

A Solid Solvent as Processing Aid for Polystyrene

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Synopsis

Many polymers suffer from excessive heat generation during processing due to high viscosity, and reduction of viscosity is desired to control the melt temperature during processing. The concept of solid solvent was recently proposed based on thermally reversible compatibility between a polymer-additive pair. Benzenesulfonamide was found to be virtually a perfect solid solvent for polystyrene, and this finding clearly proves that solid solvents can be used as processing aid for polymers to effectively reduce the viscosity.

INTRODUCTION

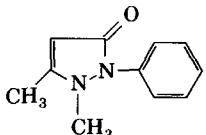
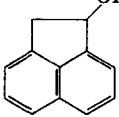
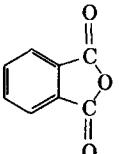
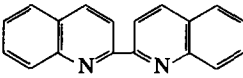
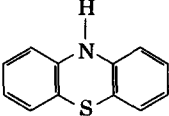
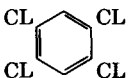
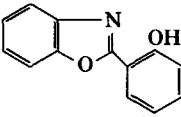
A polymer has to be melted or plasticated during processing such as extrusion, injection molding and banbury mixing, etc. Heat for melting comes mainly from viscous dissipation of the mechanical energy provided by the motor of processing equipment rather than the thermal energy provided by the heaters due to very high viscosity and very low thermal conductivity of polymeric materials. In fact, many polymers develop undesirably large amount of heat during processing, and the excess heat often causes processing difficulties. Reduction of viscosity with the concomitant lowering of melt temperature is desirable in many high speed processes.

Solvents, plasticizers, and lubricants are widely used to reduce viscosity. Solvents and plasticizers are compatible with polymers, and they can effectively reduce the viscosities of the polymers. However, they remain permanently in the polymers with consequent undesirable effects on the physical properties of the polymers. Lubricants are basically incompatible with polymers, and they are not as effective as solvents or plasticizers in reducing viscosity. Solid solvents, recently proposed as a new concept,¹ should have a thermally reversible compatibility with polymers. They become soluble in the polymers at high temperatures of processing, thus effectively reducing viscosity, but become insoluble in the polymers at low temperatures of usage, thus precipitating out of the polymers into microdomains upon cooling. A particular solid solvent identified for a particular polymer can be a powerful additive for controlling the processability of the polymer without adversely affecting the physical properties of the polymer.

It was reported previously in a partial support of the solid solvent concept that acetanilide satisfied the basic requirements of a solid solvents for polystyrene (PS), although a large amount of acetanilide remained dissolved in PS upon cooling unless annealed.¹ This paper presents the results of our

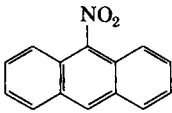
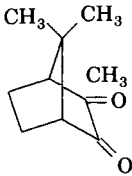
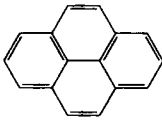
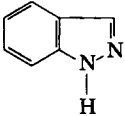
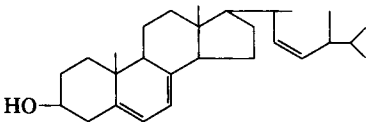
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TABLE I
Classification of LMCs According to the DSC Behavior

LMC name	Chemical structure	T_m (K)	Group ^a
Benzenesulfonamide	$C_6H_5SO_2NH_2$	423–425	A
Acetanilide	$C_6H_5NHCOCH_3$	388	B
Methyl red	$(CH_3)_2NC_6H_4N=NC_6H_4CO_2H$	452	C
Hydroxybenzoic acid	$HOC_6H_4CO_2H$	488–490	C
2,2,2-Triphenylacetaphenone	$(C_6H_5)_3C(CO)C_6H_5$	455–457	C
Antipyrine		387	C
4-Acetamidophenol	$4-HOC_6H_4NHCOCH_3$	442–445	B
4-Acetamidothiophenol	$CH_3CONHC_6H_4SH$	423–426	C(?)
Acenaphthenol		447–451	C
Phthalic anhydride		405–407	C
2,2-Biquinoline		455–469	C
Phenothiazine		458–459	C
Phenylsuccinic acid	$HO_2CCH_2CH(C_6H_5)CO_2H$	440–442	B
1,2,4,5-Tetrachlorobenzene		411–413	B(?)
Dimethyl terephthalate	$(CH_3O)_2CC_6H_4CO_2(CH_3)$	415	C
2,2-Diphenyl propionic acid	$CH_3C(C_6H_5)_2CO_2H$	445–448	C
2,2'-Biphenol	$HOC_6H_4C_6H_4OH$	383–385	C
Diphenyl sulfone	$C_6H_5SO_2C_6H_5$	396–398	C
Phenylurea	$C_6H_5NHCONH_2$	418–420	B
2(2-Hydroxyphenyl)benzoxazole		395–397	C

(Continued)

TABLE I (Continued from previous page.)

LMC name	Chemical structure	T_m (K)	Group ^a
<i>m</i> -Nitrobenzamide	$O_2NC_6H_4CONH_2$	413–416	A
9-Nitroanthracene		414–416	C
2,4,5-Trimethoxybenzoic acid	$(CH_3O)_3C_6H_2CO_2H$	416–418	B/C
<i>p</i> -Methoxybenzamide	$CH_3OC_6H_4CONH_2$	439–440	B
4,4'-Dichlorobenzophenone	$(4-ClC_6H_4)_2CO$	417–419	C
(±) Camphoroquinone		471–473	C
Triphenylamine	$(C_6H_5)_3N$	398–400	C
Pyrene		422–424	C
Indazole		420–422	C
Ergosterol	$C_{28}H_{44}O$; 	429–431	C
Sebacic acid	$HO_2C(CH_2)_8CO_2H$	404–407	A
<i>Trans</i> -Cinnamic acid	$C_6H_5CH=CHCO_2H$	405–408	C
Benzamide	$C_6H_5CONH_2$	401–402	A/B
<i>D</i> -mannitol	$HOCH_2(CHOH)_4CH_2OH$	440–443	A

^aGroup A = potential solid solvent behavior for polystyrene; group B = potential solid solvent behavior for polystyrene, but with undesirably high residual solubility; group C = permanent solvent behavior for polystyrene.

continued research on solid solvent. Over 30 low molecular weight crystalline materials (LMC) had been tested as potential solid solvent for PS, and one LMC was found to be virtually a perfect solid solvent for PS.

EXPERIMENTAL

Thermally reversible compatibility between PS and LMC was initially studied by heat capacity measurement using a Perkin-Elmer differential scanning calorimeter (DSC), Model DSC-4. For selected LMCs which exhibited potential solid solvent behavior for PS in the DSC measurement, their compatibility with PS at high temperatures was studied by viscosity measurement using an Instron Capillary Rheometer (ICR), Model 3211. A commercial PS (PS-1) with a number average molecular weight (MW) of 86,700 and a weight average MW of 229,800 was used for the ICR viscosity measurements, while a PS fraction (PS-2) with a MW of 10,000 was used for the DSC heat capacity measurements. Thirty-four LMCs tested as potential solid solvent for PS are listed in Table I together with their chemical structures and melting points. Mineral oil was also included here because of its common usage as a processing aid.

For the DSC measurements, the mixtures in powder form was packed into a sealed sample pan and heated from room temperature to about 475 K at 20 K/min measuring the heat flow. At the end of the first heating cycle, the sample was quenched down to a desired temperature by pouring liquid nitrogen at a nominal cooling rate of 320 K/min. The actual cooling rate of the sample inside the sealed pan would be much less than the nominal cooling rate. It was hoped to preserve the interaction between the polymer and the LMC in the molten state into the solid state by quenching. At the end of the second heating cycle at 20 K/min measuring the heat flow, the sample was again cooled down to a desired temperature at 20 K/min. The third heat flow measurement was made on reheating the sample at 20 K/min.

For the ICR measurements, the mixtures were heated to a desired melt temperature inside the rheometer barrel for at least 5 min before extrusion. Each mixture was extruded at least two times repeatedly at each temperature to insure complete distribution of the LMC in the polymer. The melt viscosities measured from the second path were substantially lower than those from the first path in some cases. However, the measurements from the second and third paths were about the same within a probable experimental error of $\pm 10\%$ in all cases.

RESULTS AND DISCUSSION

Figure 1 shows the DSC results of the PS-1 sample. All curves in all figures were obtained during heating at 20 K/min; curve 1 during the initial heating of the sample as received or mixed, curve 2 during the second heating after quenching, and curve 3 during the third heating after cooling at 20 K/min. The glass transition temperature (T_g) of PS-1 is found to be about 379 K from curves 2 and 3. It should be noted that T_g was taken as the midpoint of the glass transition region. Figure 2 presents the DSC results of the PS-2 sample. It is interesting to note from curve 1 that PS-2 gives a large hysteresis peak during the initial heating cycle. The T_g of PS-2 is found to be about 367 K

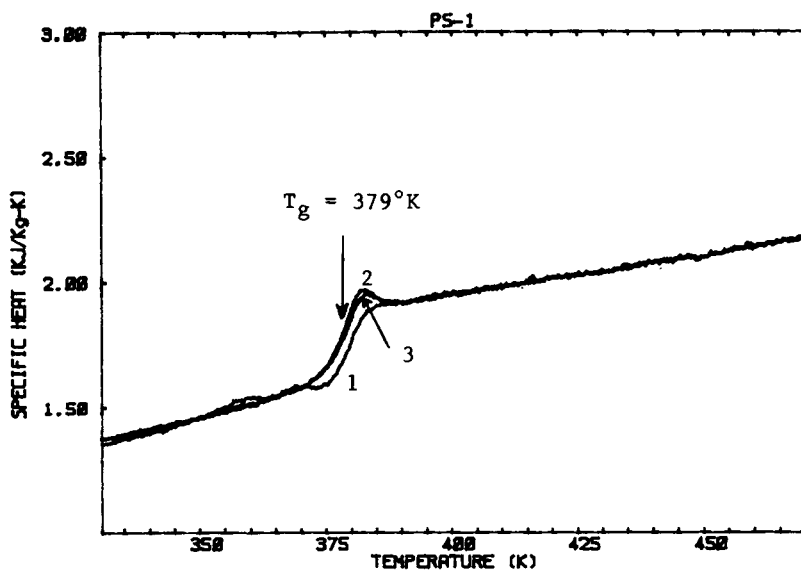


Fig. 1. DSC curves of PS-1 upon heating at 20 K/min: (1) as received; (2) after quenching; (3) after cooling at 20 K/min.

from curves 2 and 3. Our measurements of T_g for PS-1 and PS-2 are in excellent agreement with the previously reported values by other investigators.^{2,3}

Figure 3 presents the DSC results of the PS-2/5 wt % acetanilide (AA) mixture. The curve 1 obtained during the initial heating shows, as expected, a broad melting peak of AA around 390 K and the T_g of PS-2 at about 367 K.

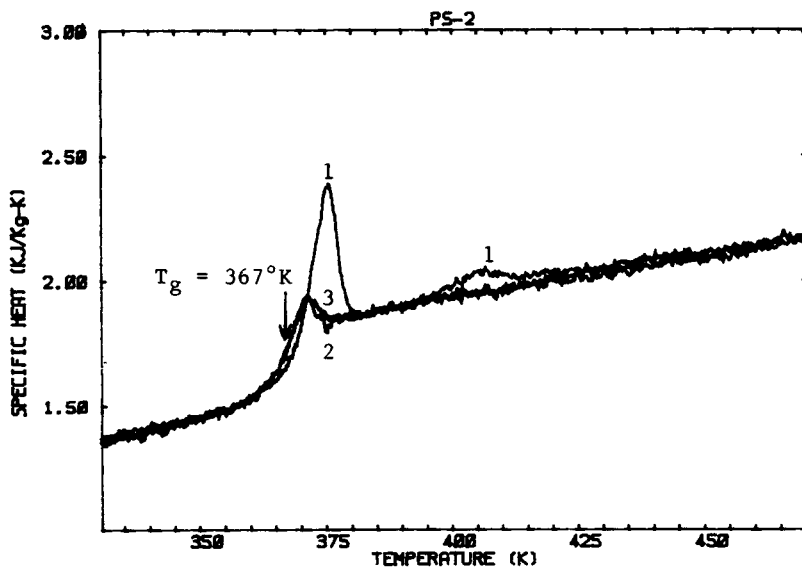


Fig. 2. DSC curves of PS-2 upon heating at 20 K/min: (1) as received; (2) after quenching; (3) after cooling at 20 K/min.

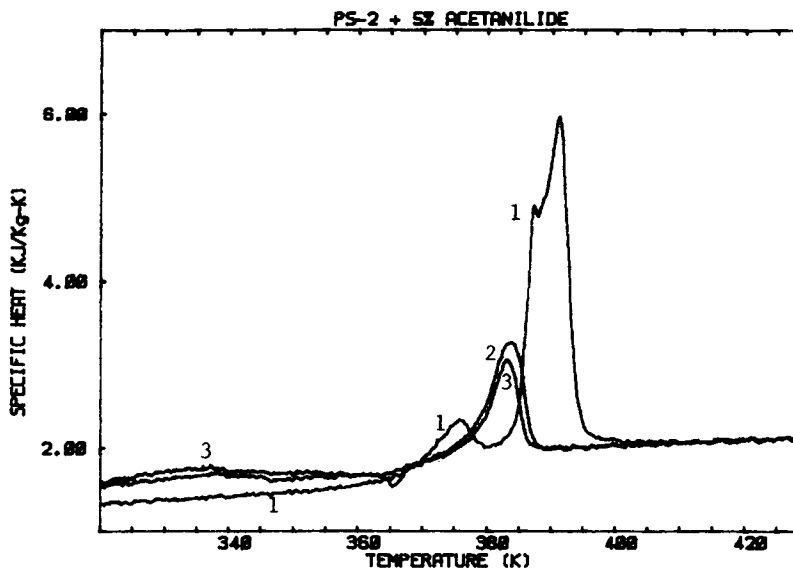


Fig. 3. DSC curves of the PS-2/5 wt % acetanilide mixture upon heating at 20 K/min: (1) initial mixture; (2) after quenching; (3) after cooling at 20 K/min.

Curves 2 and 3 show a smaller melting peak of AA around 383 K and an ill-defined T_g of PS-2 below 335 K. Both the T_m of AA and the T_g of PS-2 are significantly depressed, clearly indicating good compatibility between AA and PS-2. Although AA crystallizes out of PS-2 upon cooling, a large amount of AA remains dissolved in PS-2.

Figure 4 presents the DSC results of the PS-2/5 wt % benzenesulfonamide (BSA) mixture. All curves show a sharp melting peak at 425 K, which is the melting point of BSA. Apparently, BSA readily crystallizes out of the mixture upon cooling, and its melting point is not affected in the mixture. However, curves 2 and 3 have a slightly less area under the melting peak of BSA than curve 1, and they also show a lower T_g of PS-2 than curve 1, indicating that a very small amount of BSA remains dissolved in PS-2 and the T_g of PS-2 is effectively lowered by the small amount of residual BSA. BSA behaves almost as a perfect solid solvent for PS as far as its DSC results are concerned. It is noted that our DSC measurements do not give information on the compatibility between components at high temperatures above the melting point of LMC. Compatibility between components at high temperatures is examined in this study by measuring the viscosity of the mixture. BSA will effectively reduce the viscosity of PS acting as a solvent if it is compatible with PS at high temperatures.

Figure 5 shows the DSC results of the PS-2/5 wt % mineral oil mixture. Mineral oil is compatible with PS-2 and reduces the T_g of PS-2 from 367 K to about 347 K. Mineral oil at 5 wt % concentration acts as a plasticizer (or solvent) for PS-2 and it is irreversibly dissolved in PS-2.

Figure 6 shows the DSC results of the PS-2/5 wt % methyl red mixture. Methyl red is found to be a good solvent for PS-2. The melting peak of methyl red at about 450 K is broadened and somewhat depressed even during the

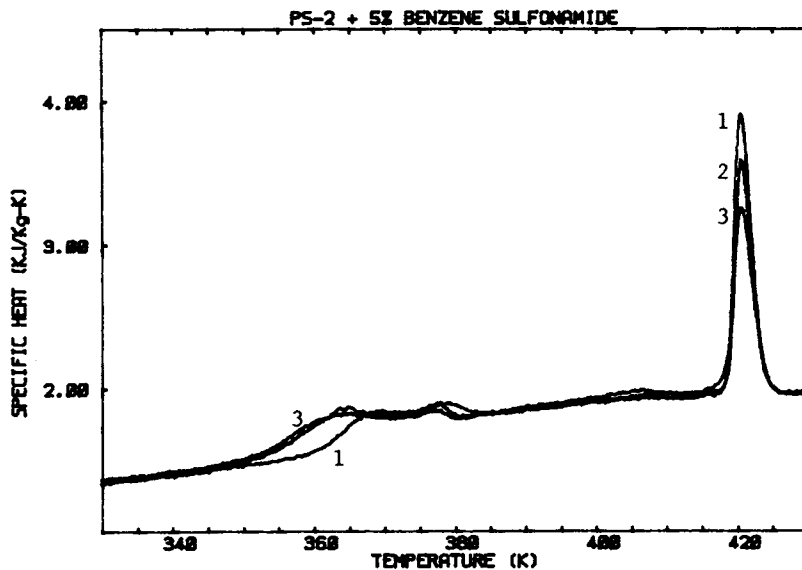


Fig. 4. DSC curves of the PS-2/5 wt % benzenesulfonamide mixture upon heating at 20 K/min: (1) initial mixture; (2) after quenching; (3) after cooling at 20 K/min.

initial heating of the mixture, as can be seen from curve 1. Methyl red does not crystallize out of PS-2 upon cooling once it is dissolved in PS-2, as shown in curves 2 and 3. The T_g of PS-2 is lowered from 367 to 357 K.

All LMCs examined by our DSC measurements may be classified into three general groups as presented in Table I: group A with a potential solid solvent behavior such as BSA (Fig. 4), group B with a potential solid solvent behavior

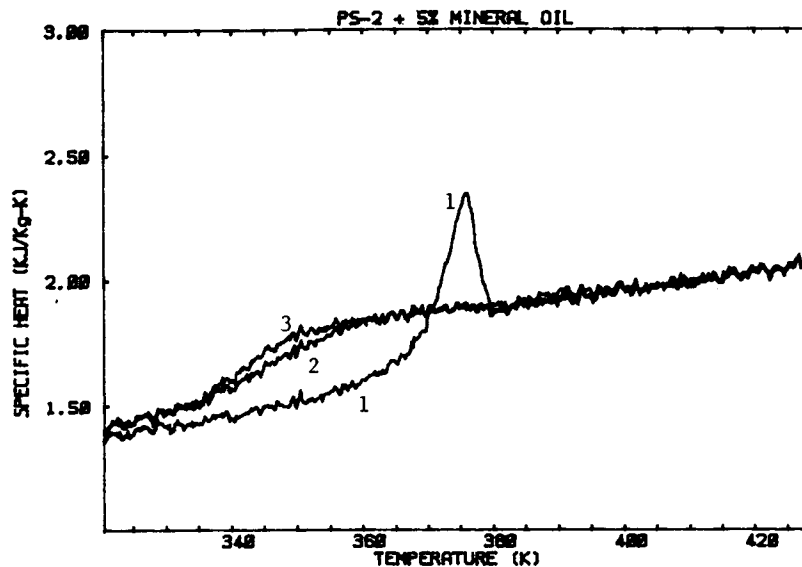


Fig. 5. DSC curves of the PS-2/5 wt % mineral oil mixture upon heating at 20 K/min: (1) initial mixture; (2) after quenching; (3) after cooling at 20 K/min.

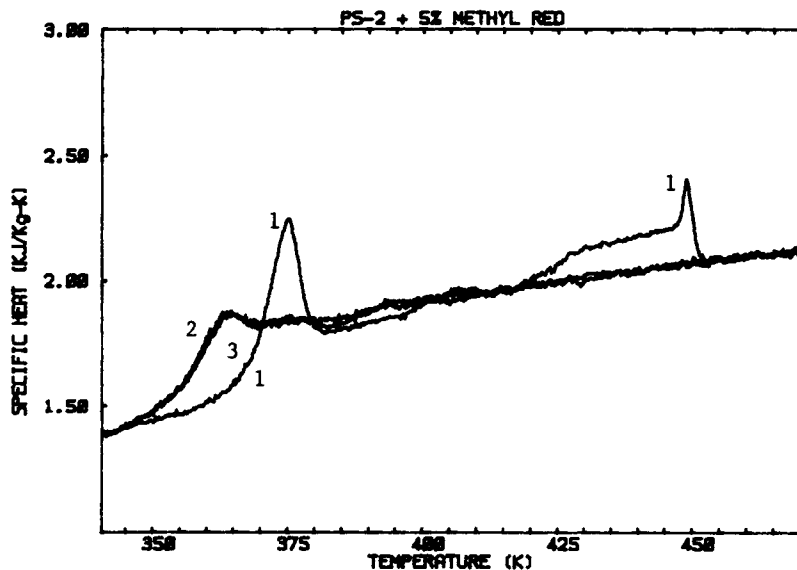


Fig. 6. DSC curves of the PS-2/5 wt % methyl red mixture upon heating at 20 K/min: (1) initial mixture; (2) after quenching; (3) after cooling at 20 K/min.

but with an undesirably high residual solubility such as AA (Fig. 3), and group C with a permanent solvent behavior such as methyl red (Fig. 6). We were surprised to find that PS was compatible with so many LMCs, as shown in Table I. We found at least five LMCs as potential solid solvent for PS, and their abilities to reduce the viscosity of PS will be studied.

Figure 7 presents the results of viscosity measurements for three selected samples. The PS sample used for viscosity measurements was PS-1. At 5 wt % concentration, BSA has the best solvent power to PS, reducing the viscosity of PS-1 measured at 490 K and 4 s^{-1} by as much as 60%. Gel permeation chromatograph measurement of the extrudate of the PS-1/BSA mixture showed an insignificant change in the molecular weight of PS-1. The extrudate, after fused and resolidified on a glass slide, showed more or less spherical domains of BSA crystals with about $6 \mu\text{m}$ diameter under an optical microscope. AA is the second, and mineral oil is the least effective solvent. From Figures 4 and 7, BSA is found to be virtually a perfect solid solvent for PS.

Comparing Figure 3 with Figure 4, AA appears to have a better solubility in PS than BSA as determined by the DSC measurements. However, the viscosity measurements shown in Figure 7 reveal that BSA is a better solvent to PS than AA, contrary to the DSC measurements. The melting and recrystallization studies of BSA and AA shown in Figures 8 and 9, respectively, clearly explain such seemingly contradicting results of the DSC and viscosity measurements. BSA recrystallizes upon cooling with a peak at 407 K, which is substantially above the T_g of PS-2 at 367 K. Therefore, BSA dissolved in PS-2 can readily recrystallize out of liquid PS-2 upon cooling. AA recrystallizes upon cooling with a peak at 340 K, which is substantially below the T_g of PS-2. AA dissolved in PS-2, although it becomes incompatible with PS-2 upon cooling, cannot easily recrystallize out of solid PS-2 because of kinetic hin-

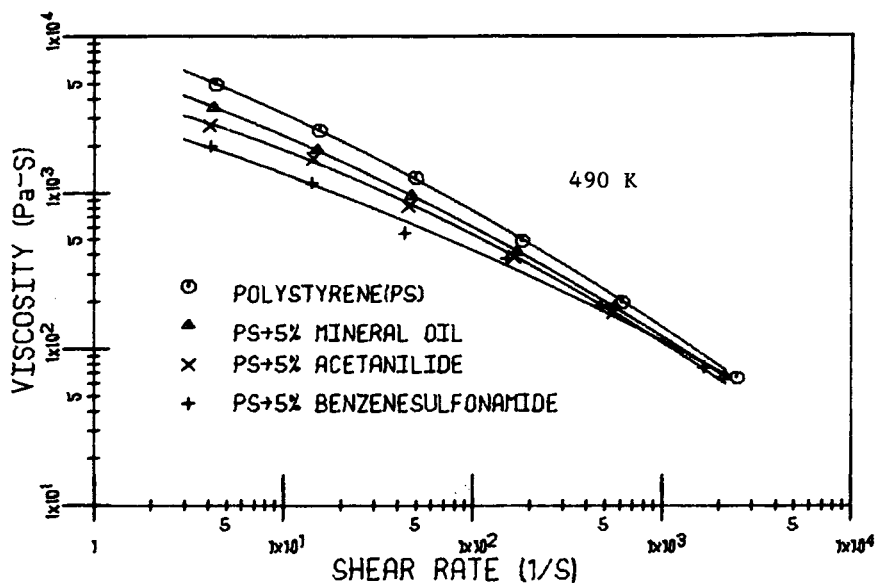


Fig. 7. Effect of LMC on the viscosity of PS-1: (○) Polystyrene (PS); (▲) PS + 5% mineral oil; (×) PS + 5% acetanilide; (+) PS + 5% benzenesulfonamide.

drance. Annealing the PS/AA mixtures in solid state causes recrystallization of AA as reported previously.¹

BSA in powder form was successfully compounded into a commercial PS in pellet form at 5 wt % on a large scale using an intermeshing, corotating twin-screw extruder. The PS strands coming out of the pelletizing die were

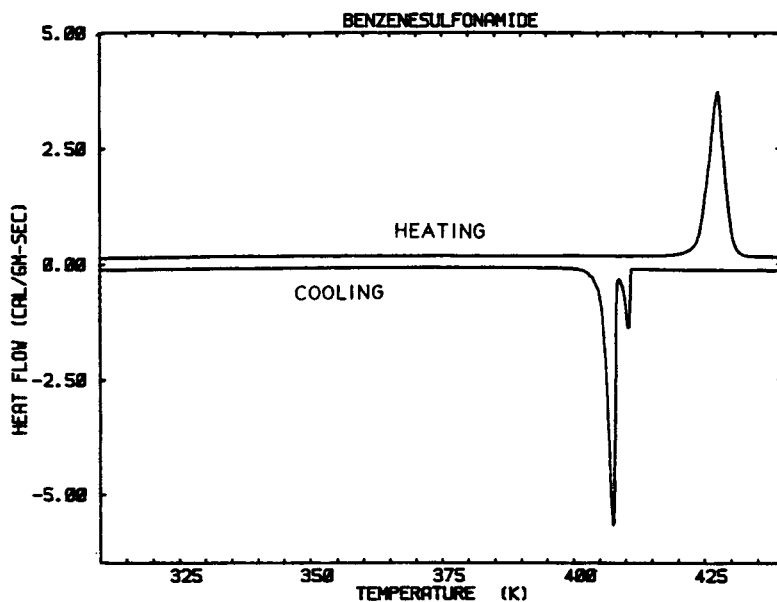


Fig. 8. Melting and recrystallization behavior of benzenesulfonamide.

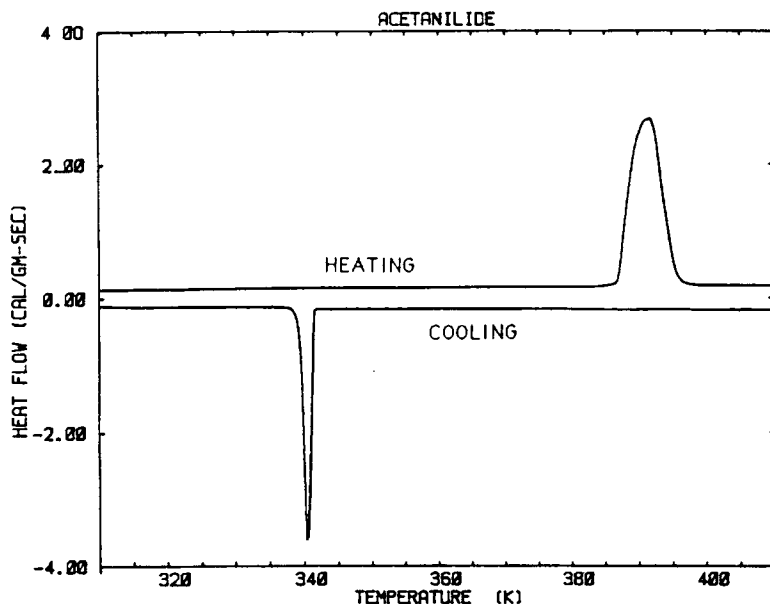


Fig. 9. Melting and recrystallization behavior of acetanilide.

initially transparent, but they quickly became milky upon cooling inside the water cooling tank as BSA crystallized out of PS. A preliminary study of using BSA as a processing aid in injection molding of PS gave a very promising result.

CONCLUSIONS

We have examined over 30 LMCs in search of a solid solvent for PS. A solid solvent should act as a solvent to the polymer at high temperatures of processing, greatly reducing the viscosity of the polymer, but crystallize out of the polymer upon cooling as discrete domains without adversely affecting the use properties of the polymer. Our DSC measurements revealed several LMCs as potential solid solvents for PS. In particular, BSA at 5 wt % concentration reduced the viscosity of a commercial PS sample measured at 490 K and 4 s^{-1} by as much as 60%. BSA was found to be virtually a perfect solid solvent for PS from our DSC and viscosity measurements.

The concept of solid solvent, theoretically based on thermally reversible solubility of a solid additive in a polymer, is proven to be feasible in this study. We will expand our study of solid solvent to block copolymers, blends, and other polymers with processing difficulties. A solid solvent causes milkiness in a transparent polymer. The effects of a solid solvent on the mechanical properties of a polymer will also have to be studied.

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