblock and endblock associating resins. Tests were done over a wide temperature range, from below the glass transition of the rubber matrix phase through the ODT (order-disorder transition); the variety of tests permits property optimization in formulating improved performance.

EXPERIMENTAL

Materials

The styrenic triblock copolymer used in this investigation is a poly(styrene-*b*-isoprene-*b*-styrene), (symbolized as SIS), Kraton D1107 of Shell Development Co. According to the supplier, this commercial SIS is 15% styrene by weight. Size exclusion chromatography (SEC) indicates that the as-supplied SIS contains approximately 20 wt% uncoupled diblock. The percentage of diblock content was determined by the area ratio of two Gaussian curves fitted to the SEC profile. [The presence of some diblock copolymer may effect the viscoelastic and adhesive properties of this material; however, in the comparative study reported here the percentage of diblock remains constant and should not influence our conclusions.] The triblock number average molecular weight, Mn, was 175,000 g/mol and the polydispersity index ca. 1.49; thus, each endblock has a Mn of about 13,000 g/mol. Two oligomer resins were chosen to mix with the SIS: an aliphatic resin, WingTack® 95 of Goodyear Co. (*W*95) and an aromatic resin, PPO 612 of General Electric Plastics Co. (PPO). The aliphatic, unsaturated oligomer resin *W*95 has a broad glass transition around 45°C as measured by differential scanning calorimetry (DSC). The aromatic oligomer resin PPO is reported to have a number average molecular weight of 1700 g/mol, a 3.3 polydispersity index, and a 160°C glass transition temperature [15]. DSC measurements in our lab show a glass transition at 155°C.

Sample Preparation

Samples with different proportions of copolymer and oligomer resins were prepared by solution blending in toluene at 10 wt% solids with 1-part antioxidant (IRGANOX® 1010) per hundred parts solids. For the TEM, SAXS, DSC, and original DMA tests, solutions were transferred to 90 × 50 mm evaporating dishes for solvent evaporation in open air at room temperature for a week. Remaining trace solvent was removed in a vacuum oven at 40°C for 3 days. The drying of the sample was finished in the vacuum oven at elevated temperature by gradually raising the oven temperature up to 120°C, and then annealing at 120°C for 24 hr.

Samples for later DMA tests with lower concentrations (< 3 wt%) of PPO were solution blended at the higher concentration of 20 wt% solids. PPO and antioxidant solutions (5 and 0.2 g/dL in toluene) were prepared first. These two solutions were combined in desired amounts in brown glass bottles and the SIS added next and dissolved with shaking. The *W*95 was added last and this solution was allowed to sit overnight before solution casting. Three and a half mL of each blended solution was placed on a Teflon watch glass (for easy removal of the dried sample) and these were placed in a vacuum oven at room temperature with a small beaker of toluene and a low purge (0.1 SLPM) of nitrogen gas. Vacuum was not applied. The beaker of toluene was removed after one day, and the low purge of nitrogen continued for three more days. Then the purge was ended and vacuum applied for two days. Finally, the temperature was raised to approximately 110°C and allowed to return to room temperature, all under vacuum. The controlled, gradual evaporation procedures were followed to insure samples of uniform composition, with no residual toluene.

Samples for peel and holding power tests were prepared by rod coating from a 20 wt% solution on 50 μm polyester film followed by air drying overnight in a laminar flow hood. Dried adhesive layer thickness on the film was 25 ± 3 μm. For such thin samples, this less complex drying procedure was judged sufficient.

Size Exclusion Chromatography

Size exclusion chromatography (Waters, 150-CALC/GPC) was used to determine the molecular weight of the copolymer. Columns with pore sizes of 50, 100 and 1,000 nm (Polymer Laboratories) were used, and calibrated with standard polystyrene homopolymers. The solvent medium was tetrahydrofuran, and sample solution was injected at a flow rate of 1 mL/min.

Differential Scanning Calorimetry

Five to fifteen mg samples were loaded in sealed aluminum pans and tested in a differential scanning calorimeter (Perkin Elmer DSC-7). The instrument was calibrated with high purity standards of indium. Scans from 20°C to 200°C at 40°C/min were run with an ice bath as the heat sink.

Dynamic Mechanical Analysis

Initial DMA tests for temperatures ranging from -100°C to 150°C were performed using a Rheometrics Mechanical Spectrometer RMS-800 with 10 mm diameter serrated plates, sample thickness of 2 to 3 mm, and operated at 1 radian/s with shear strains $\leq 5\%$, where the rheological response is within the linear viscoelastic region. Temperature scans were conducted at a heating rate of 3°C/min under a nitrogen atmosphere. Later DMA tests with the lower concentrations (< 3 wt%) of PPO were conducted with a Rheometric Scientific ARES rheometer with nitrogen convection oven using 25 mm parallel plates for all temperature scans; however, from -100°C to 40°C, the sample was drawn down to a diameter and length of approximately 5 mm each, enabling the ratio of G'' to G' in the stiff sample to be accurately measured, with some uncertainty in magnitude of the moduli owing to the approximate diameter and shape. The plates were then closed on the sample to a regular nominal gap of 1 mm for the temperature range of 20 to > 200°C, enabling accurate measurement of moduli especially in the temperature region 20 to 100°C. Moduli data from the low temperature scan were then shifted to this accurate baseline in the overlap region (20 to 40°C). Changes in sample shape, either drawing down to a smaller diameter or squeezing back to a regular thin disk, were done at 160 to 170°C.

Small Angle X-ray Scattering

Small-angle X-ray scattering (SAXS) measurements were conducted on a small-angle beamline constructed at the University of Minnesota. Cu K_a X-rays were generated by a Rigaku RU-200BVH rotating anode X-ray machine equipped with a 0.2×2 mm microfocus cathode and Franks mirror optics. Solution-cast samples were placed inside the evacuated sample chamber and maintained at the appropriate temperature by a pair of heaters mounted on a water-cooled brass block (temperature range 5–260°C, stability ±0.1°C). Two-dimensional diffraction images were collected with a multiwire area detector (HI-STAR, Siemens Analytical X-ray Instruments) at different temperatures and corrected for detector response characteristics prior to analysis. Integration times were 5 min after samples were equilibrated at temperature for 20 min. Images were converted to a one-dimensional format by integrating azimuthally along an arc ±40° from the horizontal axis. The interdomain distances were determined based on these one-dimensional profiles. Characteristic microdomain spacings, $d = 2\pi/q^*$, were extracted from these SAXS patterns where q^* represents the principal (*i.e.*, first-order) peak position.

Transmission Electron Microscopy

Ultra-thin films (50–60 nm) of solution cast samples were obtained by ultra cryomicrotomy using a Reichert Ultracut microtome (equipped with a Reichert FCS cryo-chamber and a diamond knife) and operated at −110°C. Polyisoprene (majority component) domains were preferentially stained by exposure to the vapor of a 4% aqueous OsO_4 solution for 4 hr and appear dark in the micrographs; polystyrene (minority component) domains appear relatively light. Bright field images were obtained by mass-thickness contrast on a JEOL JEM-1210 transmission electron microscopy, at an accelerating voltage of 120 kV.

RESULTS AND DISCUSSION

DMA Miscibility Studies

The selective miscibility of oligomer resin additives with the different phases in block copolymers is key to the modification of microstructure. DMA was used to determine how the glass transitions of the blocks change as a function of the concentration of the blend components. These changes indicate the miscibility of the resin additives in the separate blocks of the copolymer. The glass transitions of the polystyrene (PS) and the polyisoprene (PI) phases are evident in the DMA loss modulus spectra (G'') of the solution-cast blends (Figs. 1 and 2).

In Figure 1, the loss modulus, G'', spectra of the *W*95/SIS mixtures show only a slight initial shift in the *Tg* of PS (105°C) and then this *Tg* is independent of *W*95 addition, while the *Tg* of PI (−65°C) steadily increases and broadens with increasing *W*95 content. This indicates solubility of *W*95 in the PI domains. The *W*95 also lowers

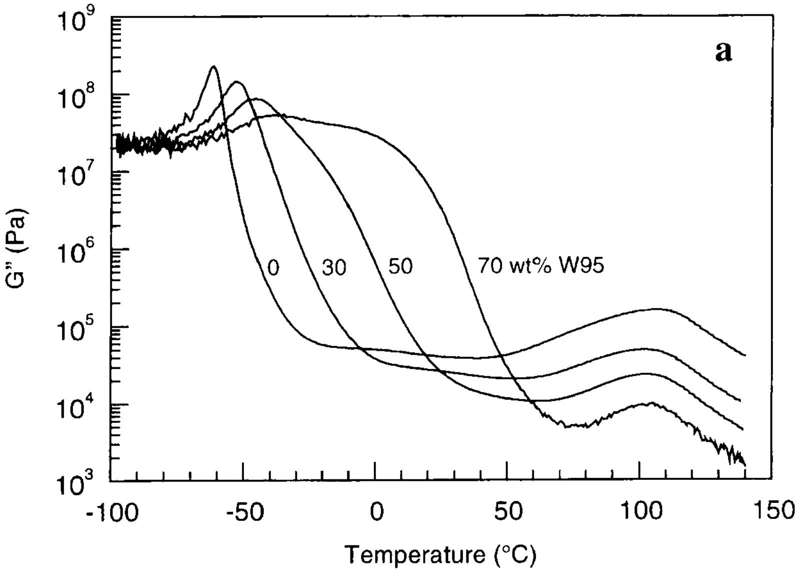


FIGURE 1 DMA (a) loss modulus and (b) storage modulus *versus* temperature for the solution-cast SIS and SIS/*W*95 mixtures, at 1 rad/s and 3°C/min.

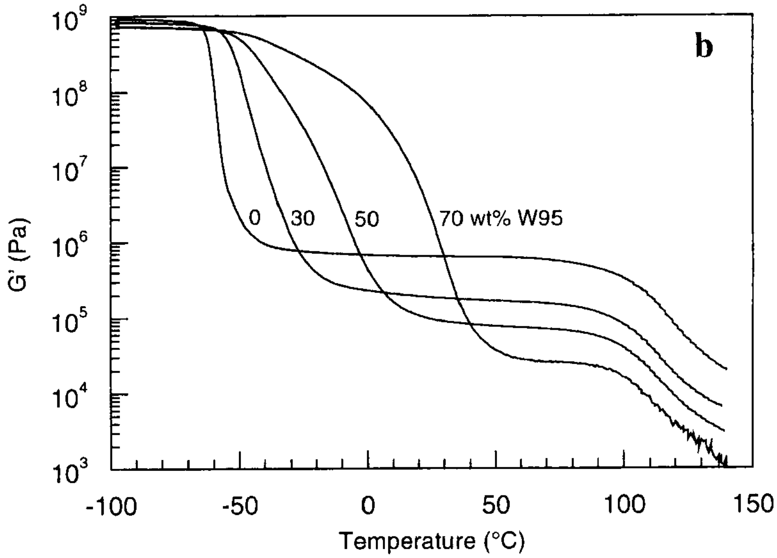


FIGURE 1 (Continued).

the level of the rubbery plateau modulus (the G' curve). Lowering the modulus below the Dahlquist criterion for tack (3×10^5 Pa) is the primary purpose of the *W*95 addition. The PI glass transition is broadened, eliminating some of the low temperature rubbery range. However, if low-temperature performance is not required, this broadening has been correlated with increased peel strength [1], as it adds more stiffness to the higher rate deformations of peeling.

Adding the PPO (Fig. 2) causes a continuous increase in the *Tg* of the PS domains while the *Tg* of PI shows an initial slight shift and is then independent of PPO concentration. PPO is, thus, preferentially dissolved in the PS domains. This verifies, as expected from chemical structure, that *W*95 is a midblock associating resin and PPO is an endblock associating resin in SIS. DMA was particularly useful for these miscibility studies. It was sensitive to the glass transitions of the blends, unlike DSC, particularly for the (low weight-fraction) polystyrene phase, where the DSC signal change at the glass transition was not distinguishable. For all the concentrations in Figure 2, the PPO addition was sufficient to cause the microstructure to change from spherical to lamellar (see the following section), and this was

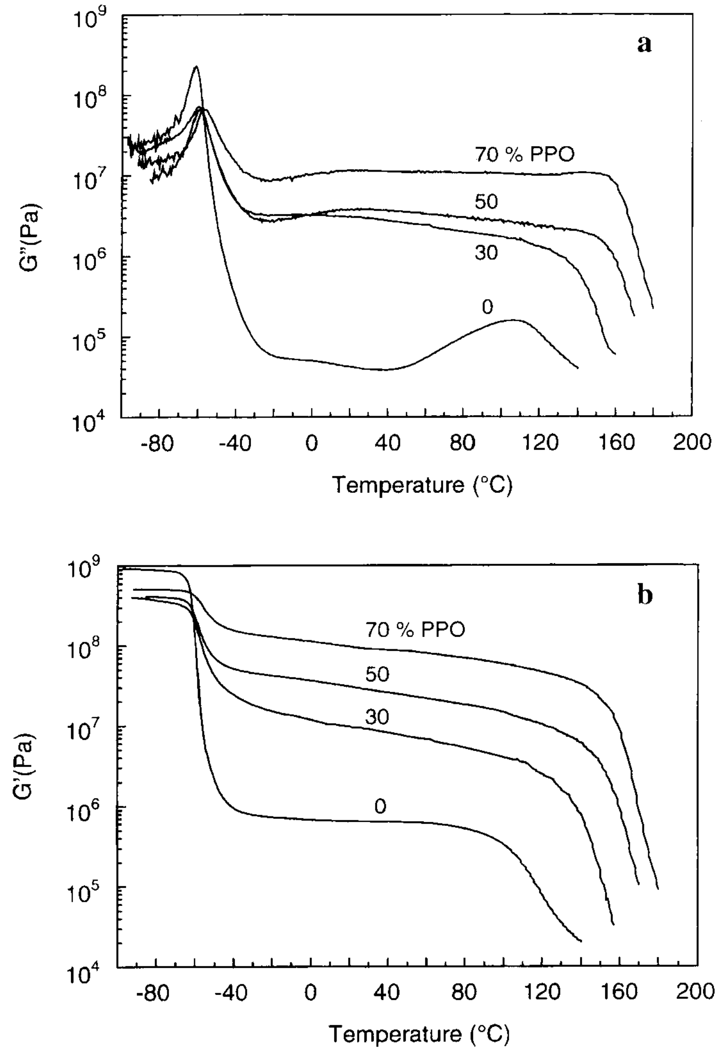


FIGURE 2 DMA (a) loss modulus and (b) storage modulus *versus* temperature for the solution-cast SIS and SIS/PPO mixtures, at 1 rad/s and 3°C/min.

accompanied by huge increases in the rubbery plateau modulus (G'). As we will subsequently show, if the PPO addition is kept small enough a spherical microstructure is maintained and the rubbery plateau modulus is then unaffected.

Microstructure

The micrograph of solution-cast SIS (Fig. 3) shows a typical body-centered cubic (BCC) structure; both 110 and 100 projections of BCC structure can be identified. In *W*95/SIS mixtures, uniform copolymer microstructures were observed for all blend compositions examined: macrophase separation was not apparent. Regular BCC microstructures were found for the 30 wt% (Fig. 4a) and 50 wt% (Fig. 4b) *W*95 blends. The degree of long-range order, as measured by the average grain size, appears to improve with increasing *W*95. A progressive decrease in PS (light, microphase-separated areas) domain size can also be observed in Figures 3, 4a and 4b (0%, 30% and 50% *W*95, respectively). Meanwhile, the *d*-spacing, as measured by SAXS, is almost unchanged in these blend compositions: Figure 5 shows the one-dimensional SAXS profiles. The *d*-spacings, extracted from these profiles as $d = 2\pi/q^*$, where q^* represents the principal (*i.e.*, first-order) peak position, are 30.5 nm, 30.4 nm and 31.0 nm for neat SIS, 30 wt%

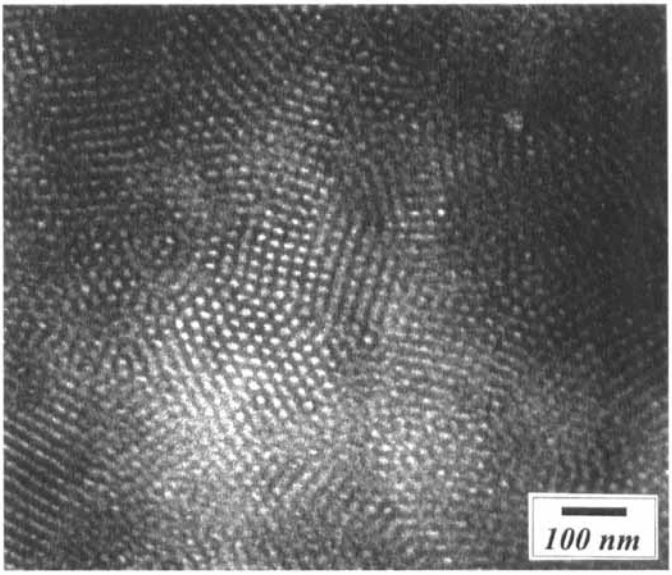


FIGURE 3 Microstucture of solution-cast neat SIS: body-centered cubic (with 110 and 100 projections visible). The polyisoprene matrix phase is stained dark and the polystyrene spherical domains appear light.

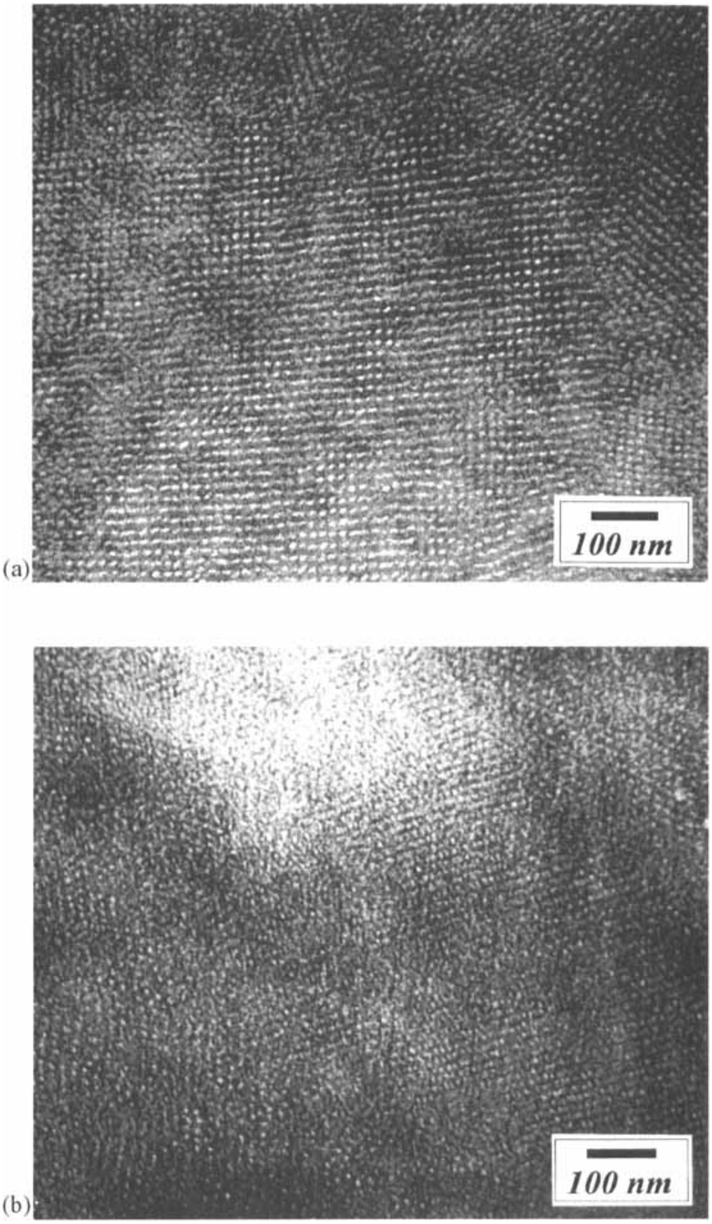


FIGURE 4 Microstructures of solution-cast SIS/*W*95 blends containing *W*95 concentrations of (a) 30 wt%, (b) 50 wt%, (c) 70 wt%. The polystyrene phase is stained dark.

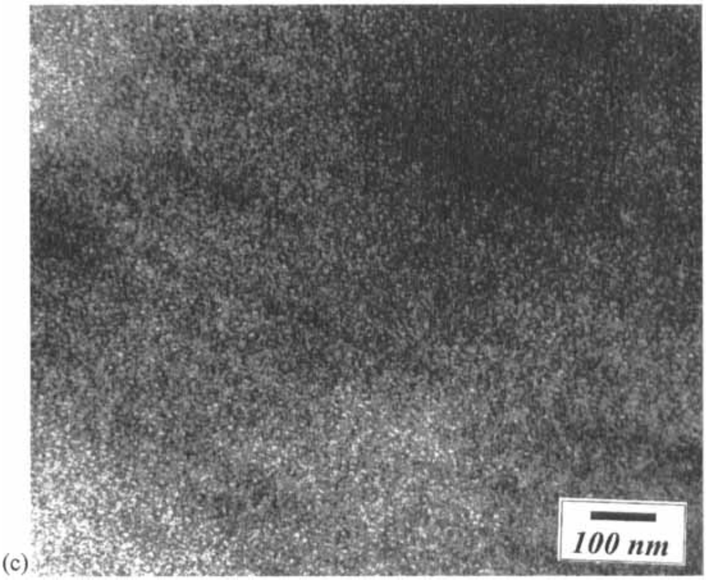


FIGURE 4 (Continued).

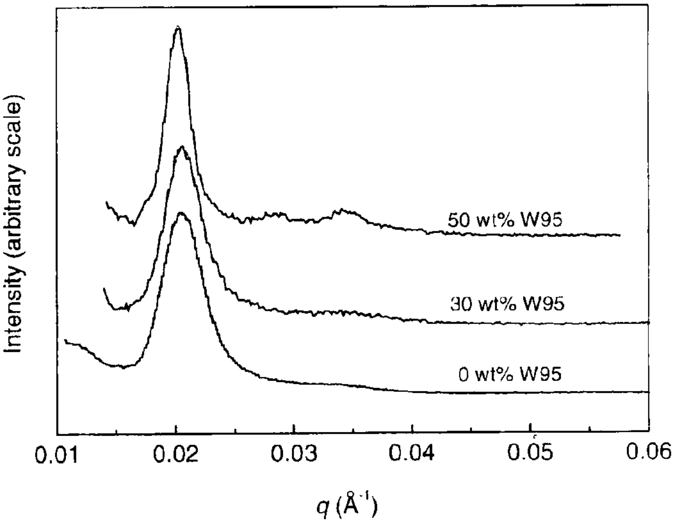


FIGURE 5 SAXS patterns from SIS/*W*95 mixtures showing that the principal peak position remains unchanged as the *W*95 concentration increases to 50 wt%. The peak position is found using a Gaussian fit. The domain spacing is $d = 2\pi/q^*$, where q^* is the principal peak position.

*W*95 and 50 wt% *W*95, respectively. Since the introduction of *W*95 swells the PI matrix phase, the only way to keep a fixed *d*-spacing in the increased volume of PI matrix phase is to increase commensurately the number of microphase-separated PS domains. This, in turn, can only be accomplished by decreasing the average number of PS chains in each domain, as observed in the decreasing domain size seen in the micrographs. When the *W*95 content is further increased, the cubic morphology begins to transform to a disorder-like morphology (Fig. 4c); however, a signature of the BCC pattern can still be identified from SAXS. This suggests a short range ordered cubic microstructure still exists.

When 10 wt% of PPO is introduced into the SIS, the cubic morphology of SIS transforms to a hexagonal cylinder morphology (Fig. 6a). Upon increasing PPO further, a typical lamellar morphology (Fig. 6b) appears, with no sign of macrophase separation. The transformation is similar to that obtained for diblock copolymer blended with polystyrene homopolymer [16]. When the PPO content is increased to 40 wt%, macrophase separation occurs as shown in

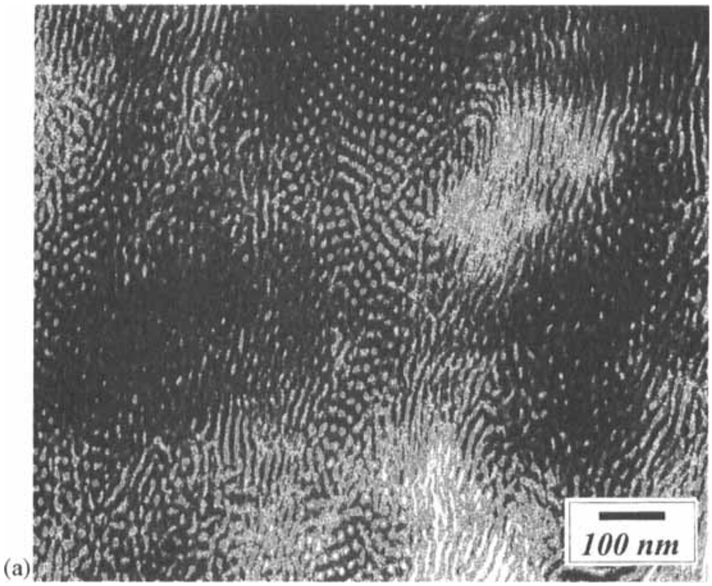
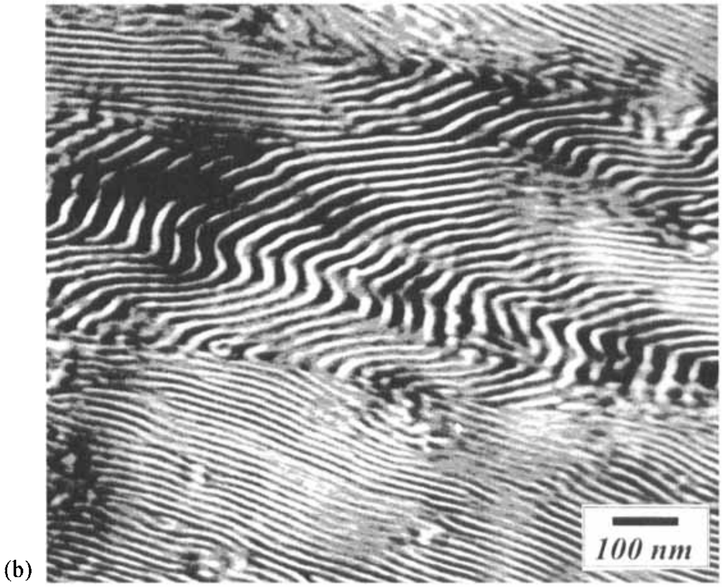


FIGURE 6 Microstructures of solution cast SIS/PPO blends containing PPO concentrations of (a) 10 wt%, (b) 30 wt%, (c) 40 wt%. The polystyrene phase is stained dark.



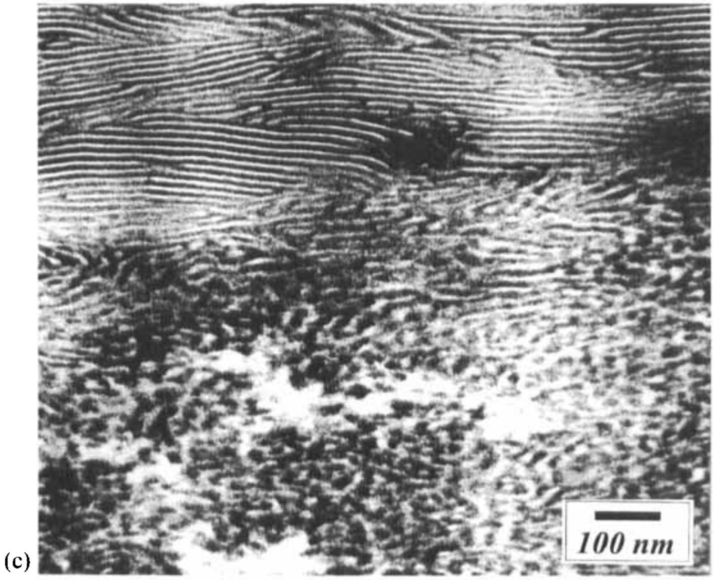


FIGURE 6 (Continued).

Figure 6c. PPO forms macrodomains with domain size ranging from submicron to micron in the continuous SIS phase. The population and domain size of the dispersed PPO phase increases with increasing PPO content while the SIS microdomain structure still exhibits a lamellar morphology. At a PPO loading of 70 wt%, PPO is still the dispersed phase in a continuous SIS matrix, but the microdomain structure disappears and a disordered morphology emerges. SAXS results show an increase in the *d*-spacing from 30.3 nm in SIS (cubic) to 37.8 nm with 10 wt% PPO (cylinder), then to 50.8 nm with 30 wt% PPO (lamellae) and, finally, to 56.0 nm with 50 wt% PPO (lamellae). This suggests the PS microdomains are significantly swollen by the PPO and that the PPO eventually separates out due to a limitation of the swelling.

Mixtures of SIS, *W*95 and PPO were prepared in order to study the morphology of SIS in the presence of both midblock and endblock associating resins. The various mixtures are designated as $x/y/z$ where x stands for the percentage of SIS, y for the percentage of *W*95 resin, and z for the percentage of PPO resin. Distinct microstructures were identified when the concentration of SIS was above 40 wt% in the mixtures. Macrophase separation occurred for mixtures containing higher concentration of PPO and lower concentration of SIS. A simplistic ternary phase diagram for the SIS/*W*95/PPO system was constructed from these observations (Fig. 7). For simplicity, we treat SIS, *W*95 and PPO as single, chemically-homogeneous components.

The phase diagram and DMA results show that when the microstructure changes from spherical BCC to hexagonal cylinders and then to lamellar, the modulus increases. These microstructure transformations are effected by increasing the ratio of the polystyrene phase to the polyisoprene phase; in this case, by increasing the amount of PPO relative to *W*95. The increase in modulus with this microstructure change is not advantageous to meeting the Dahlquist criterion for tack (modulus $< 3 \times 10^5$ Pa). To keep the modulus low, it is probably best to keep to the spherical microstructure and certainly necessary to avoid the lamellar microstructure.

Property Tests

Since relatively modest amounts of PPO (< 5 wt%) were observed to effect a significant increase in the PS phase glass transition, we focused

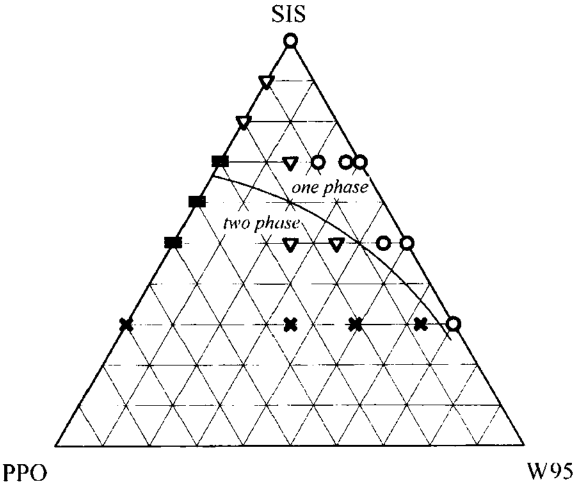


FIGURE 7 Simplistic ternary phase diagram for SIS/*W*95/PPO system, where ○ indicates body-center cubic, ∇ indicates hexagonal cylindrical, ≡ indicates lamellar, and × indicates disordered microstructure. For simplicity, SIS is treated as a single, chemically-homogeneous component, and the line demarking the "one phase" and "two phase" regions indicates where PPO phase separates out of the polystyrene domains.

on formulations where the SIS was constant at 50 wt%, the *W*95 component was added to approximately 50 wt% to lower the modulus below the Dahlquist criterion, and PPO was added in small amounts to raise the PS phase glass transition. These blends were in the ratio 50/50/0, 50/48.5/1.5 and 50/47.5/2.5 for SIS/*W*95/PPO. Room temperature peel and elevated temperature lap shear tests were conducted. The results of standard (PSTC-1, 12 inches/min (30.5 cm/min), 1 inch (2.5 cm) wide) peel tests (Fig. 8) show that the addition of these low quantities of PPO had no significant effect on peel strength. Standard lap shear tests (PSTC-7, with 1,000 g weight) at room temperature and at 50°C were not discriminating, as all samples held longer than a week. Tests at 75°C were successful in distinguishing the blends: Figure 9 shows the results where holding times at 75°C increased exponentially with PPO content, showing the practical application of this PPO for increasing the service temperature range of these PSAs.

Results for G' and G'' are shown in Figures 10a and 10b. The addition of the PPO has a small initial effect on the glass transition of

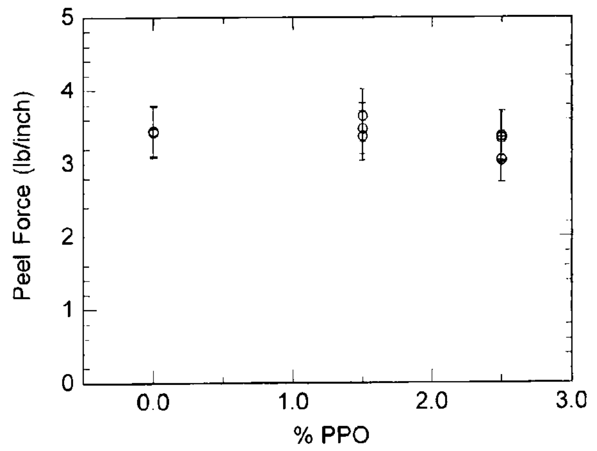


FIGURE 8 Room temperature peel force tests (PSTC-1, 12 in/min (30.5 cm/min), 1 inch (2.54 cm) width) *versus* PPO content. All formulations have 50 wt% SIS and 50 wt% additives (*W*95 plus PPO).

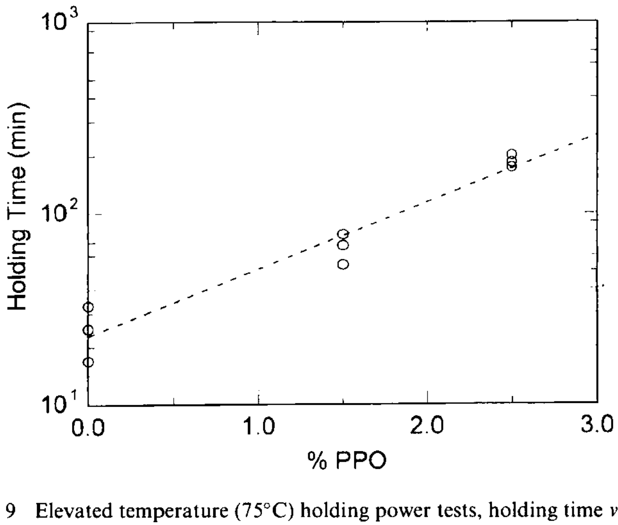


FIGURE 9 Elevated temperature (75°C) holding power tests, holding time *versus* PPO content (lap shear tests based on PSTC-7 with a 1,000 g weight). Formulations are all 50 wt% SIS and 50 wt% additives (*W*95 plus PPO).

the polyisoprene phase in these formulations. The level of the storage modulus, G', remains unchanged from very low temperatures up through the normal use range ($< 70°C$). However, the effects of PPO

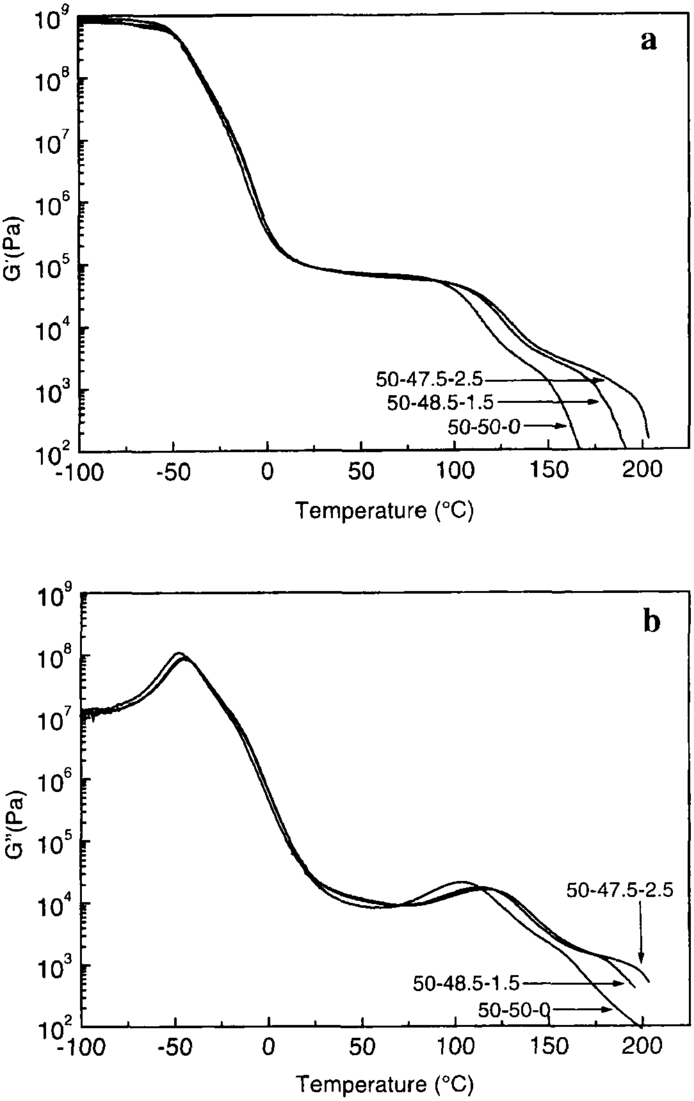


FIGURE 10 DMA (a) storage modulus and (b) loss modulus *versus* temperature for solution-cast SIS/*W*95/PPO mixtures at 1 rad/s and 3°C/min. SIS concentration is constant at 50 wt%.

are significant on the polystyrene phase glass transition, which is raised approximately 10°C in the 2.5 wt% PPO formulation (as measured from the peak in the G'' curve). At higher temperatures, the G'

curve shows a distinct change of slope that has been identified (and confirmed with SAXS) by us and by others [17] to be a signature of the order-disorder transition in block copolymers. Figure 11 summarizes the changes in the PS phase glass transition, and in the order-disorder transition, with increasing PPO addition.

Adding PPO raises the PS phase glass transition temperature; the rise in the ODT temperature is even greater. Even so, it is the glass transition that is expected to limit the upper use temperature, since the thermoplastic elastomer flows much more easily above this temperature. The ODT might be expected to influence the processing window, *e.g.*, the ranges of temperature, coating rates, and other processing parameters that allow uniform coatings. Direct manipulation of the ODT temperature is relatively unexplored in terms of influencing the properties of adhesives, or structure–processing–property relationships. Higher ODT's might increase the rate and quality of microstructure development following melt processing (in turn affecting properties), but studying this remains for future work.

The increase in the ODT and in the polystyrene glass transition is significant with modest PPO addition. This is related to the relatively small amount of polystyrene present in the D1107 block copolymer (15 wt%). The increase in the glass transition follows the Fox

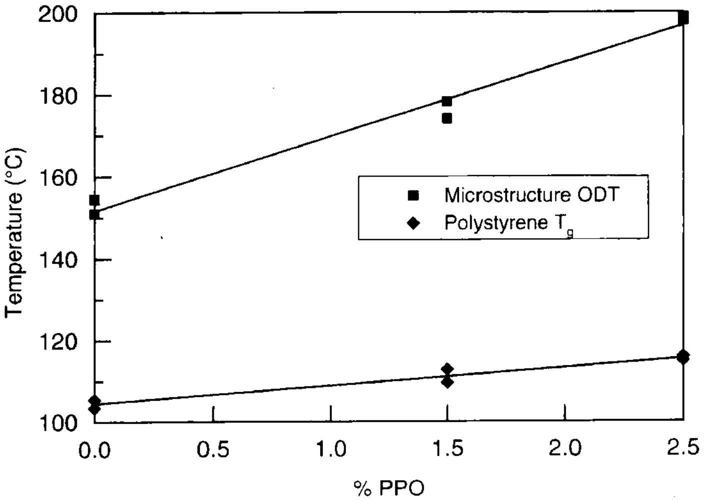


FIGURE 11 Effect of PPO addition on transition temperatures (*Tg* and ODT) of the solution-cast SIS/*W*95/PPO mixtures.

equation. As has been noted [15], block copolymers with greater proportions of polystyrene used to be thought better for PPO blends. The rationale was that the increased weight fraction of polystyrene would provide a larger reservoir for PPO, allowing more to be added, resulting in a greater increase in the polystyrene glass transition and, thus, in the service temperature. This is not necessarily so, as the increase in the glass transition will only follow the proportion of PPO to polystyrene. The same increase in glass transition will result with smaller weight fractions of PPO for lower weight fractions of polystyrene in the block copolymer.

CONCLUSIONS

The requirements of low modulus for tack and higher service temperatures are met with small additions of PPO (<3 wt%) to SIS/*W*95/PPO blends. These additions left the rubbery plateau modulus unaffected. In our work, as long as the microstructure remains spherical, the rubbery modulus is essentially unaffected by PPO addition. The modulus was lowered to meet the Dahlquist criterion for tack with addition of approximately 50 wt% *W*95. In formulating this model adhesive, DMA studies were effective in determining the miscibility of resin additives in the different blocks of the copolymer. DMA simultaneously showed the level of the rubbery modulus in the use region (criterion for tack) and changes in the glass transition and ODT temperatures. The increases observed in the polystyrene phase glass transitions were key to the higher service temperature holding power performance.

Acknowledgements

This work was supported by the Center for Interfacial Engineering, an NSF-supported Engineering Research Center at the University of Minnesota, by the Minnesota Department of Transportation, and by the National Science Council of Taiwan (NSC 87-2218-E-005-024). The assistance of Mark Johnson, Dui Bui and Joseph Huang with the measurements is gratefully acknowledged.

References

[1] *Handbook of Pressure Sensitive Adhesives Technology*, Satas, D. Ed. (Van Nostrand Reinhold, NY, NY, 1989).
[2] Kraus, G., Jones, F. B., Marrs, O. L. and Rollmann, K. W., *J. Adhesion* **8**, 235 (1977).
[3] Krenceski, M. A., Johnson, J. F. and Temin, S. C., *JMS-Rev. Macromol. Chem. Phys. C* **26**(1), 143 (1986).
[4] Kamagata, K., Kosaka, H., Hino, K. and Toyama, M., *J. Appl. Polym. Sci.* **15**, 483 (1971).
[5] Dahlquist, C. A., *Proc. Nottingham Conf on Adhesion*, Part III (Maclaren & Sons Ltd., London, 1966), Chap. 5, p. 134.
[6] Kambour, R. P., *U.S. Pat. No. 3,639,508* (1 Febuary, 1972).
[7] Crossland, R. K. and Harlan, J. T., *U.S. Pat. No. 3,917,607* (4 November, 1975).
[8] Shultz, A. R. and Gendron, B. M., *J. Appl. Polym. Sci.* **16**, 461 (1972).
[9] Bair, H. E., *Polym. Eng. Sci.* **10**, 247 (1970).
[10] MacKnight, W. J., Stoelting, J. and Karasz, F. E., *Adv. Chem. Ser.* **99**, 29 (1971).
[11] Hansen, D. R., *U.S. Pat. No. 4,104,323* (1 August, 1978).
[12] Hansen, D. R., *U.S. Pat. No. 4,141,876* (27 February, 1979).
[13] Chu, W. K. and Ruckel, E. R., *U.S. Pat. No. 5,807,915* (15 September, 1998).
[14] Tucker, P. S., Barlow, J. W. and Paul, D. R., *Macromolecules* **21**, 2794 (1988).
[15] Himes, G. R., Hansen, D. R., Fulton, S. L. and Shafer, D. L., *TAPPI Proceedings, 1996 Hot Melt Symposium*, p. 71 (1996).
[16] Winey, K. I., Thomas, E. L. and Fetters, L. J., *Macromocules* **25**, 2645 (1992).
[17] Hanley, K. J. and Lodge, T. P., *J. Polym. Sci., Polm Phys. Ed.* **33**, 3101 (1998).