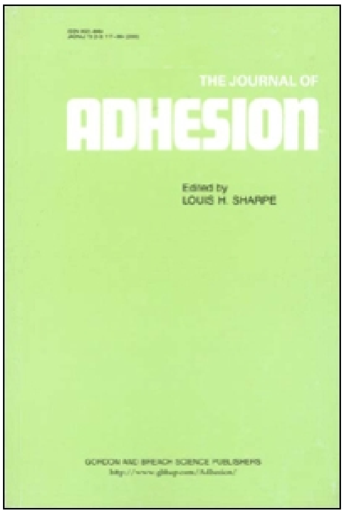

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Viscoelastic Behavior, Thermodynamic Compatibility, and Phase Equilibria in Block Copolymer-Based Pressure-Sensitive Adhesives

Chang Dae Han[a]; Jinhwan Kim[a]; Deog Man Baek[a]
[a] Department of Chemical, Engineering and Polymer Research Institute, Polytechnic University, Brooklyn, New York, U.S.A.

To cite this Article Han, Chang Dae , Kim, Jinhwan and Baek, Deog Man(1989) 'Viscoelastic Behavior, Thermodynamic Compatibility, and Phase Equilibria in Block Copolymer-Based Pressure-Sensitive Adhesives', The Journal of Adhesion, 28: 4, 201 — 230

To link to this Article: DOI: 10.1080/00218468908030171

URL: http://dx.doi.org/10.1080/00218468908030171

J. Adhesion, 1989, Vol. 28, pp. 201–230
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Viscoelastic Behavior, Thermodynamic Compatibility, and Phase Equilibria in Block Copolymer-Based Pressure-Sensitive Adhesives

CHANG DAE HAN,† JINHWAN KIM and DEOG MAN BAEK

Department of Chemical Engineering and Polymer Research Institute, Polytechnic University, Brooklyn, New York 11201, U.S.A.

(Received June 25, 1988; in final form December 20, 1988)

The viscoelastic behavior, thermodynamic compatibility, and phase equilibria in block copolymer-based pressure-sensitive adhesives were investigated. The block copolymers investigated were: (1) polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) copolymer (KRATON® D-1102, Shell Development Company) and (2) polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymer (KRATON® D-1107, Shell Development Company). The tackifying resins investigated were: (1) WINGTACK® 86 (Goodyear Tire & Rubber Company) and (2) PICCOTAC® 95BHT (Hercules Inc.). Samples of various compositions were prepared by a solution-casting method with toluene as solvent. Measurements of dynamic storage modulus (G'), dynamic loss modulus (G''), and loss tangent ($\tan\delta$) were taken, using a Rheometrics Mechanical Spectrometer. It was found that: (1) both WINGTACK 86 and PICCOTAC 95BHT were equally effective in decreasing the plateau modulus (G_N^0), and increasing the glass transition temperature (T_g) of the polyisoprene midblock of KRATON 1107; and (2) WINGTACK 86 was very effective in decreasing the G_N^0 and increasing the T_g of the polybutadiene midblock of KRATON 1102, whereas PICCOTAC 95BHT was not. The observed difference between WINGTACK 86 and PICCOTAC 95BHT in decreasing the G_N^0 and increasing the T_g of the polybutadiene midblock of KRATON 1102 (perhaps to SBS block copolymers in general) is explained by the values of the interaction parameter for WINGTACK 86 and KRATON 1102, and for PICCOTAC 95BHT and KRATON 1102. The interaction parameter was determined, using the piezoelectric quartz sorption method. Phase diagrams were constructed for the four block copolymer/tackifying resin systems investigated, using information obtained from both dynamic viscoelastic measurements and optical microscopy. It was found that when mixed with KRATON 1102, PICCOTAC 95BHT formed separate domains whereas WINGTACK 86 did not over the range of concentrations and temperatures investigated. This confirms the evidence obtained from two other independent experimental techniques, namely, dynamic viscoelastic measurements and the piezoelectric sorption method. We have concluded from the present study that PICCOTAC 95BHT is not as an effective tackifying resin as WINGTACK 86, when each is mixed with KRATON 1102. It is pointed out further that information on the order–disorder transition temperature T_r, which was determined from a rheological technique proposed by us, is valuable in determining optimal processing conditions for block copolymer-based pressure-sensitive adhesives.

KEY WORDS Block copolymer; dynamic viscoelastic properties; phase diagram; pressure-sensitive adhesives; tackifying resins; thermodynamic compatibility.

---

† To whom all correspondence should be addressed.

INTRODUCTION

The adhesive industry in the United States is probably the largest and most complex market for formulated specialty polymers. Its steady increase is expected to continue in the years to come. Among the various kinds of adhesives, the demand for pressure-sensitive and hot-melt adhesives has grown significantly. Various types of elastomers are used in this branch of the industry. Although natural rubber still has the largest volume, adhesives based on synthetic elastomers have grown very fast in recent years. The block copolymers are gaining wide acceptance, due to their excellent balance of tack, adhesion strength and shear holding characteristics. The most widely used block copolymer in pressure-sensitive adhesives has a polystyrene block on both ends of a polydiene midblock (e.g., the ABA-type triblock copolymers). The usefulness of these block copolymers as adhesives is a direct consequence of their unique structure. The polystyrene endblock, which is incompatible with the polydiene midblock, separates on a microscopic scale to form polystyrene microdomains, thereby creating a physically-crosslinked network structure.[1,2]

Since the elastomer alone is not sufficient to give rise to the desired levels of adhesion and tack, one usually adds low molecular weight hydrocarbons (e.g., aliphatic or aromatic hydrocarbons, polyterpenes, rosin and its derivatives), in order to improve its ability to wet the surface sufficiently and to form a bond of measurable strength upon contact. This low molecular-weight material is referred to as a "tackifying resin." Tackifying resins come in a variety of chemical structures and physical properties.[3] They are thermoplastics and usually form an amorphous glass at room temperature.

Choosing the proper elastomer and tackifying resin pair is one of the most important tasks in obtaining successful adhesives which meet the required performance level, as determined by tack and the resistance to peel and shear. Tack is essentially a measure of viscous flow under conditions of high strain rates and low stress levels, while shear adhesion is a measure of viscous flow at low strain rates and intermediate stress levels. Peel adhesion may be considered to be a measure of the resistance to viscous flow at intermediate strain rates and high stress levels, as well as a measure of the cohesive strength of pressure-sensitive adhesives. It is certain that in a given adhesive system these properties tend to be mutually exclusive, so that a balance must be maintained on the desired performance requirements. Hence, the determination of an optimum concentration of tackifying resin, for instance, can be one of the most important tasks in producing successful adhesives. The higher the resin concentration, the greater the peel adhesion and surface tack, but the lower the cohesive strength will be.

Several factors must be considered when formulating an adhesive. Firstly, the tackifying resin and elastomer must be compatible. Unless the resin is compatible with the elastomer, the resin will form a dispersed phase and thus will not be able to reduce the modulus of the elastomer/resin blend, making the blend undesirable as a pressure-sensitive adhesive.[4] When using an ABA-type block copolymer, a distinction must be made between the effect of midblock-associating resins and that of endblock-associating resins, for the following reasons. Aliphatic olefin-derived resins, rosin esters, polyterpenes, and terpene phenolic resins tend to associate with the polydiene midblocks and not with the polystyrene endblocks. The primary function of a midblock-associating resin is to develop tack in the thermoplastic elastomer. On the other hand, polyaromatics and the resins derived from coal tar or petroleum tend to associate with the polystyrene endblocks and not with the polydiene midblocks.

Secondly, information on the viscoelastic behavior of an adhesive is needed to evaluate its performance. The principal problem involved in the application of adhesives to substrates is rheological in nature. In order to have good tack, the viscosity of the elastomer/resin mixture must be lower than that of the elastomer itself, such that it can flow easily and is able to wet the surface sufficiently upon application. On the other hand, viscoelasticity information is required for understanding the ultimate properties of an adhesive. Since tack, shear adhesion, and peel strength are determined at different strain rates or stresses, viscoelasticity information (such as viscosity and elasticity, yield stress of the adhesive, and their dependencies on strain rate) must be well understood.

The testing of pressure-sensitive adhesives involves both bonding and debonding steps. For satisfactory performance in the bonding step, the material must be in a permanently deformable state, implying that it must possess the features typical of a liquid. However, satisfactory performance in the debonding step demands that the adhesive yield little under stress, and therefore behave essentially as a solid. A good adhesive adequately wets the substrate during its application, so that subsequent failure, when it occurs, is of a cohesive nature rather than an adhesive one. Thus, the viscoelastic behavior of adhesives is an important factor in performance evaluation. Therefore, it can be surmised that a better understanding of the significance of the type and concentration of tackifying resin on the viscoelastic behavior of pressure-sensitive and hot-melt adhesives is needed so as to provide better control of (or to improve) their end-use performance.

Very recently, we have conducted an investigation on the viscoelastic behavior, thermodynamic compatiblity, and phase equilibria in block copolymer-based pressure-sensitive adhesives that were prepared in our laboratory. In this paper we will report the highlights of our investigation.

BACKGROUND

We will review very briefly some of the previous studies, which are directly related to the results of this study.

Viscoelastic behavior of mixtures of a block copolymer and a tackifying resin

Kraus and coworkers[5–7] reported a series of experimental studies on the dynamic viscoelastic properties of mixtures of a block copolymer and a tackifying resin.

They reported that the use of a tackifying resin increased the glass transition temperature (T_g) of the polydiene midblock and decreased the dynamic storage modulus (G') in the plateau region, hereafter referred to as the plateau modulus (G_N^0). They stated that such characteristics are highly desirable for a low molecular-weight resin to be effective as a tackifying resin.

According to the classical concept of molecular viscoelasticity theory,[8] G_N^0 for dilute polymer solutions is proportional to the square of the volume fraction of the polymer ϕ_2,

$$G_N^0 = \phi_2^2 G_N^\infty \tag{1}$$

where G_N^∞ is the plateau modulus of the polymer. Note that G_N^∞ is related to the molecular weight of entanglement spacings, M_e:

$$G_N^\infty = \rho RT/M_e \tag{2}$$

where ρ is the density, R is the universal gas constant, and T is the absolute temperature. Assuming that the polystyrene microdomains in the block copolymer may be regarded as filler dispersed in a continuous polydiene matrix, Holden[9] estimated the value of G_N^∞ for ABA-type block copolymers, using the following expression:[10]

$$G_N^\infty = (\rho RT/M_e)(1 + 2.5C + 14.1C^2) \tag{3}$$

where C is the concentration of filler, which in this case is the concentration of polystyrene microdomains in the block copolymer.

When a tackifying resin is added to a block copolymer, often one cannot observe a clear plateau region in plots of G' *versus* temperature. Kraus and Rollmann[5] suggested that in such situations, the value of G_N^0 of a mixture consisting of a block copolymer and a tackifying resin can be approximated by the value of G' at the minimum value of loss tangent ($\tan \delta_{\min}$).

Class and Chu[11] studied the dynamic viscoelastic properties of mixtures of natural rubber (or a synthetic elastomer) and a tackifying resin. They reported that: (1) The molecular weight of the tackifying resin is very important for controlling the compatibility of mixtures, and macrophase separation was observed as the molecular weight of the tackifying resin was increased; (2) The T_g of compatible mixtures of an elastomer and a tackifying resin, as determined by the peak value of $\tan \delta$, can be estimated by the Fox equation:[12]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{4}$$

where T_g, T_{g1}, and T_{g2} are the peak temperatures of $\tan \delta$ for the mixture and the constituent components, respectively, and w_1 and w_2 are the weight fractions of the constituent components.

It should be pointed out that the studies referred to above have not addressed the important question as to whether or not the mixtures of block copolymer and tackifying resin used were indeed compatible. This is a very important and fundamental question, because the extent of compatibility for a tackifying resin with a block copolymer influences greatly the viscoelastic properties of the mixtures and, consequently, the adhesion characteristics of the block copolymer-based pressure-sensitive adhesives.

Thermally-induced transition behavior and phase equilibria in mixtures of a block copolymer and a tackifying resin

Today, it is a well-established fact that when an SB diblock copolymer, SBS or SIS triblock copolymer is heated above the upper (polystyrene) glass transition temperature (T_g), the microdomains of polystyrene will eventually be destroyed and then the block copolymer will form a homogeneous phase. The critical temperature at which the polystyrene microdomains are completely destroyed is often referred to as the "order–disorder transition temperature" (T_r).

An experimental determination or theoretical prediction of T_r is very important to determine optimal processing conditions for a block copolymer or its mixtures with tackifying resins, because the viscosity of a block copolymer becomes very low at and above its T_r. This is due to the fact that at temperatures below T_r, the microdomain structure of polystyrene in a block copolymer acts like a crosslinked network structure, giving rise to a very high viscosity. However, when the microdomain structure of polystyrene is completely destroyed at and above T_r, forming a homogeneous phase, the block copolymer will behave like a homogeneous molten polymer.

In recent years, Helfand and Wasserman[13–15] have developed a statistical thermodynamic theory, and Leibler [16] has also developed a statistical thermodynamic theory, both of which can be used to predict the T_r of block copolymers. Experimentally, Hashimoto and coworkers[17–19] and Roe and coworkers[20–23] have investigated the order-disorder transition behavior of SB, SBS or SIS block copolymers and determined their T_r's, using the small-angle X-ray scattering (SAXS) technique. They reported that the maximum scattered intensity present at room temperature persists well above the glass transition temperature of the polystyrene microdomains, but disappears at a critical temperature (T_r) at which the block copolymer becomes a homogeneous melt. Kraus and Hashimoto[24] conducted an experimental SAXS study on pressure-sensitive adhesive systems, and observed that the adhesive showed the same scattering pattern as the block copolymer and that the T_r of the adhesive was lower than that of the block copolymer.

Very recently, Han and coworkers[25,26] have proposed a rheological technique to determine the T_r of block copolymers, based on dynamic viscoelastic properties measured under isothermal conditions. Basically, the technique calls for logarithmic plots of dynamic storage modulus (G') *versus* dynamic loss modulus (G''), whereby the T_r of a block copolymer is determined by the temperature at which $\log G'$ *versus* $\log G''$ plots cease to vary with temperature. Earlier, Han and coworkers[27–31] have shown that when the morphological state of a polymer (a homopolymer, graft copolymer or heterogeneous polymer blend) does not vary with temperature, then $\log G'$ *versus* $\log G''$ plots become virtually independent of temperature.

When a low molecular-weight homopolymer (e.g., tackifying resin) is mixed with a block copolymer, the mixture can give rise to a complex equilibrium phase diagram, depending upon the extent of compatibility between the two components in the mixture. It is, therefore, very important for one to understand phase equilibria in a pressure-sensitive adhesive system, which consists of a tackifying resin and a block copolymer. Since the chemical structures of tackifying resins are very complex indeed, it would be very useful first to investigate phase equilibria in mixtures of a block copolymer and a homopolymer whose chemical structure is well established; for instance, polydiene, polystyrene or poly(α-methyl styrene) homopolymer. In this regard, it is worth mentioning the recent experimental studies of Roe and coworkers,[21-23] who investigated phase equilibria in mixtures of SB or SBS block copolymer with polystyrene homopolymer or polybutadiene homopolymer. Independently, Noolandi and coworkers[32,33] have developed a statistical thermodynamic theory, which allows one to construct phase diagrams for mixtures of a block copolymer and a homopolymer. The phase diagrams constructed theoretically by Whitmore and Noolandi[33] look very similar to some of the experimental results of Roe and coworkers.[22]

EXPERIMENTAL

Materials

The block copolymers used in this study were: (1) polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymer (KRATON® D-1107, Shell Development Company), and (2) polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) copolymer (KRATON® D-1102, Shell Development Company). Table I gives the molecular characteristics of the block copolymers investigated. The following two commercial tackifying resins were used: (1) WINGTACK® 86 (Goodyear Tire & Rubber Company), and (2) PICCOTAC® 95BHT (Hercules Company). The weight-average molecular weights ($\bar{M}_w$) of both WINGTACK 86 and PICCOTAC 95BHT were determined by gel permeation chromatography, and the glass transition temperatures (T_g) using differential scanning calorimetry, at a heating rate of 10°C/min. Table II gives a summary of the molecular characteristics and T_g for the tackifying resins investigated. We prepared twenty formulations, by adding different proportions of the tackifying resin (WINGTACK 86 or PICCOTAC 95BHT) to the block copolymer

TABLE I
Molecular characteristics of the block copolymers used

Sample code	Structure	Block molecular weight ($\times 10^{-3}$)	Polystyrene (wt%)	Triblock/ diblock ratio
KRATON® D-1102	SBS	10S-50B-10S	28	80/20
KRATON® D-1107	SIS	10S-120I-10S	15	80/20

TABLE II
Molecular characteristics of the tackifying resins used

Sample code	Structure	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	T_g(°C)
WINGTACK® 86	Modified polyterpene	1800	1.7	42
PICCOTAC® 95BHT	Piperylene	1100	1.7	43

TABLE III
Summary of the mixtures investigated

Block coplymer	Tackifying resin	Blend ratio
KRATON® 1102	WINGTACK® 86	90/10; 70/30; 50/50; 30/70; 10/90
KRATON® 1102	PICCOTAC® 95BHT	90/10; 70/30; 50/50; 30/70; 10/90
KRATON® 1107	WINGTACK® 86	90/10; 70/30; 50/50; 30/70; 10/90
KRATON® 1107	PICCOTAC® 95BHT	90/10; 70/30; 50/50; 30/70; 10/90

(KRATON 1102 or KRATON 1107). Table III gives a summary of the formulations used in the present investigation.

In the present investigation, an attempt was made to elucidate the structure of WINGTACK 86 and PICCOTAC 95BHT, using infrared (IR) spectroscopy and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. Based on the IR and NMR data, we have concluded that PICCOTAC 95BHT is an aliphatic hydrocarbon with cyclic structures, and WINGTACK 86 contains aliphatic hydrocarbons and poly(α-methyl styrene).

Sample preparation

Samples for viscoelastic measurements were prepared by first dissolving a predetermined amount of block copolymer and tackifying resin in toluene (10 wt% solid in solution) in the presence of an antioxidant (IRGANOX® 1010, Ciba-Geigy Group) and then slowly evaporating the solvent. The evaporation of solvent was carried out initially in open air at room temperature for a week and then in a vacuum oven at 40°C for three days. The last trace of solvent was removed by drying the samples in a vacuum oven at an elevated temperature by gradually raising the oven temperature up to 110°C. The drying of the samples was continued until there was no further change in weight. Finally, the samples were annealed at 130°C for 10 hours. The formulations employed in this investigation are given in Table III.

Measurement of dynamic viscoelastic properties

A Dynamic Mechanical Spectrometer (Rheometrics Inc.) in the parallel plate mode (8 mm diameter plates with a 2 mm gap) was used to take temperature scans of block copolymer and its mixtures with PICCOTAC 95BHT or WINGTACK 86. From temperature scans made from about −100 to 140°C at a fixed angular frequency (ω) of 10 rad/s, the dynamic storage modulus (G'), dynamic loss modulus (G''), and loss tangent ($\tan \delta$) defined as G''/G' were plotted againt temperature T. From the measurements, values of the plateau modulus (G_N^0) were determined from the plots of G' *versus* T at which $\tan \delta$ showed a minimum, i.e., values of G' at $\tan \delta_{\mathrm{min}}$.

A Model R16 Weissenberg Rheogoniometer (Sangamo Control Inc.) in the cone-and-plate mode (25 mm diameter plate and 4-degree cone angle with a 160-μm gap) was used to measure G' and G'' as a function of ω at various temperatures for mixtures of KRATON 1102 (or KRATON 1107) with WINGTACK 86 and with PICCOTAC 95BHT. The purpose of this experiment was to investigate the effect of tackifying resins (WINGTACK 86 and PICCOTAC 95BHT) on the thermally-induced order–disorder transition behavior of the block copolymer, using $\log G'$ *versus* $\log G''$ plots.

Piezoelectric sorption measurement

The piezoelectric quartz crystal sorption technique was used to determine the interaction parameter χ of the tackifying resin (WINGTACK 86 or PICCOTAC 95BHT) in polybutadiene (PB) homopolymer or polyisoprene (PI) homopolymer. This experimental technique has been successfully used to determine the solubility of a gas or a volatile liquid at elevated temperatures in a polymer[34,35] and to determine the interaction parameters χ for pairs of polymers.[36,37]

The apparatus used in this investigation was essentially the same as that described by Harris.[37] Briefly mentioned, a quartz crystal with a resonance frequency of approximately 7 MHz was used to determine the amount of solvent sorbed in a polymer sample under a given solvent partial pressure. A polymer solution of approximately 1 wt% was prepared by dissolving the polymer in chloroform. Toluene was chosen as the solvent probe, since toluene had already been used as a solvent in the preparation of the block copolymer/resin mixtures for rheological measurements. All sorption measurements were made at 25°C. The details about the construction of the apparatus and the physical principles involved are referred to in the doctoral dissertation of Harris.[37]

Turbidity measurements

As will be shown below, the determination of T_r by rheological measurements enables us to construct a phase diagram, as long as the tackifying resin added to a block copolymer does not form a separate phase and the T_r of the block copolymer decreases with increasing amounts of tackifying resin. In the present investigation we have found that mixtures of KRATON 1102 and PICCOTAC 95BHT at certain blend compositions showed evidence of *macrophase* separation at room temperature. Therefore, in order to construct a phase diagram for this system, we conducted turbidity measurements, basically a hot-stage microscope attached to a programmable temperature controller and a laser light source. This device enabled us to take photomicrographs of the sample as the temperature was raised from room temperature to about 200°C, at which point the sample showed evidence of thermal degradation.

RESULTS AND DISCUSSION

Viscoelastic behavior of block copolymer-based pressure-sensitive adhesives

Plots of log G' and tan δ *versus* temperature are given in Figure 1 for mixtures of KRATON 1107 and WINGTACK 86, and in Figure 2 for mixtures of KRATON 1107 and PICCOTAC 95BHT. It can be seen in these figures, over the concentration range investigated, that the addition of WINGTACK 86 or PICCOTAC 95BHT to KRATON 1107 decreased the plateau modulus G_N^0 which, in the present case, is approximated by the value of G' at the minimum value of the loss tangent, i.e., by the value of $G'(\tan \delta_{\min})$. Note in Figures 1 and 2 that the peak of tan δ in the lower transition region, representing the T_g of the polyisoprene phase in KRATON 1107, is shifted toward higher temperatures as the amount of tackifying resin in the mixture is increased. This is a clear indication that the tackifying resins, WINGTACK 86 and PICCOTAC 95BHT, are compatible with the polyisoprene midblock of KRATON 1107 over the concentration range investigated.

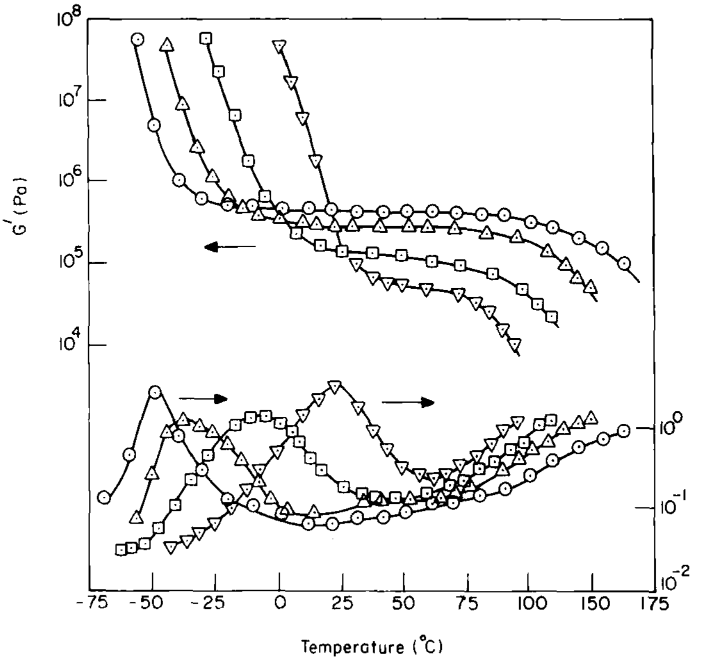

FIGURE 1 Log G' and log tan δ *versus* temperature: (○) KRATON 1107; (△) 70/30 KRATON 1107/WINGTACK 86; (□) 50/50 KRATON 1107/WINGTACK 86; (▽) 30/70 KRATON 1107/WINGTACK 86.

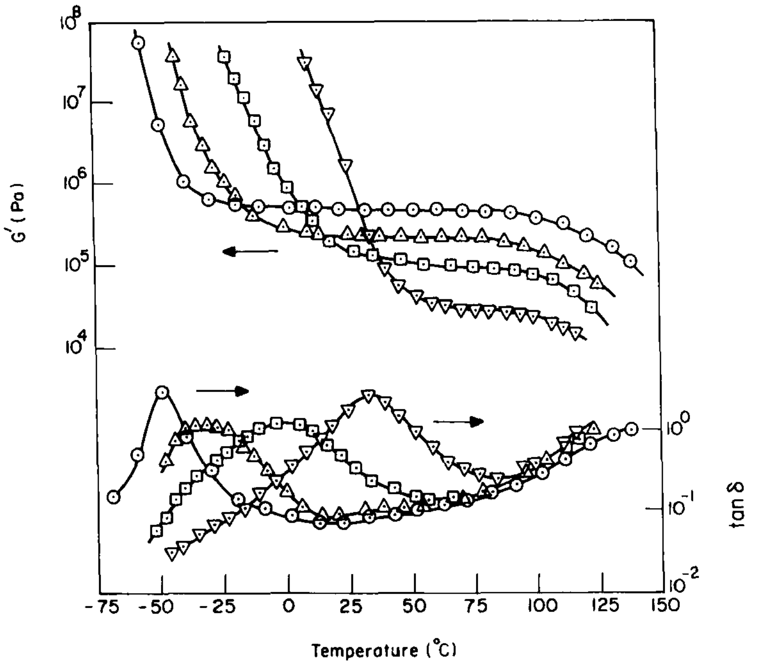

FIGURE 2 Log G' and log tan δ *versus* temperature: (⊙) KRATON 1107; (△) 70/30 KRATON 1107/PICCOTAC 95BHT; (⊡) 50/50 KRATON 1107/PICCOTAC 95BHT; (▽) 30/70 KRATON 1107/PICCOTAC 95BHT.

The experimentally determined values of T_g, read off from Figures 1 and 2, are given in Table IV for mixtures of KRATON 1107 and WINGTACK 86, and mixtures of KRATON 1107 and PICCOTAC 95BHT. Figure 3 gives plots of the reciprocal of T_g (absolute temperature) *versus* weight fraction of tackifying resin, in which the solid line represents the prediction given by Eq. (4) (see Table II for the T_g's of the tackifying resins). It can be seen that the experimentally obtained T_g values follow closely the theoretical predictions.

TABLE IV
Glass transition temperature (T_g) for mixtures of KRATON 1107 and tackifying resin

Material	T_g(°C)
(a) KRATON 1107/WINGTACK 86	
100/0	−50
70/30	−34
50/50	−4
30/70	26
(b) KRATON 1107/PICCOTAC 95BHT	
100/0	−50
70/30	−30
50/50	0
30/70	32

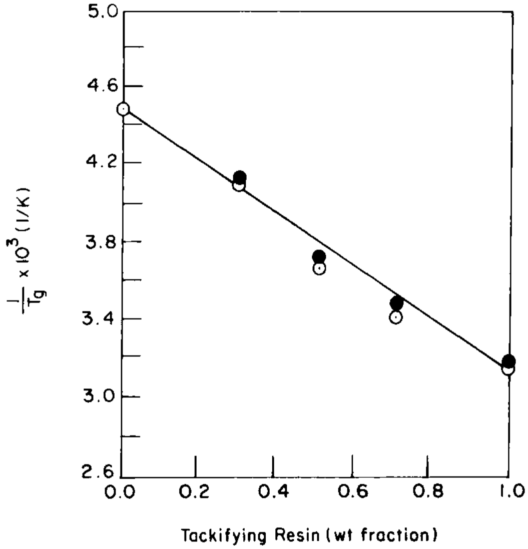

FIGURE 3 $1/T_g$ *versus* weight fraction of tackifying resin: (⊙) KRATON 1107/PICCOTAC 95BHT; (●) KRATON 1107/WINGTACK 86 mixtures.

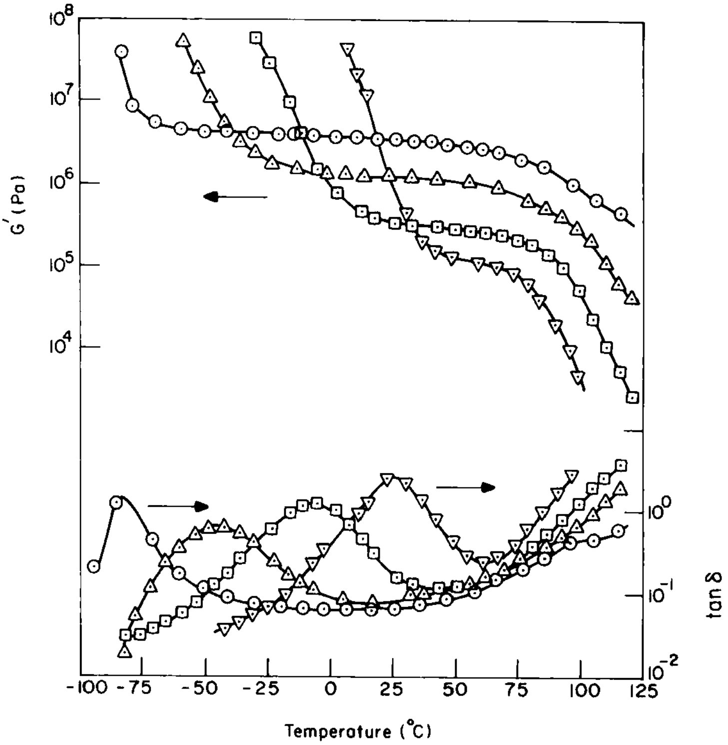

FIGURE 4 Log *G*′ and log tan δ *versus* temperature: (⊙) KRATON 1102; (△) 70/30 KRATON 1102/WINGTACK 86; (⊡) 50/50 KRATON 1102/WINGTACK 86; (▽) 30/70 KRATON 1102/WINGTACK 86.

On the basis of the experimental observations made above, that $G'(\tan \delta_{\min})$ of KRATON 1107 decreases and the T_g of the polyisoprene phase in KRATON 1107 increases with increasing amount of WINGTACK 86 or PICCOTAC 95BHT, it can be concluded that these two tackifying resins are equally compatible with KRATON 1107, over the concentration range investigated.

Plots of log G' and tan δ *versus* temperature are given in Figure 4 for mixtures of KRATON 1102 and WINGTACK 86, and in Figure 5 for mixtures of KRATON 1102 and PICCOTAC 95BHT. Figure 6 gives plots of the reciprocal of T_g (absolute temperature) *versus* weight fraction of WINGTACK 86 for mixtures of KRATON 1102 and WINGTACK 86. In these figures we observe some significant differences in the effect of the respective tackifying resins on the viscoelastic behavior of KRATON 1102, namely: (1) over the concentration range investigated the $G'(\tan \delta_{\min})$ of KRATON 1102 decreased with increasing amount of WINGTACK 86, whereas the $G'(\tan \delta_{\min})$ of KRATON 1102 initially decreased and then increased with increasing amount of PICCOTAC 95BHT; (2) the peak of tan δ in the lower transition region, representing the T_g of the polybutadiene phase in KRATON 1102, is shifted steadily to higher temperatures with increasing amount of WINGTACK 86, whereas the peak of tan δ in the

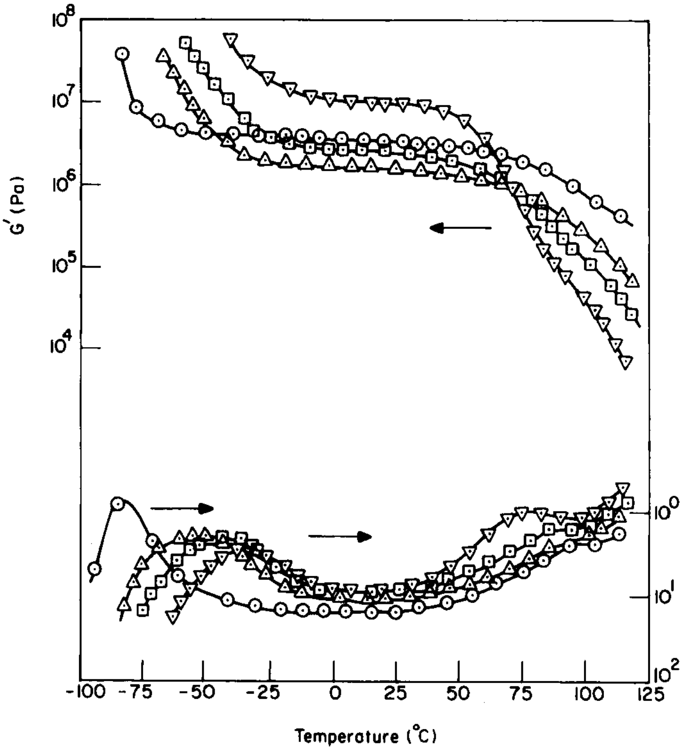

FIGURE 5 Log G' and log tan δ *versus* temperature: (○) KRATON 1102; (△) 70/30 KRATON 1102/PICCOTAC 95BHT; (□) 50/50 KRATON 1102/PICCOTAC 95BHT; (▽) 30/70 KRATON 1102/PICCOTAC 95BHT.

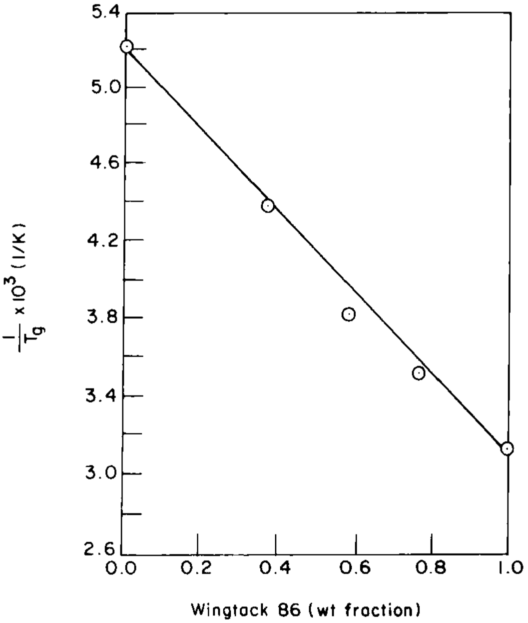

FIGURE 6 $1/T_g$ *versus* weight fraction of WINGTACK 86 for KRATON 1102/WINGTACK 86 mixtures.

lower transition region of KRATON 1102 is not shifted much as the concentration of PICCOTAC 95BHT in the mixture is increased above 30 wt%. A summary of the values of T_g determined from Figures 4 and 5 are given in Table V.

It is worth pointing out that when a tackifying resin (PICCOTAC 95BHT in the present case) increases the modulus of the block copolymer (KRATON 1102 in the present case), there are two possible reasons: one is that the tackifying resin is associated with the polystyrene domains of the block copolymer, and the other is

TABLE V
Glass transition temperature (T_g) for mixtures of KRATON 1102 and tackifying resin

Material	T_g(°C)
(a) KRATON 1102/WINGTACK 86	
100/0	−80
70/30	−45
50/50	−6
30/70	23
(b) KRATON 1102/PICCOTAC 95BHT	
100/0	−80
70/30	−55
50/50	−44
30/70	−37

that the tackifying resin forms a separate phase. As will be shown below, PICCOTAC 95BHT is not compatible with polystyrene homopolymer and, therefore, there is little chance that PICCOTAC 95BHT is associated with the polystyrene domains in KRATON 1102, especially when the amount of PICCOTAC 95BHT in the mixture is as much as 50 wt%. This then leads us to speculate that PICCOTAC 95BHT forms a separate phase. On the basis of the experimental results presented above, it is concluded that WINGTACK 86 is compatible with KRATON 1102, and that PICCOTAC 95BHT is not. Other evidence supporting this conclusion will be presented below.

The interaction parameter χ for an elastomer and a tackifying resin

When presenting the results of viscoelastic behavior, we have noted that the compatibility (or miscibility) of WINGTACK 86 with KRATON 1102 is much greater than that of PICCOTAC 95BHT with KRATON 1102 (compare Figure 4 with Figure 5), and that the compatibility of PICCOTAC 95BHT with KRATON 1107 is much greater than with KRATON 1102 (compare Figure 2 with Figure 5). In order to help understand the physical origins of the experimental observations, we investigated the thermodynamic compatibility of the various mixtures referred to above using the piezoelectric sorption method (see Experimental Section). Since the block copolymers (KRATON 1102 and KRATON 1107) consist of two components, polybutadiene and polystyrene in KRATON 1102, and polystyrene and polyisoprene in KRATON 1107, we decided to determine the interaction parameter χ_{23} between a homopolymer (polybutadiene, polyisoprene or polystyrene) and a tackifying resin (WINGTACK 86 or PICCOTAC 95BHT). For this purpose, we used the following nearly monodisperse homopolymers: (a) polybutadiene with the weight-average molecular weight ($\bar{M}_w$) 2760; (b) polyisoprene homopolymer with $\bar{M}_w = 75{,}000$; and (c) polystyrene homopolymer with $\bar{M}_w = 12{,}200$.

Before proceeding to take the piezoelectric sorption measurements with the various formulations of the pressure-sensitive adhesives that we had prepared, we first checked the accuracy of our measurements with the literature data of Saeki *et al.*,[38] by plotting the weight fraction activity coefficient (a_1/w_1) of toluene *versus* the weight fraction (w_1) of toluene in the polystyrene solution. Figure 7 gives a comparison between the study of Saeki *et al.*[38] and this study, which proved to be very satisfactory. Note that the data of Saeki *et al.*[38] were also obtained by the piezoelectric sorption method.

Table VI gives a summary of the values of the interaction parameters χ_{23} for the various formulations investigated in the present study. In determining the values of χ_{23}, we have used the Scott theory:[39]

$$\ln a_1 = \ln \phi_1 + (1 - 1/N_2)\phi_2 + (1 - 1/N_3)\phi_3 + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(1 - \phi_1) - \chi_{23}\phi_2\phi_3 \tag{5}$$

where a_1 is the activity of the solvent, which must be measured in a ternary

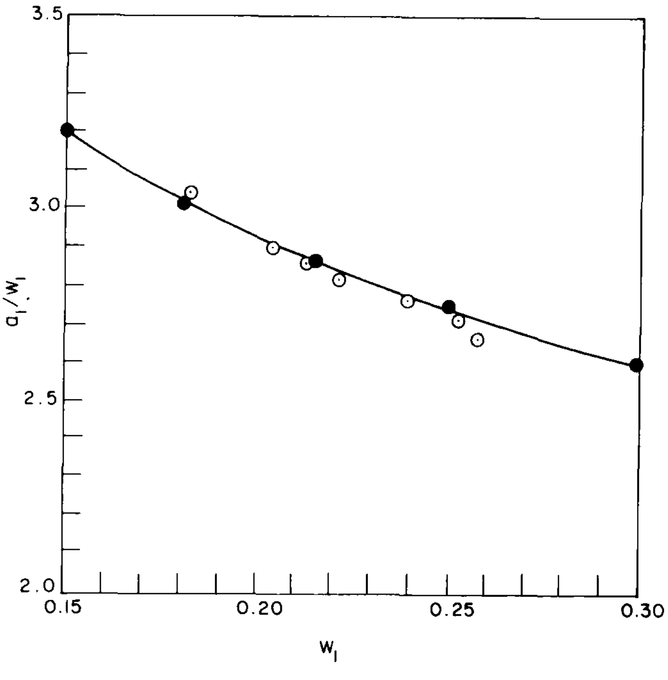

FIGURE 7 a_1/w_1 *versus* w_1 for polystyrene/toluene mixtures at 25°C: (○) This study; (●) Saeki *et al.*[38] The sold curve drawn is taken from the study of Saeki *et al.*

solution, ϕ_i ($i = 1, 2, 3$) are the volume fractions of the solvent and two polymers, and N_2 and N_3 are the polymerization indices of components 2 and 3, respectively, which are related to the molar volumes V_2 and V_3 by

$$N_2 = V_2/V_r \quad \text{and} \quad N_3 = V_3/V_r \tag{6}$$

where V_r is the reference volume, which is usually taken as the molar volume of the solvent in a three-component system. In Eq. (5), χ_{12} is the interaction parameter between polymer 1 (i.e., component 2) and the solvent, and χ_{13} is the interaction parameter between polymer 2 (i.e., component 3) and the solvent, which can be determined from the following expressions:[39]

$$\ln a_1 = \ln \phi_1 + (1 - 1/N_2)\phi_2 + \chi_{12}\phi_2^2 \tag{7}$$

and

$$\ln a_1 = \ln \phi_1 + (1 - 1/N_3)\phi_3 + \chi_{13}\phi_3^2 \tag{8}$$

Note that the activity of the solvent a_1 appearing in Eqs. (7) and (8) must be measured in the respective binary systems, i.e., polymer 1/solvent and polymer 2/solvent systems.

In the present investigation, toluene was used as the solvent and the activity of toluene, a_1, in binary and ternary solutions was determined using the following

TABLE VI
Summary of the values of the interaction parameter χ_{23} for mixtures of a tackifying resin and a homopolymer[a]

Weight fraction of polymer	χ_{23}	$-T\,\Delta S_{\text{mix}}$ (cal/cm^3)	ΔH_{mix} (cal/cm^3)	ΔF_{mix} (cal/cm^3)	Comment on film clarity
(a) Polyyubutadiene/WINGTACK 86 Mixture					
0.674	−0.58	−0.201	−0.702	−0.903	Clear
0.465	−0.41	−0.191	−0.578	−0.769	Clear
0.268	−0.10	−0.136	−0.114	−0.250	Clear
(b) Polyisoprene/WINGTACK 86 Mixture					
0.690	−0.51	−0.196	−0.604	−0.800	Clear
0.305	−0.57	−0.142	−0.695	−0.837	Clear
(c) Polyisoprene/PICCOTAC 95BHT Mixture					
0.747	−0.59	−0.304	−0.614	−0.918	Clear
0.471	−0.04	−0.303	−0.056	−0.359	Clear
0.284	0.11	−0.219	0.129	−0.090	Clear
(d) Polybutadiene/PICCOTAC 95BHT Mixture					
0.714	−0.20	−0.317	−0.224	−0.541	Clear
0.485	0.13	−0.313	0.184	−0.129	Opaque
0.289	0.61	−0.230	0.728	0.498	Opaque
(e) Polystyrene/WINGTACK 86 Mixture					
0.703	−0.47	−0.209	−0.573	−0.782	Clear
0.511	−0.01	−0.202	−0.014	−0.216	Opaque
(f) Polystyrene/PICCOTAC 95BHT					
0.714	0.13	−0.331	0.155	−0.176	Opaque

[a] All measurements were conducted at 25°C.

expression:[40]

$$a_1 = (P_1/P_1^0)\exp[-(B_{11} - v_1)(P_1^0 - P_1)/RT] \tag{9}$$

where P_1 is the system pressure of toluene in the vapor phase, P_1^0 is the saturated vapor pressure of toluene, B_{11} is the second virial coefficient of toluene, v_1 is the molar volume of the solvent, T is the absolute temperature, and R is the universal gas constant. The values of χ_{12} and χ_{13} as determined from Eqs. (7) and (8) were used to determine the values of χ_{23} by Eq. (5).

It should be mentioned that in the use of the piezoelectric sorption method, the weight fraction of the probe solvent w_1 sorbed by a thin polymer film is then calculated using the following relation:[41]

$$w_1 = \Delta f'/(\Delta f' + \Delta f_0) \tag{10}$$

where $\Delta f'$ is a decrease in frequency due to the sorption of a probe solvent (toluene in the present study) by the polymer, coated on the quartz crystal, and Δf_0 is a decrease in frequency due to the mass of the polymer, coated on the quartz crystal.

Note that in calculating χ_{23} from Eq. (5), information on the volume fraction of solvent ϕ_1 is needed and therefore ϕ_1 must be determined from the experimentally determined w_1, using information on the specific volume at a desired temperature. When examining Eqs. (5)–(8), it becomes clear that a small error in the values of ϕ_1 can significantly affect the computed values of χ_{12} and χ_{13}, and hence values of χ_{23}.

At this juncture, the magnitude of errors involved must be mentioned in the determination of the interaction parameters χ_{23} using Eq. (5). In calculating w_1 from the frequency measurements using Eq. (10), the values of w_1 were found to vary within ±2%, depending on the amount of polymer that was coated on the piezoelectric quartz crystal. This amount of error in w_1 can produce an error of ±0.02 in the value of χ_{12} (or χ_{13}) for a binary system but can give rise to much larger errors in χ_{23} for a ternary system, since the values of χ_{23} were determined by dividing the difference of two small values, namely, the value of $\ln a_1$ on the left-hand side of Eq. (5) and the value of the terms, excluding the term $\chi_{23}\phi_2\phi_3$, on the right-hand side of Eq. (5), by $\phi_2\phi_3$. Note that values of ϕ_2 and ϕ_3 are always less than 1. Therefore, small errors in ϕ_2 and ϕ_3 can significantly affect the final values of χ_{23} as determined from Eq. (5). In the present investigation, a variation in the value of χ_{23} within ±0.20 can be expected when the error in w_1 is within ±2%.

The following observations are worth noting on the values of χ_{23} given in Table VI. (1) For mixtures of polybutadiene homopolymer and WINGTACK 86, the values of χ_{23} are *negative* over the concentration range of WINGTACK 86 investigated and that χ_{23} moves toward a positive value with increasing concentration of WINGTACK 86 in the mixture. The negative values of χ_{23} observed for the mixtures of polybutadiene homopolymer and WINGTACK 86 over the concentration range investigated seem to suggest that WINGTACK 86 is compatible with KRATON 1102. This, then, explains why in dynamic viscoelastic measurements the T_g of the polybutadiene phase in KRATON 1102 shifted toward higher temperatures (see Figure 4); (2) For mixtures of polyisoprene homopolymer and WINGTACK 86, the values of χ_{23} are *negative* over the concentration range of WINGTACK 86 investigated, indicating that WINGTACK 86 is compatible also with KRATON 1107. The negative values of χ_{23} observed for the mixtures seem to explain why the T_g of the polyisoprene phase in KRATON 1107 shifted toward higher temperatures as the amount of WINGTACK 86 in the mixture increased (see Figure 1); (3) For mixtures of PICCOTAC 95BHT with polyisoprene or polybutadiene homopolymer, the value of χ_{23} remains *negative* in the polyisoprene/PICCOTAC 95BHT mixtures containing up to about 50 wt% of PICCOTAC 95BHT, but becomes slightly *positive* when the PICCOTAC 95BHT increases to about 70 wt%.

Within the uncertainty limits of the errors involved in the analysis of the piezoelectric sorption data described above, for all intents and purposes the 30/70 polyisoprene/PICCOTAC 95BHT mixture can be considered to be compatible. This observation seems to explain why the addition of PICCOTAC 95BHT to KRATON 1107 increased the T_g of the polyisoprene phase and lowered the plateau modulus of KRATON 1107 (see Figure 2). Note, however, that the value of χ_{23} is negative for the 70/30 polybutadiene/PICCOTAC 95BHT mixture, but becomes positive for the 50/50 and 30/70 polybutadiene/PICCOTAC 95BHT mixtures. The concentration of PICCOTAC 95BHT at which χ_{23} is negative is much lower in the mixtures with polybutadiene homopolymer than with polyisoprene homopolymer, meaning that the miscibility limits (or extent of compatibility) of PICCOTAC 95BHT with KRATON 1102 would be much lower than with KRATON 1107. This observation now explains why in the 50/50 and 30/70 KRATON 1102/PICCOTAC 95BHT mixtures, the plateau modulus increased while the T_g of the rubbery polydiene phase in the KRATON 1102/PICCOTAC 95BHT mixtures hardly increased, for amounts of PICCOTAC 95BHT in the mixture above 50 wt% (see Figure 5); (4) For mixtures of polystyrene homopolymer with WINGTACK 86 or PICCOTAC 95BHT, at about the same level of tackifying resin in the mixture, the value of χ_{23} is *negtaive* for the polystyrene/WINGTACK 86 mixture, while it is *positive* for the polystyrene/PICCOTAC 95BHT mixture, which means that WINGTACK 86 is compatible with polystyrene within the concentration range investigated. This observation is not surprising, in view of the fact that WINGTACK 86 contains a significant amount of poly(α-methyl styrene), as detected by IR spectroscopy. And yet, since the major portion of WINGTACK 86 consists of aliphatic hydrocarbons, it is believed to have fairly limited miscibility with polystyrene homopolymer. Thus, the addition of a large amount of WINGTACK 86 to polystyrene homopolymer is expected to give rise to *macrophase* separation.

It should be mentioned that values of the interaction parameter do not necessarily have to be *negative* for a tackifying resin to be compatible with a block copolymer, because the entropic contribution ($T\,\Delta S_{\text{mix}}$) of the tackifying resin, which is negative, can offset a positive value of the enthalpic contribution (ΔH_{mix}) when the value of the interaction parameter is positive, giving rise to a negative value for the free energy of mixing, ΔF_{mix}. This can be illustrated best by looking at the values of $-T\,\Delta S_{\text{mix}}$, ΔH_{mix}, and ΔF_{mix}, given in Table VI. Note that the value of ΔH_{mix} and $-T\,\Delta S_{\text{mix}}$ given in Table VI were determined, using the Flory–Huggins theory:[42,43]

$$\Delta F_{\text{mix}} = RT\left(\frac{\phi_1}{V_1}\ln\phi_1 + \frac{\phi_2}{V_2}\ln\phi_2 + \frac{\chi}{V_r}\phi_1\phi_2\right) \tag{11}$$

where ϕ_i $(i = 1, 2)$ are the volume fractions, and V_i $(i = 1, 2)$ are the molar volumes, of the constituent components, V_r is the reference volume of one of the components (i.e., the volume of a segment or a lattice), R is the universal gas constant, T is the absolute temperature, and χ is the interaction parameter which is equivalent to χ_{23} in Eq. (5). It can be seen that when the contribution of $-T\,\Delta S_{\text{mix}}$ outweighs the contribution of ΔH_{mix}, the value of ΔF_{mix} becomes negative (i.e., the mixture is compatible) even when the value of χ_{23} is slightly positive.

Let us now examine whether or not the use of the solubility parameter δ would give the same information as that of the interaction parameter χ, in predicting the compatibility of a tackifying resin with a block copolymer. For this purpose, let us compare the compatibilities of PICCOTAC 95BHT with polyisoprene and polybutadiene, respectively. It can be seen in Table VI that, over the concentration range investigated, the values of χ_{23} for PICCOTAC 95BHT and polyisoprene homopolymer are negative for PICCOTAC 95BHT concentrations up to about 50 wt% and then become slightly positive at higher concentrations. Nevertheless, the values of ΔF_{mix} are negative over the entire range of PICCOTAC 95BHT concentrations investigated. On the other hand, for the PICCOTAC 95BHT/polybutadiene mixtures, the values of χ_{23} are negative for PICCOTAC 95BHT concentration up to about 30 wt% but increase rapidly, becoming positive, as the concentration is increased further, and values of ΔF_{mix} are positive at concentrations of PICCOTAC 95BHT above approximately 50 wt%. This observation now explains the limited compatibility of PICCOTAC 95BHT with KRATON 1102, observed in the viscoelastic measurements displayed in Figure 5.

The chemical structure of PICCOTAC 95BHT is not clearly known to us, but it is reported that piperylene is a major monomer for PICCOTAC 95BHT.[3] Let us then use piperylene to evaluate the solubility parameter δ of PICCOTAC 95BHT. Using the group contribution method, the value of δ for PICCOTAC 95BHT is estimated to be 8.20 $(\mathrm{cal/cm^3})^{1/2}$ using the data of Fedors,[44] 8.33 $(\mathrm{cal/cm^3})^{1/2}$ using the data of van Krevelen,[45] 7.76 $(\mathrm{cal/cm^3})^{1/2}$ using data of Small,[46] 8.16 $(\mathrm{cal/cm^3})^{1/2}$ using the data of van Krevelene,[47] and 7.92 $(\mathrm{cal/cm^3})^{1/2}$ using the data of Hoy.[48] The average of the five values is 8.09 $(\mathrm{cal/cm^3})^{1/2}$. Since the values of the solubility parameter for polyisoprene and polybutadiene are 8.50 and 8.55 $(\mathrm{cal/cm^3})^{1/2}$, respectively, the difference in solubility parameters between PICCOTAC 95BHT and polyisoprene, $(\delta_{\mathrm{PI}} - \delta_{\mathrm{Pic95}})$, is 0.41 $(\mathrm{cal/cm^3})^{1/2}$, and the difference in solubility parameters between PICCOTAC 95BHT and polybutadiene, $(\delta_{\mathrm{PB}} - \delta_{\mathrm{Pic95}})$, is 0.46 $(\mathrm{cal/cm^3})^{1/2}$. When these values are used for different values of ϕ_1 (volume fraction of PICCOTAC 95BHT), we cannot explain why PICCOTAC 95BHT is compatible with KRATON 1107, while it becomes incompatible (i.e., forms a separate phase) with KRATON 1102. Therefore, we conclude that the solubility parameter has very limited usefulness in predicting compatibility between a tackifying resin and a block copolymer.

Phase diagrams of block copolymer-based pressure-sensitive adhesives

In the development of formulas for block copolymer-based pressure-sensitive adhesives, it is important to have phase diagrams available. The construction of a phase diagram for mixtures of a block copolymer and a tackifying resin is not as easy as that for binary mixtures of simple liquids, because block copolymers have microdomain structures at temperatures below a certain critical value, referred to above as the order–disorder transition (or microphase separation transition) temperature T_r. As mentioned above, the size of the microdomains is too small to be detected by ordinary optical microscopy, and thus the determination of T_r for a block copolymer or its mixtures with a homopolymer has often been done by

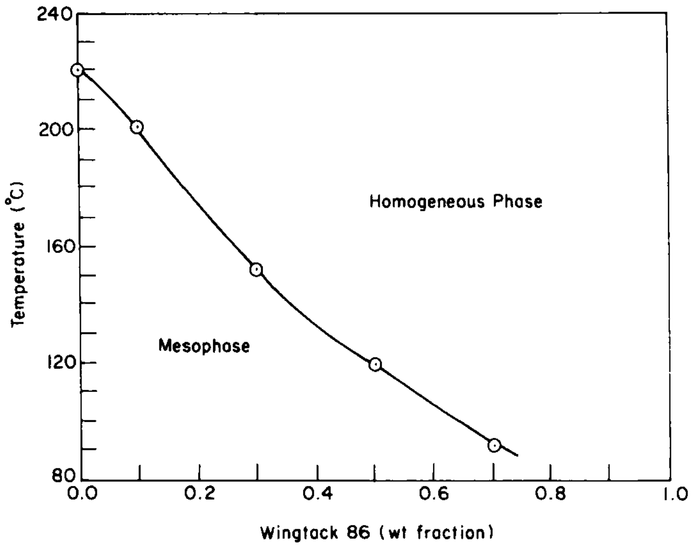

FIGURE 8 Phase diagram for KRATON 1102/WINGTACK 86 mixtures.

small-angle X-ray scattering.[17–24] In the present investigation, however, we have used a rheological technique, introduced very recently by us,[25,26] to determine the values of T_r for block copolymer and its mixtures with a tackifying resin.

Figure 8 gives a phase diagram for mixtures of KRATON 1102 and WINGTACK 86, and Figure 9 gives a phase diagram for mixtures of KRATON 1107 and WINGTACK 86. Note in Figures 8 and 9 that the region below the solid

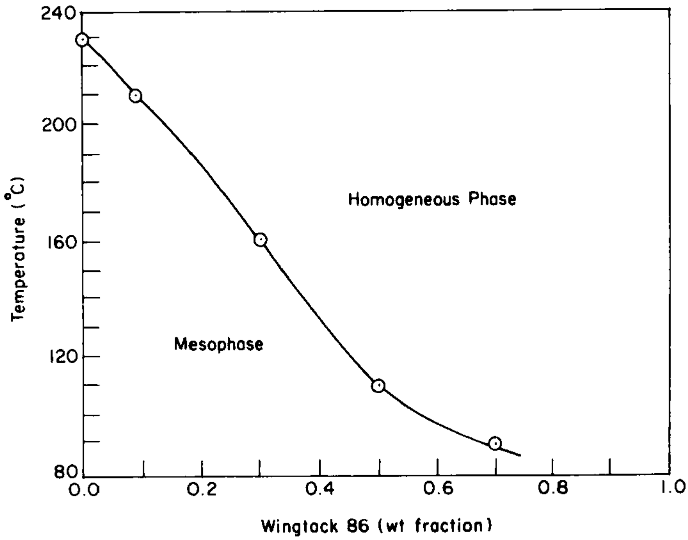

FIGURE 9 Phase diagram for KRATON 1107/WINGTACK 86 mixtures.

curve represents the mesophase (mixtures of the block copolymer and the tackifying resin) and that the region above the solid curve represents the mixtures, where the block copolymer and the tackifying resin form a homogeneous, single phase.

The circular symbols in Figures 8 and 9 are values of temperature (i.e., T_r), which were determined from logarithmic plots of dynamic storage modulus G' *versus* dynamic loss modulus G'' for the block copolymer (KRATON 1102 or KRATON 1107) and its mixtures with WINGTACK 86. In order to illustrate the method used to determine T_r, let us look at Figure 10, log G' *versus* log G'' plots for KRATON 1102. It can be seen in Figure 10 that the log G' *versus* log G'' plots do not change with temperature at 220°C and above. According to the criterion suggested in our previous papers,[25,26] the lowest temperature at which log G' *versus* log G'' plots cease to vary with temperature is the T_r, at which point the microdomain structures in the block copolymer dissolve completely. Figure 11 gives log G' *versus* log G'' plots for the 90/10 KRATON 1102/WINGTACK 86 mixture, and Figure 12 for the 70/30 KRATON 1102/WINGTACK 86 mixture. It

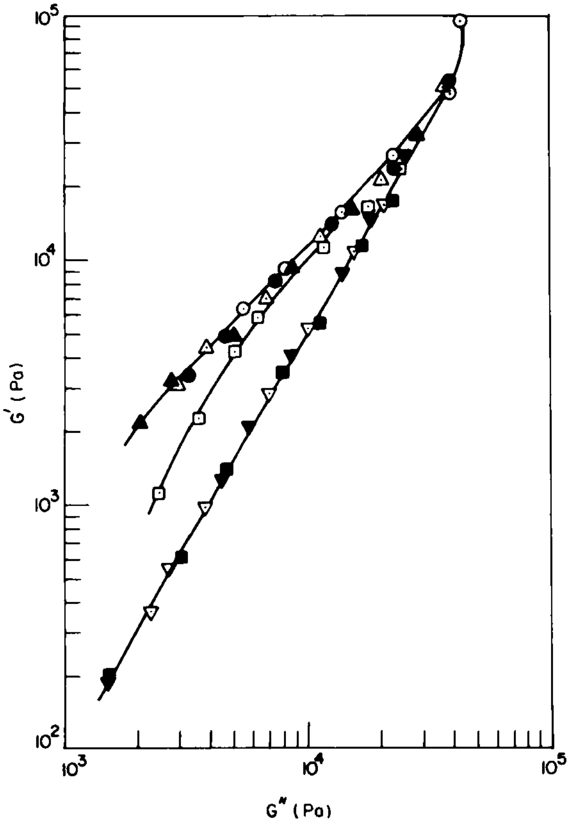

FIGURE 10 Log G' *versus* log G'' plots for KRATON 1102 at various temperatures (°C): (○) 160; (●) 180; (△) 190; (▲) 200; (□) 210; (■) 220; (▽) 230; (▼) 240.

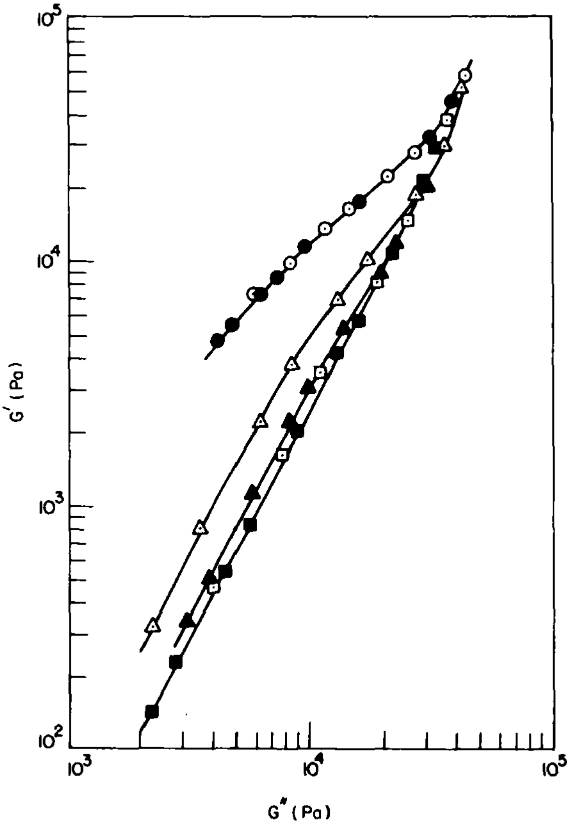

FIGURE 11 Log G' *versus* log G'' plots for the 90/10 KRATON 1102/WINGTACK 86 mixture at various temperatures (°C): (⊙) 140; (●) 170; (△) 180; (▲) 190; (⊡) 200; (■) 210.

can be seen in Figures 11 and 12 that T_r decreased as the concentration of WINGTACK 86 in the mixture increased. Due to space limitations here, log G' *versus* log G'' plots for mixtures of other blend compositions are not presented, but a summary of the T_r's determined are given in Table VII. It is of interest to observe in Figure 8 that the temperature at which the microdomain structures dissolve completely decreases steadily with increasing amounts of WINGTACK 86 in KRATON 1102. Based on the information given in Figure 9, a similar observation can be made for the KRATON 1107/WINGTACK 86 mixtures.

It should be mentioned that when the light-scattering experiments and hot-stage microscopy were performed for the mixtures of WINGTACK 86 with KRATON 1102 or KRATON 1107, and for the mixtures of PICCOTAC 95BHT with KRATON 1107, no evidence of the occurrence of *macrophase* separation over the temperature range investigated was obtained. However, there was evidence of *macrophase* separation occurring in certain compositions of the

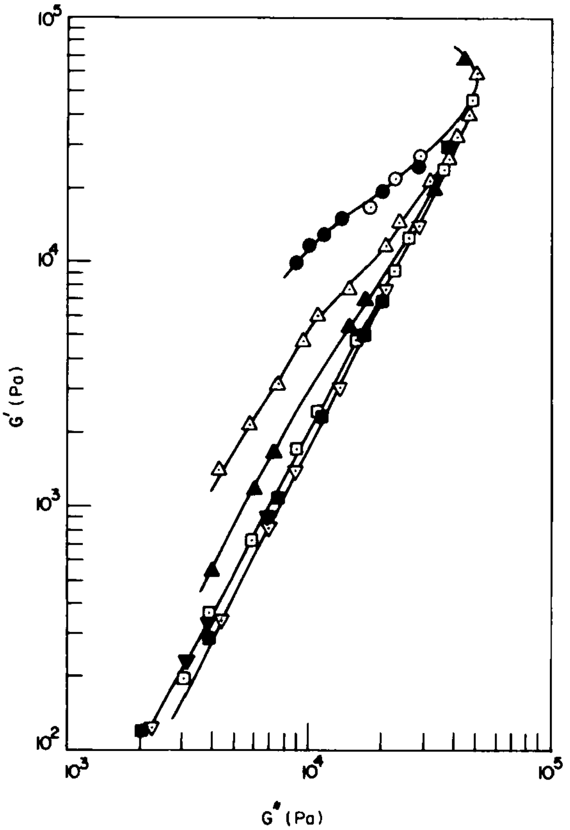

FIGURE 12 Log G' *versus* log G'' plots for the 70/30 KRATON 1102/WINGTACK 86 mixture at various temperatures (°C): (⊙) 100; (●) 110; (△) 120; (▲) 140; (⊡) 150; (■) 160; (▽) 180; (▼) 200.

TABLE VII
Summary of the order–disorder transition temperature (T_r) for mixtures of a block copolymer and a tackifying resin

Material	T_r(°C)
KRATON 1102	220
KRATON 1102/WINGTACK 86 = 90/10	200
KRATON 1102/WINGTACK 86 = 70/30	150
KRATON 1102/WINGTACK 86 = 50/50	120
KRATON 1102/WINGTACK 86 = 30/70	90
KRATON 1107	230
KRATON 1107/WINGTACK 86 = 90/10	210
KRATON 1107/WINGTACK 86 = 70/30	160
KRATON 1107/WINGTACK 86 = 50/50	110
KRATON 1107/WINGTACK 86 = 30/70	90
KRATON 1107/PICCOTAC 95BHT = 70/30	200
KRATON 1107/PICCOTAC 95BHT = 50/50	180
KRATON 1107/PICCOTAC 95BHT = 30/70	160
KRATON 1102/PICCOTAC 95BHT = 90/10	200

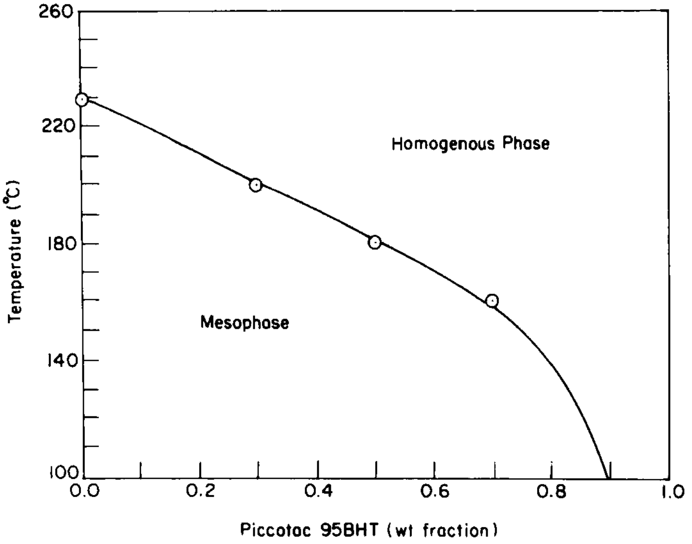

FIGURE 13 Phase diagram for KRATON 1107/PICCOTAC 95BHT mixtures.

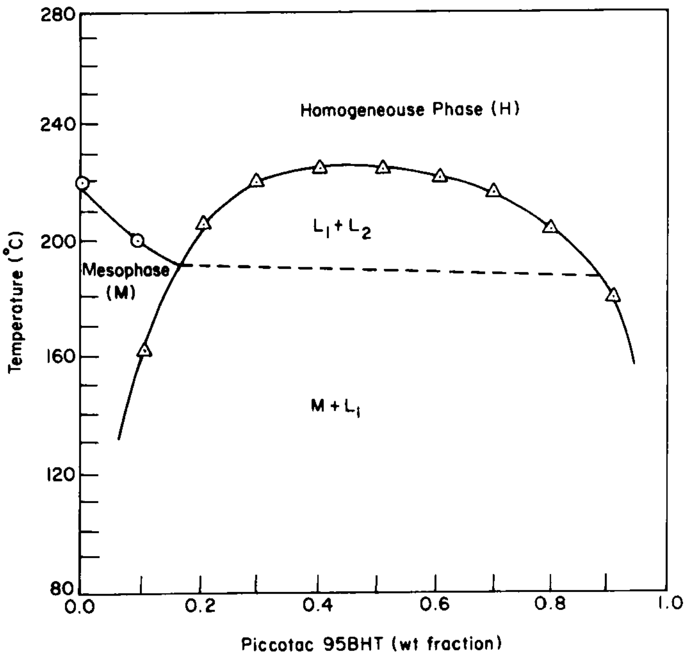

FIGURE 14 Phase diagram for KRATON 1102/PICCOTAC 95BHT mixtures.

mixtures of PICCOTAC 95BHT with KRATON 1102 over the temperature range investigated.

Figure 13 gives a phase diagram for the KRATON 1107/PICCOTAC 95BHT mixtures, and Figure 14 gives a phase diagram for the KRATON 1102/PICCOTAC 95BHT mixtures. These phase diagrams were constructed using information obtained from both the rheological technique and hot-stage microscopy. The phase diagram for the KRATON 1107/PICCOTAC 95BHT mixtures looks very similar to the phase diagrams for the KRATON 1102/WINGTACK 86 mixtures (see Figure 8) and KRATON 1107/WINGTACK 86 mixtures (see Figure 9). But the phase diagram for the KRATON 1102/PICCOTAC 95BHT mixtures looks much more complex. Note in Figure 14 that the cicruclar symbols on the curve separating the mesophase and the homogeneous phase are the values of T_r determined from $\log G'$ *versus* $\log G''$ plots and that the triangular symbols represent the phase boundary as determined by hot-stage microscopy. Due to the limited magnifications available, the phase boundary determined by the hot-stage microscope is considered to be approximate. Note further in Figure 14 that region $M + L_1$ represents the mixtures of *microphase* separated KRATON 1102 (denoted by M) and *macrophase* separated PICCOTAC 95BHT (denoted by L_1), and that region $L_1 + L_2$ represents two-phase mixtures of PICCOTAC 95BHT (denoted by L_1) and completely disordered KRATON 1102 (denoted by L_2). It can be concluded from these figures that PICCOTAC 95BHT has a very limited solubility in KRATON 1102, as compared with WINGTACK 86. This conclusion supports the validity of the hypotheses made above when we examined the viscoelastic behavior of the mixtures.

Processability of block copolymer-based pressure-sensitive adhesives

Information on viscosity is very valuable for determining the processability of block copolymer-based pressure-sensitive adhesives. According to Cox and Merz,[49] only when linear viscoelastic data are available do plots of complex viscosity $|\eta^*(\omega)|$ *versus* angular frequency ω become very useful in predicting the relationship between steady shear viscosity $\eta(\dot{\gamma})$ and shear rate $\dot{\gamma}$. Note that values of $|\eta^*|$ can be calculated using the definition, $|\eta^*(\omega)| = [\eta'(\omega)^2 + \eta''(\omega)^2]^{1/2}$, where $\eta'(\omega)$ is equal to $G''(\omega)/\omega$ and $\eta''(\omega)$ is equal to $G'(\omega)/\omega$.

Figure 15 gives logarithmic plots of $|\eta^*|$ *versus* ω for the 50/50 KRATON 1102/WINGTACK 86 mixture at the following temperatures: 90, 100, 110, 120, and 140°C. Similar plots are given in Figure 16 for the 50/50 KRATON 1107/WINGTACK 86 mixture at the following temperatures: 100, 110, 130, 140, and 160°C, in Figure 17 for the 50/50 KRATON 1102/PICCOTAC 95BHT mixture at the following temperatures: 120, 130, 140, 150, and 160°C, and in Figure 18 for the 50/50 KRATON 1107/PICCOTAC 95BHT mixture at the following temperatures: 120, 140, 160, 180, and 190°C. It can be seen in Figures 15 to 18 that the $\log|\eta^*|$ *versus* $\log \omega$ plots exhibit Newtonian behavior at temperatures above its T_r, but yield behavior at temperatures below its T_r (see

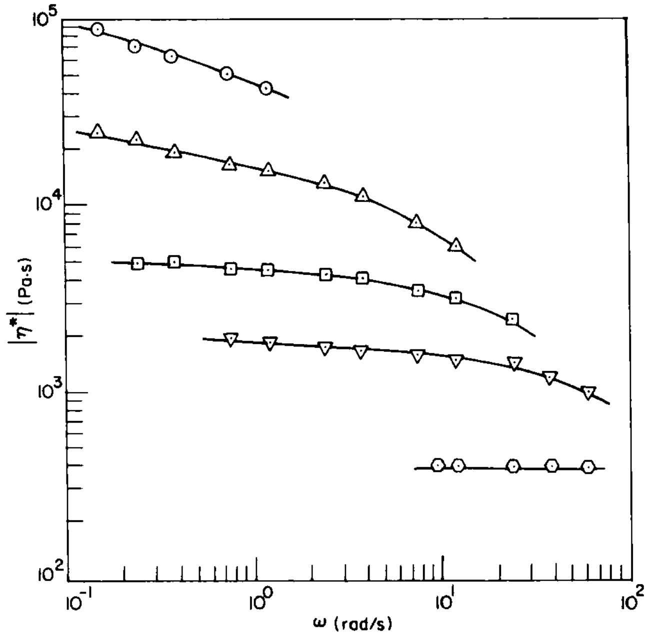

FIGURE 15 Log $|\eta^*|$ *versus* log ω for the 50/50 KRATON 1102/WINGTACK 86 mixture at various temperatures (°C): (⊙) 90; (△) 100; (⊡) 110; (▽) 120; (⬡) 140.

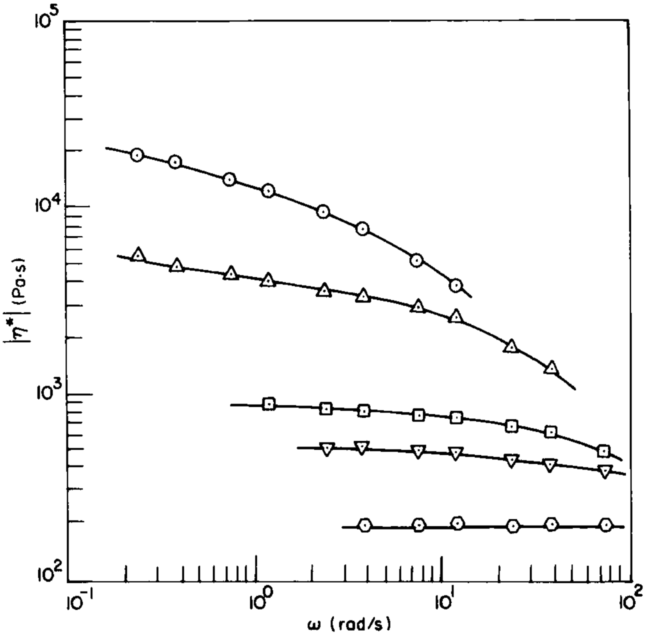

FIGURE 16 Log $|\eta^*|$ *versus* log ω for the 50/50 KRATON 1107/WINGTACK 86 mixture at various temperatures (°C): (⊙) 100; (△) 110; (⊡) 130; (▽) 140; (⬡) 160.

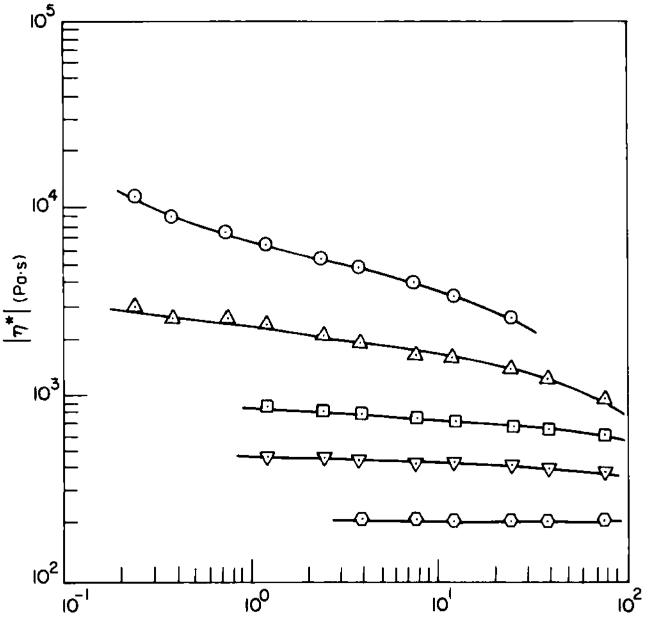

FIGURE 17 Log $|\eta^*|$ *versus* log ω for the 50/50 KRATON 1102/PICCOTAC 95BHT at various temperatures (°C): (⊙) 120; (△) 130; (⊡) 140; (▽) 150; (⬡) 160.

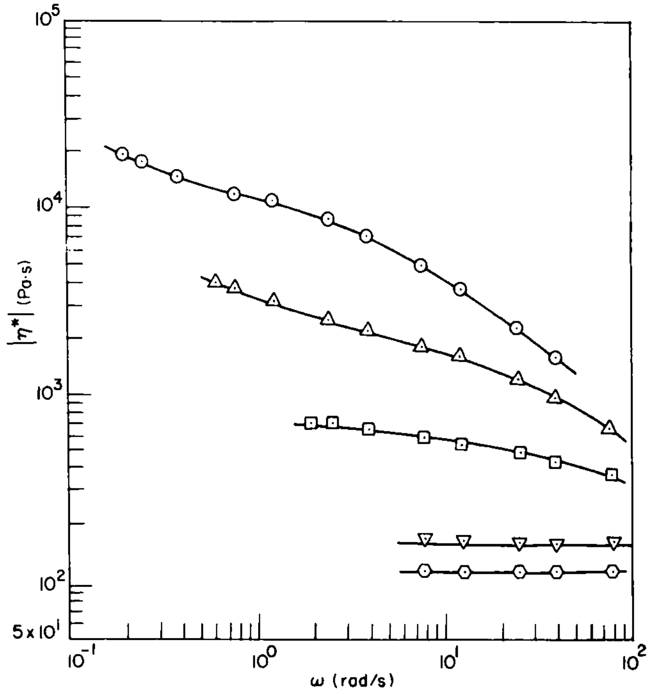

FIGURE 18 Log $|\eta^*|$ *versus* log ω for the 50/50 KRATON 1107/PICCOTAC 95BHT at various temperatures (°C): (⊙) 120; (△) 140; (⊡) 160; (▽) 180; (⬡) 190.

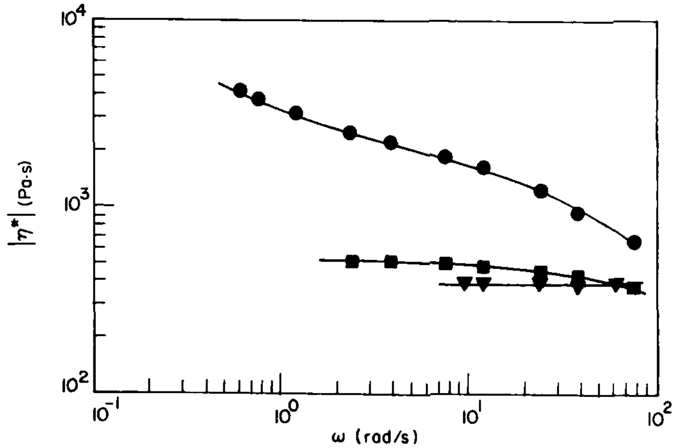

FIGURE 19 Log $|\eta^*|$ *versus* log ω at 140°C: (●) 50/50 KRATON 1107/PICCOTAC 95BHT; (▲) 50/50 KRATON 1107/WINGTACK 86; (■) 50/50 KRATON 1102/WINGTACK 86.

Table VII and Figure 13 and 14 for values of the T_r of the block copolymer/tackifying resin systems investigated). From the processing point of view, it is highly desirable to have viscosities as low as possible. This, then, suggests to us that the processing temperature chosen should be above the T_r of a given pressure-sensitive adhesive. In this regard, information on the T_r of a pressure-sensitive adhesive is very valuable to determine the optimum processing conditions.

To illustrate the point emphasized above, let us observe the plots of log $|\eta^*|$ *versus* log ω at 140°C, given in Figure 19, for mixtures containing different tackifying resins at a fixed blend composition, 50/50 block copolymer/tackifying resin mixture. It can be seen in Figure 19 that the viscosities of the 50/50 KRATON 1102/WINGTACK 86 and 50/50 KRATON 1107/WINGTACK 86 mixtures are much lower than the viscosities of the 50/50 KRATON 1107/PICCOTAC 95BHT mixture. Note that the T_r's of the 50/50 KRATON 1102/WINGTACK 86 and 50/50 KRATON 1107/WINGTACK 86 mixtures are 120°C and 110°C, respectively, which are below the processing temperature 140°C, whereas the T_r of the 50/50 KRATON 1107/PICCOTAC 95BHT mixture is 180°C which is above the processing temperature of 140°C (see Table VII for information on the T_r's of the block copolymer/tackifying resin mixtures employed). It is then clear why the viscosities of the 50/50 KRATON 1102/WINGTACK 86 and 50/50 KRATON 1107/WINGTACK 86 mixtures are much lower than the viscosities of the KRATON 1107/PICCOTAC 95BHT.

CONCLUDING REMARKS

In this paper we have presented experimental results for the viscoelastic behavior, the Flory–Huggins interaction parameter, and phase diagrams of block copolymer-based pressure-sensitive adhesives. It has been found that different experimental techniques produced consistent results regarding the compatibility of a tackifying resin with a block copolymer. We have demonstrated that the use of the Flory–Huggins interaction parameter is much more reliable than the use of the Hildebrand solubility parameter in determining the compatibility for a tackifying resin with a block copolymer. It should be mentioned that in order to determine the interaction parameter for a tackifying resin and a block copolymer using Scott's theory, Eq. (5), together with the piezoelectric sorption method, one must have accurate information on the molar volumes, V_1 and V_2, of the repeat units of the tackifying resin and the block copolymer. Unfortunately, the chemical structures of most of the tackifying resins in commercial use today are very complex and not clearly understood. Thus, under such circumstances, the accurate determination of the interaction parameter χ_{23} using Eq. (5) would be very difficult, if not impossible. This, then, suggests that, in the future, efforts should be directed towards the elucidation of the chemical structures of tackifying resins.

We have found that values of the interaction parameter χ_{23} for certain mixtures of a tackifying resin and a block copolymer are negative. Earlier, using gas-liquid chromatography, Su *et al.*[50] also obtained negative values of χ_{23} in poly(vinyl chloride) (PVC) plasticized by di-n-octyl phthalate (DnOP). Note that in analyzing experimental data to determine values of χ_{23}, they also used Eq. (5). They observed that the value of χ_{23} was negative up to 0.25 volume fraction of DnOP but it became less negative and finally positive at 0.55 volume fraction of DnOP. They then concluded that the compatibility of PVC with DnOP depended upon the composition of the mixtures investigated.

Kraus and Rollmann[5] reported that a plateau modulus in the vicinity of 3×10^5 Pa gives a satisfactory tack property for applications in pressure-sensitive adhesives. Based on this criterion, we can conclude that the 50/50 and 30/70 KRATON 1107/WINGTACK 86 mixtures (see Figure 1), the 50/50 and 30/70 KRATON 1107/PICCOTAC 95BHT mixtures (see Figure 2), and the 30/70 KRATON 1102/WINGTACK 86 mixture (see Figure 4) may be considered to be effective formulas for pressure-sensitive adhesives. The present study shows that, on an equal weight basis, WINGTACK 86 is more effective in lowering the plateau modulus of KRATON 1107 than that of KRATON 1102. Due to very limited compatibility with KRATON 1102, PICCOTAC 95BHT was found to form a separate phase.

We have constructed phase diagrams of block copolymer-based pressure-sensitive adhesives, using information obtained from both the dynamic viscoelastic measurements and a light scattering method (or hot-stage microscopy).

Acknowledgment

We wish to acknowledge with gratitude that the Shell Development Company supplied us with the block copolymers, KRATON® D-1102 and KRATON® D-1107, Hercules Incorporated supplied us with PICCOTAC® 95BHT, and the Goodyear Tire and Rubber company supplied us with WINGTACK® 86 used in this investigation.

References

1. A. Noshay and J. McGrath, *Block Copolymers* (Academic Press, New York, 1977).
2. J. J. Burke and V. Weiss, Eds., *Block and Graft Copolymers* (Syracuse University Press, Syracuse, New York, 1973).
3. J. A. Schlademan, in *Handbook of Pressure-Sensitive Adhesive Technology*, D. Satos, Ed. (Van Nostrand Reinhold, New York, 1982), p. 360.
4. M. Sheriff, R. W. Knibbs and P. G. Langely, *J. Appl. Polym. Sci.* **17,** 3423 (1973).
5. G. Kraus and K. W. Rollmann, *ibid.* **21,** 3311 (1977).
6. G. Kraus, F. B. Jones, O. L. Marrs and K. W. Rollmann, *J. Adhesion* **8,** 235 (1977).
7. G. Kraus, K. W. Rollmann and R. A. Gray, *ibid.* **10,** 221 (1979).
8. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd Edition (Wiley, New York, 1980).
9. G. Holden, in *Block and Graft Polymerization*, R. J. Ceresa, Ed. (Wiley, New York, 1973), Chap 6.
10. E. Guth and O. Gold, *Phys. Rev.* **53,** 322 (1938).
11. J. B. Class and S. G. Chu, *J. Appl. Polym. Sci.* **30,** 805, 815, 825 (1985).
12. T. G. Fox, *Bull. Am. Phys. Soc.* **1,** 123 (1956).
13. E. Helfand and Z. Wasserman, *Macromolecules* **9,** 879 (1976).
14. E. Helfand and Z. Wasserman, *ibid.* **11,** 960 (1978).
15. E. Helfand and Z. Wasserman, *ibid.* **13,** 994 (1980).
16. L. Leibler, *ibid.* **13,** 1602 (1980).
17. T. Hashimoto, Y. Tsukahara and H. Kawai, *J. Polym. Sci., Polym. Lett. Ed.* **18,** 585 (1980).
18. T. Hashimoto, *et al.*, *Macromolecules* **16,** 361 (1983).
19. T. Hashimoto, K. Kowaka, M. Shibayama and H. Kawai, *ibid.* **19,** 754 (1986).
20. R. J. Roe, M. Fishkis and J. C. Chang, *ibid.* **14,** 1091 (1981).
21. W. C. Zin and R. J. Roe, *ibid.* **17,** 183 (1984).
22. R. J. Roe and W. C. Zin, *ibid.* **17,** 189 (1984).
23. S. Nojima and R. J. Roe, *ibid* **20,** 1866 (1987).
24. G. Kraus and T. Hashimoto, *J. Appl. Polym. Sci* **27,** 1745 (1982).
25. C. D. Han and J. Kim, *J. Polym. Sci. Part B: Polym. Phys.* **25,** 1741 (1987).
26. C. D. Han, J. Kim and J. K. Kim, *Macromolecules*, **22,** 383 (1989).
27. C. D. Han and K. W. Lem, *Polym. Eng. Rev.* **2,** 135 (1983).
28. H. K. Chuang and C. D. Han, *J. Appl. Polym. Sci.* **29,** 2205 (1984).
29. C. D. Han and H. K. Chuang, *ibid.* **30,** 2431 (1985).
30. C. D. Han and H. H. Yang, *ibid.* **33,** 1199 (1987).
31. C. D. Han and M. S. Jhon, *ibid.* **32,** 3809 (1986).
32. M. Hong and J. Noolandi, *Macromolecules* **16,** 1083 (1983).
33. D.Whitmore and J. Noolandi, *ibid.* **18,** 2486 (1985).
34. D. C. Bonner and Y. L. Cheng, *J. Polym. Sci., Polym. Lett. Ed.* **13,** 259 (1975).
35. S. Saeki and D. C. Bonner, *Polymer* **19,** 319 (1978).
36. J. E. Harris, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.* **23,** 676 (1983).
37. J. E. Harris, PhD Dissertation (ChemE), University of Texas, Austin, Texas, 1981.
38. S. Saeki, J. C. Holste and D. C. Bonner, *J. Polym. Sci., Polym. Phys. Ed.* **19,** 307 (1981).
39. R. L. Scott, *J. Chem. Phys.* **17,** 279 (1949).
40. J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd Edition (Prentice-Hall, Englewood Cliffs, New Jersey, 1986).
41. H. Z. Sauerbrey, *Z. Phys.* **155,** 206 (1959).
42. P. J. Flory, *J. Chem. Phys.* **10,** 51 (1942)).
43. M. L. Huggins, *J. Phys. Chem.* **4,** 151 (1942).
44. R. F. Fedors, *Polym. Eng. Sci.* **14,** 147 (1974).
45. D. W. van Krevelen, *Properties of Polymers* (Elsevier, New York, 1976), Chap. 7.
46. P. A. Small, *J. Appl. Chem.* **3,** 71 (1953).
47. D. W. van Krevelen, *Fuel* **44,** 236 (1965).
48. K. L. Hoy, *J. Paint Technol.* **42,** 76 (1970).
49. W. P. Cox and E. H. Merz, *J. Polym. Sci.* **28,** 619 (1958).
50. C. S. Su, D. Patterson and H. P Schreiber, *J. Appl. Polym. Sci.* **20,** 1025 (1976).