Thermochimica Acta, 54 (1982) 349–356
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

THE INVESTIGATION OF THE COMPATIBILITY AND PHASE SEPARATION OF POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) AND STYRENE–FLUOROSUBSTITUTED STYRENE COPOLYMER BLENDS BY DIFFERENTIAL SCANNING CALORIMETRY

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(Received 30 October 1981)

ABSTRACT

The compatibility of random copolymers of styrene and *p*-fluorostyrene, P(S–*p*FS), and styrene and *o*-fluorostyrene, P(S–*o*FS), with poly-(2,6-dimethyl-1,4-phenylene oxide), PPO, has been studied by differential scanning calorimetry (DSC). It was found that compatibility depends on copolymer composition as well as on the position of substituted fluorine. P(S–*p*FS) copolymers of *p*-fluorostyrene content less than 56 mole % are miscible with PPO in all proportions, using the criteria of a single glass transition and optical clarity. However, P(S–*o*FS) copolymers with less than 91 mole % of *o*-fluorostyrene are compatible with PPO. Copolymers P(S–*p*FS) containing 46–56% of *p*FS undergo phase separation upon annealing at elevated temperatures indicating that a lower critical solution temperature (LCST) exists. At the same time, P(S–*o*FS) copolymers with less than 80% of *o*-fluorostyrene blended with PPO do not show phase separation even by annealing at 325°C for the same time.

INTRODUCTION

It is known that blends of polystyrene (PS) and PPO meet all criteria for compatibility over the entire composition range [1–4]. However, relatively small changes in chemical structure of either polymer component are sufficient to render the resulting system entirely incompatible [3,5,6]. Recent studies have shown that complete substitution with chlorine at the *para* or *ortho* position in PS thus leads to a polymer incompatible with PPO [5]. Random copolymers of *p*- and *o*-chlorostyrene form homogeneous blends with PPO between compositions 23 and 64% of *p*ClS [6,7]. It was also shown that all compatible blends exhibit an LCST [6]. In the case of styrene–*o*(*p*)-chlorostyrene copolymers, it was shown that they may be compatible with PPO depending only on the copolymer compositions [3,5,7]. Consequently, it was of interest to investigate the behaviour of corresponding fluorinated compounds.

Both homopolymers poly(p-fluorostyrene)(PpFS) and poly(o-fluorostyrene)(PoFS) are found to be incompatible with PPO; such blends exhibit two glass transitions at temperatures characteristic of the pure component phases [8]. Furthermore, it was found that compatibility behaviour in the systems poly(pFS–oFS) and PPO depends on the copolymer composition [9]. This paper describes the compatibility behaviour of P(S–pFS), P(S–oFS) and PPO mixtures, and the thermally induced phase separation of homogenous blends.

EXPERIMENTAL

Materials

PPO (General Electric Company) was purified by dissolution in toluene and reprecipitation into an excess of methanol. Molecular weights of purified PPO were determined in tetrahydrofuran (THF) by gel permeation chromatography (GPC) at 25°C and were $\overline{M}_n = 16.900$, $\overline{M}_w = 34.800$.

The copolymers P(S–pFS) and P(S–oFS) were prepared by solution polymerization in toluene at 60°C using 2,2′-bis(azoisobutyronitrile) (AIBN) as a free radical initiator [5,8]. The respective monomers (Columbia Chemical Company) were purified by distillation. The resulting polymers were purified by precipitation from toluene solution into methanol. Copolymer compositions were determined by fluorine analysis. Conversion was held below 60% in order to minimize copolymer composition drift. Molecular weights were obtained by GPC at 25° in THF. Data on copolymers are presented in Table 1. The reactivity of o- and p-fluorostyrene with respect to the styrene radical was calculated using the Fineman–Ross equation [10]. For copolymer pairs, pFS(r_1) and styrene the reactivity ratios are $r_1 = 0.92$ and $r_2 = 0.80$. This result is in agreement with published data [11]. The reactivity ratios for systems oFS (r_1) and styrene are $r_1 = 1.06$ and $r_2 = 0.80$. Introduction of a fluorine atom in the *para* or *ortho* position of polystyrene has little effect on the reactivity of the styrene molecule.

Blend and film preparation

The copolymers given in Table 1 were blended with PPO by coprecipitation from dilute toluene solution (3–4 wt.%) into a large quantity of methanol (12:1). The precipitates were dried under vacuum at 80°C for 50 h. The dried precipitated blends were compression moulded into films at temperatures that are discussed in the results section.

Differential scanning calorimetry and thermogravimetric measurements

All DSC studies were done using a Perkin Elmer DSC-2 instrument under a nitrogen atmosphere using heating rates of 20°C min^{-1} with a sample size of 15–25 mg. All materials were amorphous, and the only distinctive features of the thermograms were glass transitions (T_gs). The T_g was determined as the temperature at which the heat capacity achieved one half of the entire step change observed.

Annealing experiments were also carried out in the DSC. An experiment consisted of heating the sample known to be homogeneous at the selected annealing temperature, at the rate of 320°C min^{-1}, and holding it at this temperature for 15 min. This period was selected as a balance between avoiding degradation and allowing enough time for equilibrium to be established. Samples were then quenched to ambient temperatures also as rapidly as possible in the instrument. Subsequent scanning at 20°C min^{-1} revealed either one or two discontinuities in the heat capacity, according to whether or not the phase separation temperature had been exceeded.

Thermogravimetric analysis (TG) experiments were carried out on a Perkin-Elmer, TGS-2 instrument at a heating rate of 20°C min^{-1}, with a nitrogen atmosphere.

RESULTS AND DISCUSSION

Pure materials

Glass transition temperatures for all the copolymers studied are listed in Table 1. Samples were annealed for at least one minute approximately 30°C above the expected T_g, quenched to ambient temperature as rapidly as possible in the instrument and then scanned at 20°C min^{-1}. This procedure allowed the polymers to flow and wet the sample pans. T_g data for the pure non-blended polymers are very close. It is as expected because the T_gs of corresponding homopolymers are similar in values. Clear films resulted for pure polymers when moulded at 180°C.

Copolymer blends

P(S-*p*FS) copolymers containing from 8 to 56 mole % of *p*FS are compatible with PPO using the criteria of single calorimetric relaxation and film clarity. Two T_gs are present in blends containing copolymers with a higher content of *p*FS (Fig. 1). Films of compatible blends were transparent, and those of incompatible blends cloudy. These results are similar to the results obtained for corresponding chlorinated copolymers with PPO as reported elsewhere [3,5,7].

Copolymers of P(S-*o*FS) having 91% or less of *o*FS are compatible with PPO in all proportions of component. DSC thermograms for these systems exhibit only a single, compositionally dependent T_g. The T_gs of these blends as well as T_gs of blends of P(S-*p*FS) copolymers with PPO are depressed from that predicted by the assumption of linear additivity. For example, the observed T_gs of P(S-49*o*FS)-PPO blends fall 4, 8, 11, 12 and 4°C below T_g calculated by the equation of linear addivity for mixtures of PPO weight fractions of 0.2, 0.4, 0.5, 0.6 and 0.8, respectively. It was found that T_gs of these systems may be empirically fitted by the Wood

TABLE 1

Molecular weights and T_gs of P(S-*p*FS) and P(S-*o*FS) copolymers

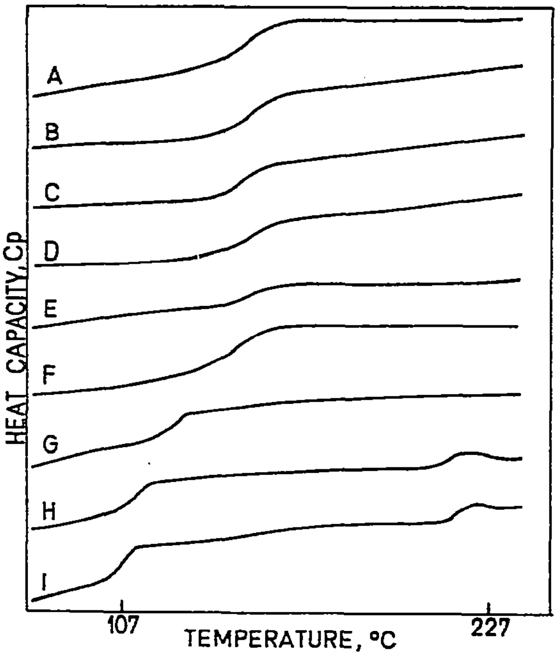
Sample	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	T_g (°C)
P(S-pFS) [a]			
P(S-8*p*F)	0.97	0 54	100
P(S-16*p*FS)	0.99	0.56	101
P(S-25*p*FS)	0.97	0.51	103
P(S-36*p*FS)	0.96	0.49	103
P(S-46*p*FS)	0.99	0.52	103
P(S-49*p*FS)	0.95	0.51	103
P(S-56*p*FS)	0.99	0.49	103
P(S-67*p*FS)	1.04	0.53	104
P(S-78*p*FS)	1.03	0.51	105
P(S-oFS) [a]			
P(S-8*o*FS)	0.98	0.52	101
P(S-18*o*FS)	0.95	0.53	101
P(S-29*o*FS)	1.10	0.57	100
P(S-40*o*FS)	1.23	0.64	98
P(S-49*o*FS)	1.14	0.59	98
P(S-58*o*FS)	1.33	0.69	97
P(S-68*o*FS)	1.34	0.68	96
P(S-80*o*FS)	1.39	0.71	96
P(S-84*o*FS)	1.51	0.78	96
P(S-91*o*FS)	1.45	0.72	96

[a] Numbers indicate mole fractions of *p*- or *o*-fluorostyrene in the copolymer. The data represent polystyrene equivalent molecular weights.

copolymer equation [12], with parameter $k \simeq 0.9$. Similar depressions in the corresponding chloro compound were observed [5]. Such observations are common for random copolymer systems. The next important feature of the blend thermograms is the apparent width of the transition. The glass transition for the single phase blends is spread over a much larger temperature range as compared with that of the unblended pure materials. The observed transition width behavior may be explained on the basis of phase homogeneity [5,13].

Thermally induced phase separation

To further analyze the behaviour of all copolymer blends with PPO which are compatible at the moulding temperature of 210°C, these samples were annealed at higher temperatures for an arbitrarily selected period of time, and this is explained in the experimental section. Some of these blends became heterogeneous at higher temperatures. In these, two T_g values were observed which did not correspond to those of the pure components, indicating rather a separation into mixed phases.



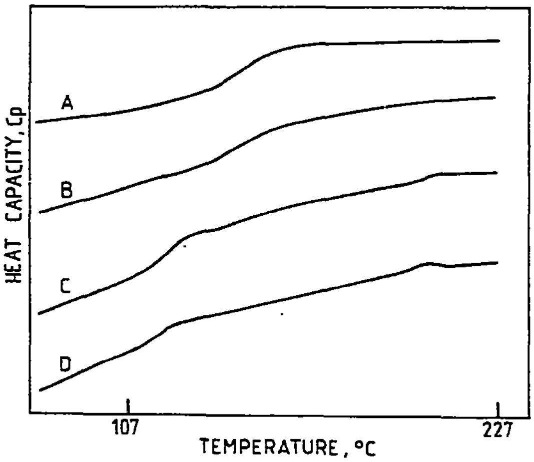
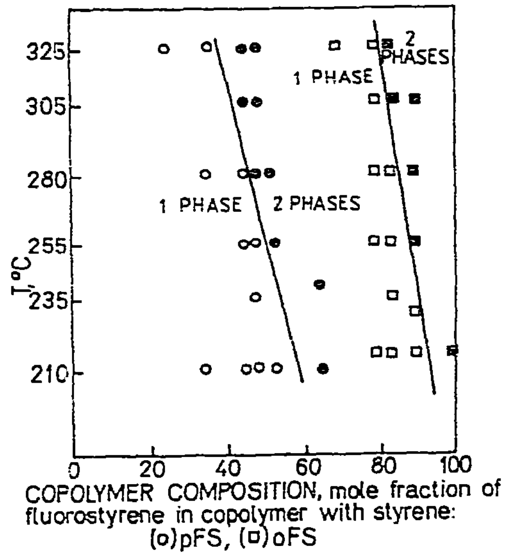


Fig. 1. DSC thermograms of 50/50 by weight of PPO and P(S-*p*FS) copolymer blends containing: A, 8: B, 16: C, 25: D, 36: E, 46: F, 49: G, 56: H, 67: I, 78: in mole % of *p*FS.

Fig. 2. DSC thermograms illustrating phase separation of 50/50 by weight of PPO-P(S-*p*FS) blends containing 49 mole % of *p*FS: A, as moulded at 210°C; B, annealed for 15 min at 255°C; C, annealed for 15 min at 305°C.

Figure 2 shows DSC thermograms for 50/50 wt.% PPO and P(S-49*p*FS) copolymer blends. Each curve represents the thermogram of independently annealed samples. The sample moulded at 210°C shows one T_g. Annealing of another sample at 255°C produces a glass transition region which is wider. The samples annealed at 280°C and 305°C exhibit two T_gs. This behaviour indicates the existence of a lower critical solution temperature (LCST) for these mixtures. To determine phase stability for other P(S-*p*FS) copolymers and PPO blends, samples were also annealed under the same conditions. The results are presented in Fig. 3. It is evident that phase stability depends on copolymer composition. Samples with a higher content of styrene in the copolymer are compatible with PPO even at 325°C. This is as expected in the light of the polystyrene compatibility with PPO [3,5]. Assuming that the composition of the separated phases can be determined by using the known T_g versus blend composition curve for the homogeneous blends, a phase diagram can be constructed. Figure 4 shows such a diagram for the blends of PPO with P(S-*p*FS) copolymer containing 46 mole % of *p*FS. Blends with the composition 50/50 wt.% exhibit phase separation at 305°C, but blends with the composition 40/60 and 60/40 show phase separation at 325°C. The separation of blends containing 80% of one component was not detected even at 325°C. It should be noted that the amount of materials in



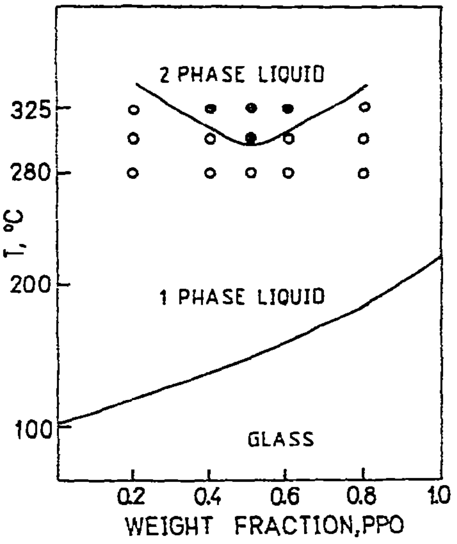


Fig. 3. Compatibility of 50/50 by weight of PPO–P(S–*p*FS) versus copolymer composition: ○, one phase; ●, two phases, and 50/50 PPO–P(S–*o*FS): □, one phase; ■, two phases.

Fig. 4. Phase diagram for PPO/P(S–*p*FS) copolymer blends containing 46 mole % of *p*FS at different PPO wt.%: ○, one phase; ●, two phases.

the minor phase was too small to be detected with certainity by the DSC technique. These results show that the degree of compatibility depends on the blend composition.

All compatible PPO–P(S–*o*FS) copolymer blends were exposed to the same thermal treatment as described for the blends of copolymers of *p*FS and styrene with PPO. It was found that raising the temperature up to 325°C does not influence the compatibility of the blends containing 80% or less of *o*-fluorostyrene. All thermograms within annealing temperatures from 255 to 325°C show the same glass transition temperature, closely corresponding to the T_g of the non-annealed sample of the corresponding blend. PPO–P(S–*o*FS) copolymer blends with a higher content of *o*FS (80 and 91%) are compatible with PPO at the moulding temperature but show phase separation by annealing at temperatures of 305 or 325°C, respectively. These results are also shown in the Fig. 3.

From the copolymer P(S–49*o*FS) and PPO, blends were prepared containing different amounts of components and were annealed also at temperatures up to 325°C. From the DSC thermograms it is evident that the annealing temperature has no influence on those samples. Each of these blends shows its own T_g after annealing.

With all the materials studied here, visual observations correlate with the results of calorimetry. From Fig. 3 it can be inferred that P*o*FS more 'nearly' mixed with PPO than *p*FS. However, P*p*ClS and P*o*ClS are quire similar in their behaviour when mixed with PPO. It was found that the P(S–*p*ClS) copolymer containing less than 76% of *p*ClS and P(S–*o*ClS) copolymers containing less than 72% of *o*-chlorostyrene are compatible with PPO [3,5,7].

Phase separation found in these systems appears to be completely reversible. Adequate periods of annealing below the LCST but above the T_gs of PPO and fluorostyrene copolymer result in the homogenization of previously phase separated blends. The time necessary to reform the single phase blend is highly dependent on the annealing temperatures and the degree of separation started with.

Polymer stability was investigated via thermogravimetric analysis. Namely, annealing experiments were carried out at temperatures over 300°C. Such high temperatures raise the question of whether polymer degradation is occurring and obscuring the results. Because of this, TG experiments were conducted for P(S–46*p*FS) and P(S–49*o*FS) copolymers and their 50/50 blends with PPO. Weight loss was monitored from 50 to 330°C. All samples lost less than 1% of weight up to 330°C. Although TG detects only weight loss, this is usually a good first approximation for testing the thermal stability of polymers. It is concluded that thermal degradation is not an important factor at temperatures of about 300°C for PPO and P(S–*p*FS) or P(S–*o*FS) blends.

CONCLUSIONS

In both poly(styrene–*p*-fluorostyrene) and poly(styrene–*o*-fluorostyrene) copolymers, it was found that copolymer composition has a pronounced influence on the compatibility with PPO.

The compatible P(S–*p*FS) copolymer–PPO blends show phase separation depending on the height of the annealing temperatures.

Copolymers P(S–*o*FS) having less than 91% of *o*FS are compatible with PPO in all proportions of components.

PPO–P(S–*o*FS) copolymers containing less than 80% of *o*FS did not show any phase separation in blends with PPO up to 325°C.

It was also found that blends of *o*-fluorostyrene copolymers with PPO are more stable than the blends of *p*- or *o*-chlorostyrene–styrene copolymers with PPO.

Using TG, it was found that thermal degradation is not an important factor at the temperature of interest (about 300°C).

REFERENCES

1 A.R. Shultz and B.M. Gendron, J. Appl. Polym. Sci., 7 (1972) 251.
2 J. Stoelting, F.E. Karasz and W.J. MacKnight, Polym. Eng. Sci., 10 (1970) 133.
3 A.R. Shultz and B.M. Beach, Macromolecules, 7 (1974) 902.
4 A.F. Yee, Polym. Prepr., 17 (1976) 145.
5 J.R. Fried, F.E. Karasz and W.J. MacKnight, Macromolecules, 11 (1978) 150.
6 P. Alexandrovich, F.E. Karasz and W.J. MacKnight, Polymer, 18 (1977) 1022.
7 P. Alexandrovich, Ph.D. Dissertation, University of Massachusetts, 1978.

8 R. Vukovič, F.E. Karasz and W.J. MacKnight, Hem. Ind., 35 (1981) 361.
9 R. Vukovič, V. Kureševič, F.E. Karasz and W.J. MacKnight, 27th Int. Symp. Macromolecules, Strasbourg, July 1981, p. 1231.
10 M. Fineman and S.D. Ross, J. Polym. Sci., 5 (1956) 756.
11 A.R. Gantmacher, Yu.L. Spirin and S.S. Ledvedev, Vysokomol. Soedin., 1 (1959) 1526.
12 L.A. Wood, J. Polym. Sci., 28 (1958) 319.
13 R. Buchdahl and L.E. Nielsen, J. Polym. Sci., 15 (1955) 1.