

The Concept of Solid Solvent as a Processing Aid

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Synopsis

The concept of solid solvent entails the use of low-molecular weight crystalline materials (LMC) as a processing aid. A LMC as an ideal solid solvent mixed into a polymer is expected to become a solvent for the polymer at high processing temperatures, reducing the melt viscosity and thus enhancing the processability, but to become a nonsolvent for the polymer at low use temperatures precipitating out of the polymer without adversely affecting the properties of the polymer. The feasibility of such a concept was examined using acetanilide as a potential solid solvent for polystyrene (PS) and two ABA-type block copolymers containing PS end blocks. Acetanilide demonstrated the essential features required of a solid solvent supporting the concept of solid solvent. It had a high solubility in PS at high temperatures very effectively reducing the melt viscosity of PS and the block copolymers, and it precipitated out of PS at low temperatures although it had an undesirably high residual solubility. The concept of solid solvent appears to be a viable one.

INTRODUCTION

One of the most important advantages of polymeric materials over other classes of materials lies in the ease of processing. Polymers can be quite easily and inexpensively processed into desired shapes. Some polymers, however, possess a high viscosity usually accompanied by a high elasticity at the processing temperatures, causing processing difficulties. In particular, polymer blends and block copolymers with a multiphase structure often exhibit such behavior. A significant reduction of the viscosity at the processing temperatures is desirable to enhance the processability for those polymers.

Solvents (or plasticizers) are very effective in reducing the viscosity of polymers.¹ They can reduce the viscosity by a factor much greater than their weight or volume fractions, but they also adversely affect the properties at the use temperatures resulting in a lower modulus and a lower use temperature range for instance, unless they are removed from the products after processing. Thus, the use of solvents as processing aids is impractical. Lubricants are used to improve the processability for some polymers, but their effects on viscosity are far less than solvents because lubricants are basically nonsolvents to polymers even at the processing temperatures.

The concept of solid solvent is to use low-molecular weight crystalline materials (LMC) as a processing aid for polymers. LMC materials as an ideal solid solvent should become compatible with a polymer and act as a solvent in the liquid state above its melting point, significantly reducing the viscosity of the polymer, but should become incompatible and crystallize out of the polymer as discrete domains below its melting point without

adversely affecting the properties of the polymer. A drastic increase in the compatibility between a LMC and a polymer upon melting of the LMC can be expected because the entropy of mixing between the liquid LMC without any structural constraint and the polymer is drastically greater than that between the solid LMC with the crystalline structural constraint and the polymer. A higher entropy of mixing results in a lower free energy of mixing, making the mixed state a thermodynamically more stable state when the free energy of mixing eventually becomes negative.²

Several LMC-polymer systems, which exhibit the essential behavior as postulated in this paper for a solid solvent, have been reported by some investigators in their study of the effects of LMC on the physical properties of polymers.³⁻⁶ Linnig et al.³ found that crystalline organic compounds having a β -naphthyl group increased the modulus of various rubbers to a remarkable degree. In particular, 5% of phenyl- β -naphthylamine (PBNA) with a partial solubility in rubber was found to be comparable in its stiffening effect on rubber to about 40 phr of a good reinforcing carbon black. Joseph et al.⁴ in their study of the reinforcement potential of LMC in glassy polymers found that acetanilide and anthracene were soluble in styrene-acrylonitrile copolymer (SAN) at high temperatures above their melting points, but they crystallized out of the polymer at temperatures below their melting points into small domains of the order of $10\mu\text{m}$ in width and length and much smaller dimension in thickness. From dynamic mechanical measurements, they found that LMC gave little reinforcement to glassy polymers and concluded that the elastic moduli of organic crystals were about the same as those of organic polymers in the glassy state. None of these investigators, however, explored the potential of LMC as a processing aid. Byler⁷ studied the effect of molding lubricants on the viscosity of ABS. He found that a fatty acid amide at 4 phr could reduce the viscosity of an ABS sample measured at 200°C and 100 S^{-1} by 30% and that the fatty acid amide crystallized out of the ABS upon cooling. His results strongly support the concept of solid solvent.

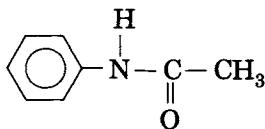
The reduction of viscosity by the use of an appropriate LMC as a solid solvent is expected to be significant for polymers with a single-phase structure in the molten state. The reduction of viscosity by a solid solvent for polymers with a multiphase structure in the molten state such as block copolymers will be even greater if the solid solvent not only acts as a solvent for one or more of the phases but also promotes mixing between the phases. It is well known⁸ that block copolymers made of incompatible polymers have multiphase structure, each component polymer being separated into its own phase. The multiphase structure leads to unusual physical properties, very different from those of the component polymers. A number of block copolymers is now widely used as thermoplastic elastomers.^{9,10} Our study,^{11,12} and others¹³ have shown that the multiphase structure in block copolymers often persists to high temperatures of processing, well above the glass transition or melting points of the component polymers, causing unusually high melt viscoelasticity and consequent processing difficulty. Phase separation in block copolymers occurs due to thermodynamic incompatibility between the component polymers. As the mobility of polymer segments increases (for example, with increasing temperature or by adding

solvent), mixing between different polymer segments will occur and eventually a homogeneous phase will be attained. Once the multiphase structure disappears, a normal melt viscoelasticity and greatly improved processability are expected. The use of solid solvent may allow processing of otherwise intractable block copolymers. The concept of solid solvent may also be beneficial to polymers with processing difficulty due to thermal instability such as polyvinyl chloride by permitting a lower processing temperature.

We have been investigating the feasibility of the concept of solid solvent, in particular as applied to block copolymers. This paper reports our preliminary results on the interaction between one particular polymer-solid solvent pair and its extension to block copolymers.

EXPERIMENTAL

A commercially available block copolymer, Kraton 1101 from Shell Chemical Company, was used as a model block copolymer in our study. Kraton 1101 is a styrene-butadiene-styrene (S-B-S) block copolymer, and it has the polystyrene (PS) block molecular weight of 11,000 each and the polybutadiene (PB) block molecular weight of 54,000 with 29% PS content according to Pillai et al.¹⁴ The microstructure of the PB block is 45% *trans*-1,4 40% *cis*-1,4 and 15% 1,2. The nominal molecular information on Kraton 1101 given by Shell is 102,000 total molecular weight with 31% PS content.¹⁵ We have to work with an uncertain molecular information, but this does not interfere with the goal of our present study. The PS blocks and the PB blocks are incompatible and they separate into their own phases. Owing to the multiphase structure, Kraton 1101 exhibits an elastomeric behavior at the low temperatures of usage but a very high viscoelasticity at the high temperatures of processing. Based on a previous study,⁴ acetanilide was chosen as a potential solid solvent for the PS phase in Kraton 1101. Acetanilide purchased from Fisher Scientific Company comes as a flake but it is easily crushed into a fine powder. It has the following chemical structure and Fisher Scientific gives its melting point at 115°C.



When Kraton 1101 mixed with acetanilide was heated to high temperatures for viscosity measurement, the PB phase in Kraton 1101 reacted with acetanilide resulting in undesirable crosslinking. An experimental Kraton G also from Shell Chemical Company identified as TRW-7-1615 was later added to our study to avoid the undesirable cross-linking reaction found in the mixture of Kraton 1101 and acetanilide. The Kraton G is a styrene-ethylene butylene-styrene (S-EB-S) block copolymer and it has no unsaturation in its chemical structure. It has PS end-block molecular weight of about 7,000 with about 30% PS content, and about 38% butylene content in the EB segment.¹⁵

The compatibility between PS and acetanilide was studied first using a commercial PS (PS-1) with a number average molecular weight of 86,700 and a weight average molecular weight of 229,800 and then using a PS fraction (PS-2) with a molecular weight of 10,000 which was comparable to the PS block molecular weight in Kraton 1101.

A Perkin-Elmer differential scanning calorimeter, model DSC-4, equipped with a dedicated microprocessor supplied by LMS, Inc. was used to measure the thermodynamic properties of the samples. The viscosity of the samples was measured using an Instron capillary rheometer (ICR), model 3211.

The polymer samples were broken into small particles, and mixed with the acetanilide powder. For the DSC measurements, the mixture was packed into a sealed sample pan and heated from room temperature to about 180°C at 10°C/min measuring the heat flow. The sample was held at the highest temperature for about 20 minutes to allow acetanilide to diffuse into the polymer. The sample was then cooled down to a desired temperature at 10°C/min, and the second heat flow measurement was made on reheating the sample at 10°C/min. At the end of the second heating cycle, the sample was quenched down to a desired temperature by pouring liquid nitrogen at a nominal cooling rate of 320°C/min. The actual cooling rate of the sample inside the sealed pan would be less than the nominal cooling rate. It was hoped to preserve the interaction between the polymer and acetanilide in the molten state into the solid state by quenching. The third heat flow measurement was made on reheating the sample at 10°C/min. Other thermal treatments were given to some samples for a more detailed study. All DSC curves were taken upon heating at 10°C/min unless noted otherwise.

For the ICR measurements, the mixture was extruded at least two times repeatedly at each temperature to insure a complete distribution of acetanilide in the polymer. The melt viscosity measured from the second path was substantially lower than that from the first path for the PS-acetanilide mixtures, but the measurements from the second and third paths were about the same.

RESULTS AND DISCUSSION

Figure 1 shows the DSC results of the PS-1 sample. The first curve was obtained from the initial heating of the sample as received, and second curve after cooling at 10°C/min, the third curve after quenching, and the fourth curve after annealing for about 21 h at 102°C. The glass transition temperature (T_g) of PS-1 is found to be about 106°C from the 3rd curve. Although the thermal history has a definite influence on the hysteresis of the glass transition with a slower cooling rate causing a greater hysteresis, it has an insignificant effect on the location of the T_g . Figure 2 presents the DSC results of the PS-2 sample. The first and second curves were obtained after 10°C/min cooling and quenching, respectively. The T_g of PS-2 is found to be about 94°C from both curves. Our measurements of T_g for the PS-1 and PS-2 samples are in an excellent agreement with the previously reported values by other investigators.^{16,17} Figure 3 presents the DSC results of acetanilide. Acetanilide shows a sharp melting peak at 116°C, very close to the melting point (T_m) reported by Fisher Scientific, and the thermal

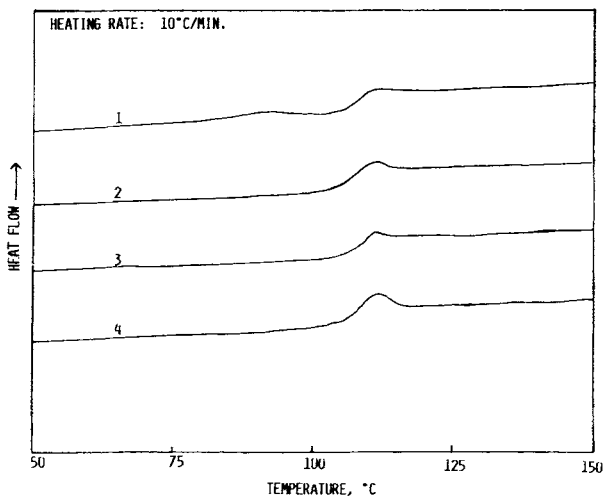


Fig. 1. DSC curves of PS-1; 1: as received, 2: cooled at 10°C/min, 3: quenched, and 4: annealed at 102°C for about 21 hours.

history has no effect on the melting behavior as expected for a low-molecular weight material. Acetanilide gives a sharp crystallization peak at about 64°C when it is cooled at 10°C/min. We can conclude from Figures 1-3 that the thermal treatments used in our experiments will have virtually no effect on the T_g of the PS samples or the T_m of acetanilide. Any change in the T_g of the PS samples or the T_m of acetanilide found for the PS/acetanilide mixtures may be attributed to the interaction between the materials.

Figure 4 presents the DSC results for the PS-1/acetanilide mixture with the acetanilide concentration of 5.97% by weight. The first curve taken during the initial heating cycle of the mixture shows that the T_g of PS-1 and the T_m of acetanilide are virtually unaffected by each other. All PS-1/acetanilide mixtures gave a similar result during the initial heating cycle.

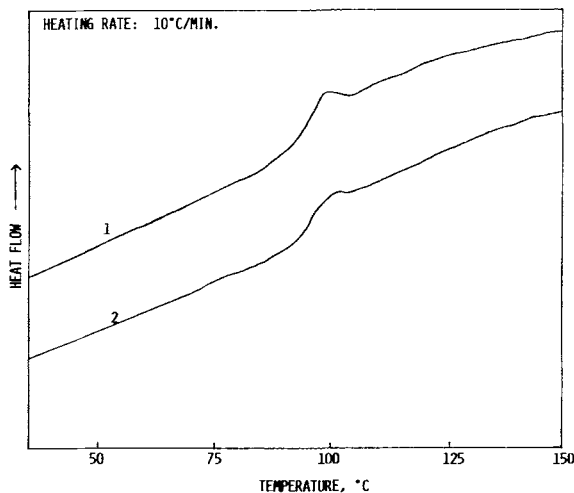


Fig. 2. DSC curves of PS-2; 1: cooled at 10°C/min, and 2: quenched.

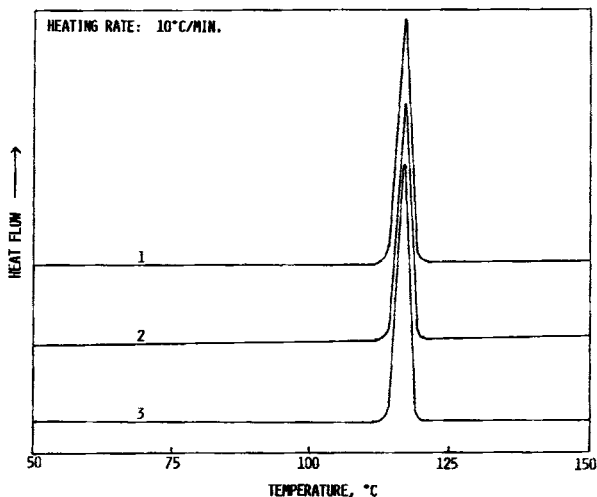


Fig. 3. DSC curves of Acetanilide; 1: as received, 2: cooled at 10°C/min, and 3: quenched.

The T_g of PS-1 in the mixture is found to be 79°C, a large depression of 27°C. The second and third curves show no indication of the acetanilide crystal. The entire amount of acetanilide apparently had dissolved into the polymer during the initial heating cycle and none of the dissolved acetanilide recrystallized out of the polymer during cooling. The dissolved acetanilide could not be recrystallized by annealing.

The DSC results for the PS-1/acetanilide mixture with 18.9% acetanilide are presented in Figure 5. The first curve was obtained after cooling the mixture at 10°C/min. Recrystallization of the dissolved acetanilide around 95°C and melting of the crystallized acetanilide with the melting peak at about 112°C are clearly seen. Depression of the T_m of acetanilide by about 4°C is observed. In order to study the recrystallization mechanism of ace-

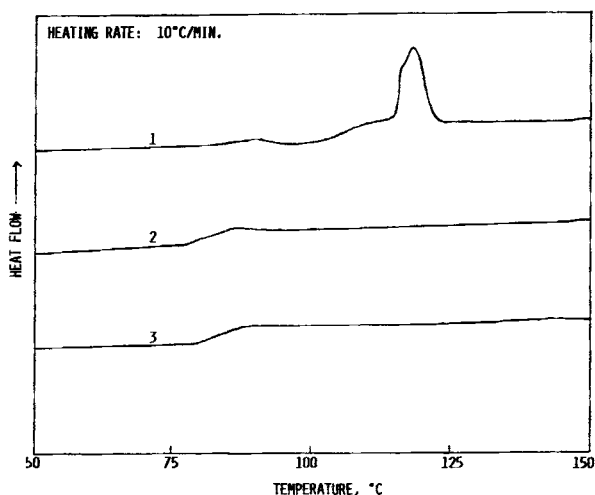


Fig. 4. DSC curves of PS-1 with 5.97 wt% acetanilide; 1: initial mixture, 2: cooled at 10°C/min, and 3: quenched.

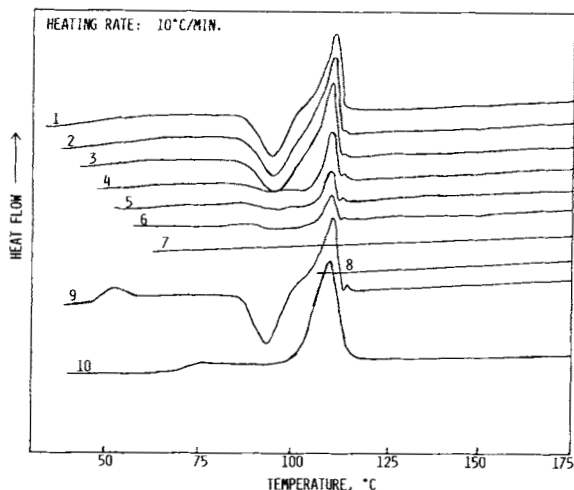


Fig. 5. DSC curves of PS-1 with 18.9 wt % acetanilide; 1: heated to about 175°C and cooled at 10°C/min to about 30°C, 2 through 8: cooled at 10°C/min to different levels of temperature, 9: quenched, and 10: annealed at 102°C for about 70 h.

tanilide, the mixture was cooled down to different temperatures at 10°C/min and the 2nd–8th curves were obtained on heating at 10°C/min. The recrystallization mechanism is found to be a classic nucleation and growth of crystals for liquid to solid-phase transition in a dense phase.² Acetanilide did not recrystallize out of the mixture upon cooling and the mixture had to be cooled down to a sufficiently low temperature before the nuclei could grow, with a lower cooling temperature resulting in a higher degree of recrystallization. The 9th curve was obtained after quenching the mixture at the end of the 8th curve. The T_g of PS-1 in the mixture after quenching is found to be about 49°C. It is clear that the entire 18.9% acetanilide dissolves into the polymer at about 180°C and all of acetanilide remains to be dissolved in the polymer upon quenching considering the thermal history and also comparing the areas under the recrystallization and melting peaks. The 10th curve was obtained after annealing the mixture for about 70 h at 102°C. It shows the T_g of PS-1 in the mixture at about 71°C and little recrystallization. In another experiment, the T_g of PS-1 in the mixture was found at about 69°C after simply heating the mixture to 102°C at 10°C/min. Apparently, the annealing treatment or even a quick heating to 102°C caused a large fraction of the dissolved acetanilide to recrystallize out of the polymer. The T_g of PS-1 in the mixture increases as the concentration of dissolved acetanilide decreases upon acetanilide recrystallization.

Figure 6 was constructed after a series of annealing experiments to control the amount of dissolved acetanilide. The amount of dissolved acetanilide was determined by quantitatively analyzing the DSC curves. The solubility of acetanilide in the PS-1 sample at 102°C is found to be about 8%. Excess acetanilide above 8% dissolved in the polymer can be recrystallized by a simple thermal treatment. Recrystallization of the dissolved solid solvent is an essential requirement for the concept of solid solvent.

Figure 7 presents the DSC results of the PS-2/acetanilide mixture with 10% acetanilide. The first and second curves were obtained after cooling

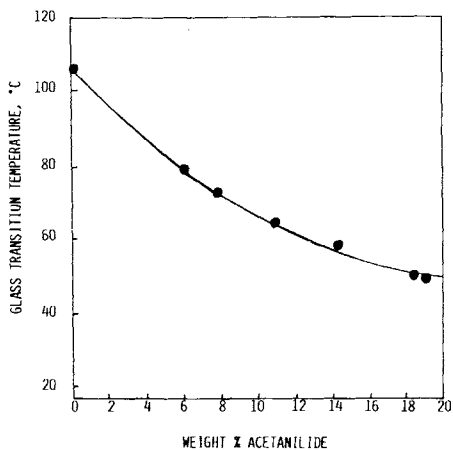


Fig. 6. Glass transition temperature of the PS-1/acetanilide mixture as a function of acetanilide concentration.

at 10°C/min and quenching, respectively. The curves show the T_g of PS-2 in the mixture at about 62°C, a depression of 32°C, and the melting peak of acetanilide at 112°C. The observation of a large acetanilide melting peak without an accompanying recrystallization peak even for the quenched sample is interesting since it indicates acetanilide recrystallization out of PS-2 during cooling unlike for the case of PS-1. The solubility of acetanilide is expected to be greater in PS-2 than in PS-1 since PS-2 has a much lower molecular weight than PS-1. However, lower melt viscosity and lower T_g of PS-2 compared with those of PS-1 are believed to have enhanced acetanilide recrystallization in PS-2 during cooling. The finding, that acetanilide recrystallizes out of PS-2 during cooling, is a quite encouraging sign for the use of acetanilide as a solid solvent for Kraton 1101 since the PS phase in Kraton 1101 and PS-2 have a similar molecular weight.

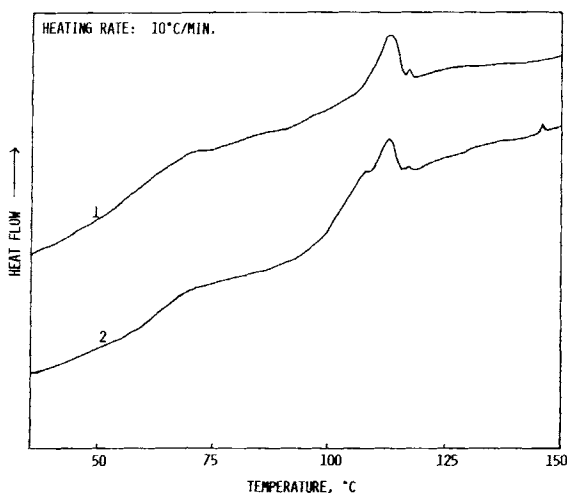


Fig. 7. DSC curves of PS-2 with 10 wt% acetanilide; 1: heated to about 150°C and cooled at 10°C/min, and 2: quenched.

The DSC results of Kraton 1101 are presented in Figure 8. The heat flow curve clearly shows the T_g of the PB phase at -95°C . The PS phase gives a broad glass transition and the T_g is not easily seen from the heat flow curve. We found in this particular case that the T_g of the PS phase at about 79°C could be determined easier from the specific heat curve although it required more work of running a sapphire standard. Our values of T_g for the PB and PS phases in Kraton 1101 agree quite well with those reported by others.¹⁶⁻¹⁸ The T_g of the PS phase in Kraton 1101, even if we take the PS block molecular weight to be the lower value of 11,000 among the reported values, is much lower than the value expected for the PS phase by itself due to the effects of the soft PB blocks and the interface.

Figure 9 presents the DSC results for the Kraton 1101/acetanilide mixture with 3.1% acetanilide. The T_g of the PB phase at -95°C was not influenced by acetanilide, but the glass transition of the PS phase became very broad, making determination of the T_g of the PS phase impractical. Although the absence of any acetanilide melting peak and the unchanged T_g of the PB phase in Figure 9 appear to indicate that all acetanilide was preferentially dissolved into the PS phase, we later found through melt viscosity measurements and solution tests that some acetanilide stayed in the PB phase and caused crosslinking of the PB phase at high temperatures. The Kraton G sample was added in our experiments at this point in order to avoid undesirable chemical reactions between the block copolymer samples and acetanilide.

Figure 10 presents the DSC results of the Kraton G/acetanilide mixture with 3% acetanilide. The 1st curve obtained during the initial heating shows the T_g of the EB phase at about -58°C and the T_m of acetanilide at 116°C . Although not shown here, the Kraton G sample by itself gives the T_g of the EB phase at about -58°C and a very broad melting peak around 15°C , virtually identical to those of Figure 10 except the acetanilide melting peak. The T_g of the PS phase in the Kraton G sample could not be easily detected by our DSC measurements. Returning to Figure 10, the second and the

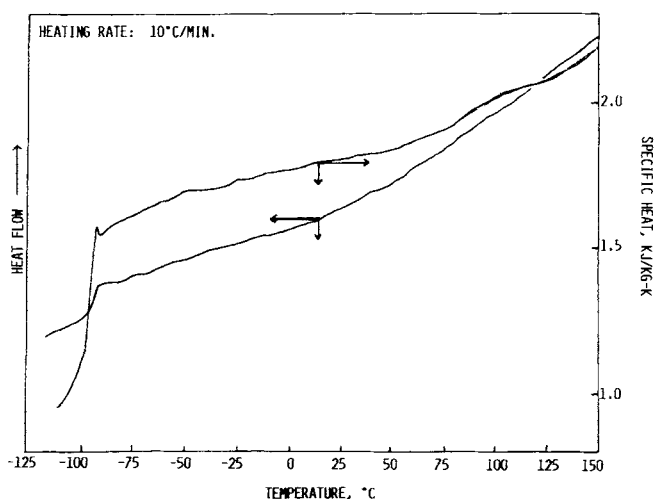


Fig. 8. DSC curves of Kraton 1101; cooled at $10^\circ\text{C}/\text{min}$.

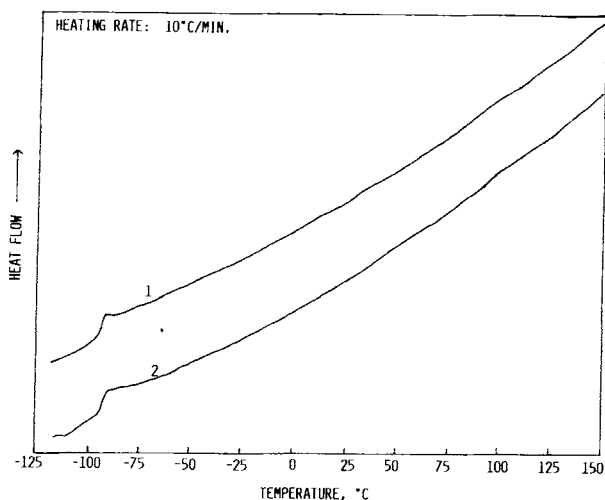


Fig. 9. DSC curves of Kraton 1101 with 3.1 wt% acetanilide; 1: heated to about 150°C and cooled at 10°C/min, and 2: quenched.

third curves obtained after cooling at 10°C/min and quenching, respectively, show a broad but definite acetanilide melting peak at about 105°C. The very broad melting peak around 15°C is believed to come from crystals composed of repeated ethylene segments in the EB phase.¹⁵ It is clear that acetanilide does not influence the T_g of the EB phase and recrystallizes in the Kraton G sample upon cooling. Acetanilide certainly appears to be a potential solid solvent for the Kraton G sample.

Figure 11 and 12 show the effect of acetanilide on the melt viscosity of the PS-1 sample. It is clearly seen that acetanilide acts as a solvent to PS in the molten state and can greatly reduce the viscosity of polystyrene. For example, 5% acetanilide reduced the viscosity of PS-1 measured at 217°C and 3.5 S^{-1} by as much as 2.16-fold.

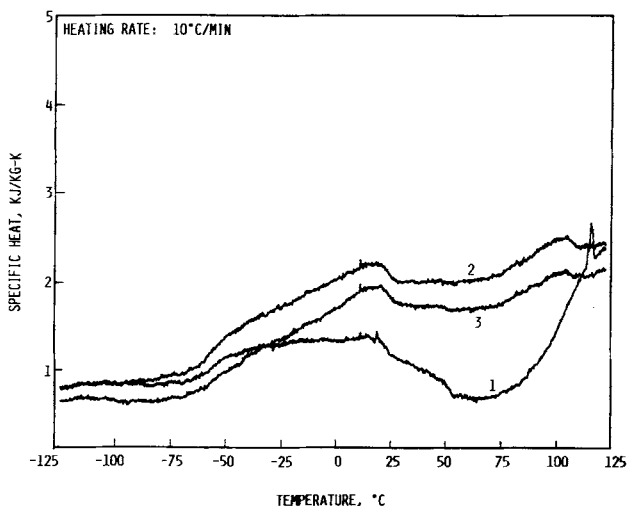


Fig. 10. DSC curves of the Kraton G sample with 3 wt% acetanilide; 1: initial mixture, 2: cooled at 10°C/min, and 3: quenched.

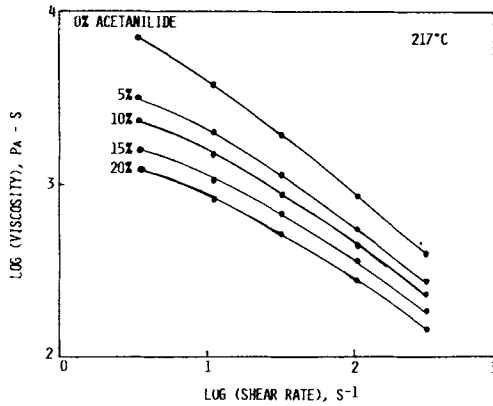


Fig. 11. Melt viscosity of the PS-1/acetanilide mixtures as a function of shear rate at 217°C.

Figure 13 shows the effect of 3.3% acetanilide on the melt viscosity of Kraton 1101. Our initial measurements were made at 175°C and 200°C, and we unexpectedly found that acetanilide increased the viscosity of Kraton 1101. Our suspicion of possible chemical reactions between acetanilide and PB was confirmed by solution tests. Kraton 1101 dissolves in a 30/70 mixture of cyclohexane and heptane at room temperature upon stirring. The extrudate of the Kraton 1101/acetanilide mixture extruded at 175°C did not dissolve in the same solvent mixture, but the extrudate extruded at 130°C dissolved. It probably is safe to assume that acetanilide reacted with the PB phase at 175°C resulting in crosslinking of the PB phase. Kraton 1101 is highly elastic as well as highly viscous even at 200°C. It is highly viscoelastic at 130°C and exhibits flow instabilities similar to a stick-slip phenomenon even at low shear rates. The shear stress goes through a maximum and a minimum almost periodically at a given shear rate. Such fluctuations are indicated in Figure 13. The addition of 3.3% acetanilide reduces the viscosity of Kraton 1101 by about 14% on the average and greatly reduces the stress fluctuation, an indication of reduced melt elasticity. The full potential of acetanilide as a solid solvent for Kraton 1101

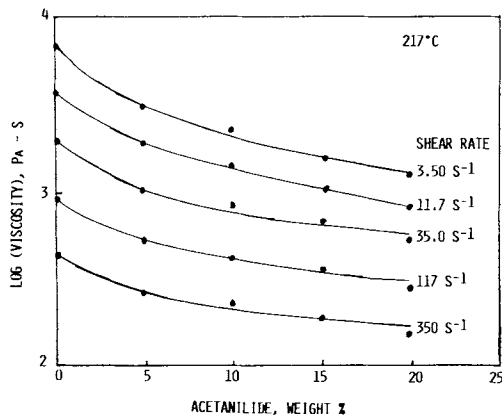


Fig. 12. Melt viscosity of the PS-1/acetanilide mixture as a function of acetanilide concentration at 217°C.

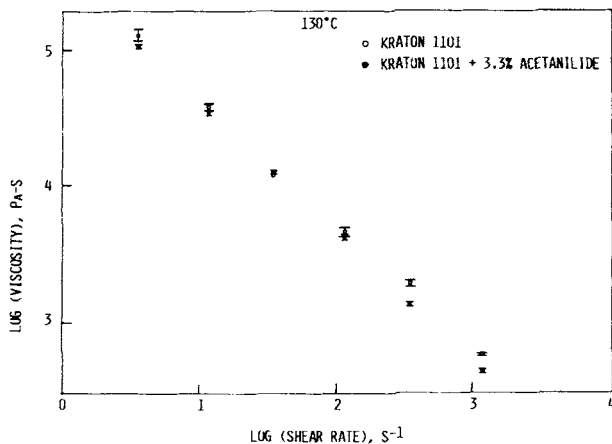


Fig. 13. Effects of 3.3 wt% acetanilide on the melt viscosity of Kraton 1101 at 130°C.

could not be evaluated because of the complication caused by chemical reactions between them.

Figure 14 shows the effect of 3% acetanilide on the melt viscosity of the Kraton G sample. The Kraton G sample is highly viscous and elastic even at 230°C, giving highly unstable flow except at very low shear rates. Thus, the true effect of acetanilide on the melt viscosity can be observed only at the low shear rates shown in Figure 14. At the shear rate of 3.6 S^{-1} , the addition of 3% acetanilide reduces the melt viscosity of the Kraton G sample by about 16% at 200°C and by about 27% at 230°C. The solvent effect of acetanilide increases as temperature increases.

Our experimental results presented here taken together with some relevant results of previous investigators³⁻⁷ strongly support the concept of solid solvent.

CONCLUSION

The concept of solid solvent has been examined using acetanilide as a potential solid solvent for PS and two block copolymers containing PS blocks (Kraton 1101 and an experimental Kraton G). The concept entails using a

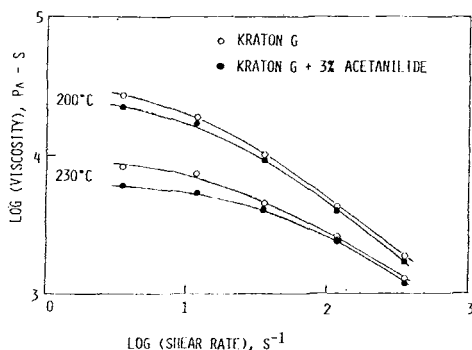


Fig. 14. Effect of 3 wt% acetanilide on the melt viscosity of the Kraton G sample at 200°C and 230°C.

LMC as a processing aid. An ideal solid solvent mixed into a polymer is expected to become a solvent to the polymer greatly reducing the viscosity of the polymer at high processing temperatures, but to precipitate out of the polymer without adversely affecting the properties of the polymer at low use temperatures.

Acetanilide is found to satisfy the basic requirements of a solid solvent for PS although it clearly is not an ideal solid solvent for PS. Acetanilide has a high solubility in PS at high processing temperatures greatly reducing the viscosity of PS, and it precipitates out of PS (note PS-2 and the Kraton G) at low temperatures exhibiting the essential behavior of a solid solvent. However, it has an undesirably high level of residual solubility in PS. Acetanilide also is found to effectively reduce the viscosity of two ABA-type block copolymers containing PS end blocks.

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