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Miscibility of partially imidized styrene–maleic anhydride copolymers with styrene–acrylonitrile copolymers

Tae Oan Ahn and Sang-Soo Lee
Department of Chemical Technology, Seoul National University, Seoul 151-742, Korea

and Lee Soon Park
Department of Polymer Science, Kyungpook National University, Daegu 702-701, Korea

and Han Mo Jeong*
Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea
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The miscibility of blends of poly(styrene-*co*-acrylonitrile) (SAN) and partially imidized poly(styrene-*co*-maleic anhydride) (SMI) was investigated using differential scanning calorimetry. SMIs with various contents and chemical structures of the imide unit were used in this study. The SANs whose acrylonitrile content is 20–32 wt% were miscible with these SMIs. It was observed that the type of substituent on the imide in SMI also affects the miscibility of the blend.

(Keywords: miscibility; styrene–acrylonitrile copolymer; styrene–maleic anyhydride copolymer)

Introduction

There has been much interest in miscible polymer blends in which one or both of the component polymers are random copolymers[1–5]. An example is the binary blend of poly(styrene-*co*-acrylonitrile) (SAN) and poly(styrene-*co*-maleic anhydride) (SMA)[5]. The miscibility of this pair depends on the copolymer compositions of SAN and of SMA: they are miscible when the styrene unit concentrations in the two copolymers are comparable.

The acrylonitrile (AN) unit content in commercialized SAN is mostly less than 35 wt%. The thermal resistance of these SANs can be enhanced by blending with other polymers which have a higher glass transition temperature (T_g) than SAN. Polymers which are miscible with SAN can be used more effectively for this purpose.

When some of the maleic anhydride (MA) units in SMA are imidized, the T_g increases. In this study, the miscibility of partially imidized SMA (SMI) with SANs whose content of AN is less than 35 wt% was investigated.

Experimental

The characteristics of polymers used in this study are shown in *Table 1*. Several kinds of SMI were prepared by the partial imidization of SMA having 50 mol% of MA[6]. In *Table 1*, SMI-T, SMI-A and SMI-C represent SMI having *N*-tolylmaleimide, *N*-phenylmaleimide and *N*-(*p*-chlorophenyl)maleimide units, respectively. Their chemical structures are shown in *Table 2*.

Blends of SAN/SMI were prepared by the solution/precipitation method. The polymers were weighed and dissolved in tetrahydrofuran to give solutions containing 2 wt% of polymer. The solution was precipitated in n-hexane and the collected precipitate was dried for 3 days at 60°C, followed by further drying at a temperature just above the glass transition temperature of SMI for 24 h to ensure complete evaporation of solvent and non-solvent.

The T_g values of copolymers and blends were determined using a Perkin–Elmer DSC-4 differential scanning calorimeter with a heating rate of 20°C min^{-1}. The temperature at the half-height of the heat capacity change was taken to be T_g. All the blends were annealed at 20°C above the T_g of the higher T_g component for 5 min, to erase the previous thermal histories, and cooled to ambient temperature before scanning. Miscibility was monitored using the criterion that a miscible blend exhibits a single T_g whereas a phase-separated blend shows two separate T_gs.

Results and discussion

As previously reported[5], the SMA used in this study was expected to show immiscibility with the SANs in *Table 1* and the expected result was obtained, as shown in *Figure 1*. In SMA blends with SANs of low AN content, two separate T_gs, corresponding to the constituent polymers, were observed. As the AN content was increased, two T_gs situated nearer to each other than those of the pure component polymers were observed, showing increased partial miscibility[7].

In *Figures 2* and *3* we can observe increased miscibility of SAN/SMI blends compared with SAN/SMA blends. The SANs blended with SMAs partially imidized with *p*-toluidine (SMI-T) show two T_gs of separate phases when the AN content in SAN is less than 10 wt%. When the AN content in SAN is 10–20 wt%, the blends have

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* To whom correspondence should be addressed

Table 1 Polymers used in this study

Designation	Composition[a]	$\bar{M}_w$[b]	T_g (°C)
SAN6	5.7 wt% AN	212 000	107.0
SAN10	9.5 wt% AN	198 000	107.5
SAN16	15.5 wt% AN	129 000	108.2
SAN20	19.5 wt% AN	189 000	110.0
SAN25	25.2 wt% AN	194 000	109.5
SAN31	30.5 wt% AN	280 000	111.0
SAN32	32.1 wt% AN	220 000	111.4
SMA	50 mol% MA	300 000	172.5
SMI-T24	24.1 mol% imide	[c]	205.0
SMI-T40	36.3 mol% imide	[c]	207.0
SMI-T48	47.5 mol% imide	[c]	211.5
SMI-A46	45.5 mol% imide	[c]	186.5
SMI-C42	41.6 mol% imide	[c]	219.7

[a] Composition obtained with elemental analysis and ^{1}H n.m.r. analysis[6]

[b] Weight-average molecular weights determined by g.p.c. calibrated with PS standards

[c] Prepared by the partial imidization of SMA having 50 mol% of maleic anhydride and $\bar{M}_w$ of 300 000

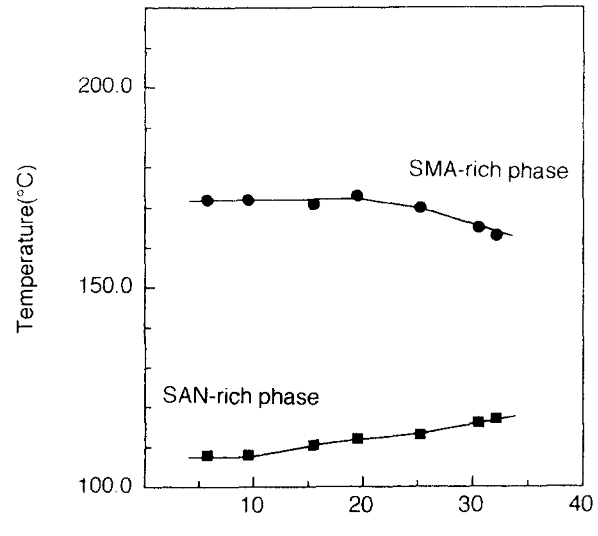
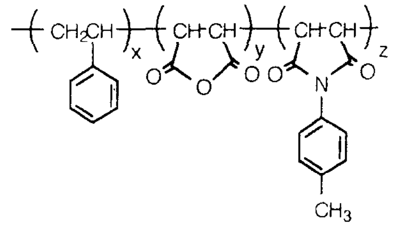
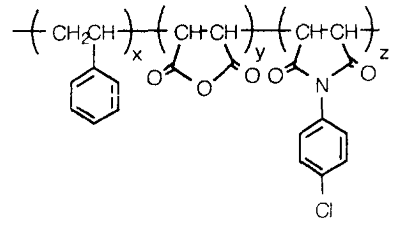
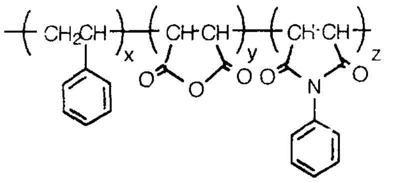


Figure 1 T_g behaviours of SAN/SMA (50/50 by weight) blends

Table 2 Chemical structures of partially imidized SMI

Designation	Structure[a]
SMI-T	
SMI-C	
SMI-A	

[a] x = 50 mol%, $y + z$ = 50 mol%, and z is shown in the composition column of *Table 1*

partial miscibility, showing two T_gs shifted nearer to each other, or a very broad glass transition. As the AN content in SAN is further increased above 20 wt%, SAN/SMI-T blends have a single T_g, exhibiting miscibility. However, we can see that the miscibility behaviour of SAN with SMI-T is little changed with the content of imidized unit when the *N*-tolylmaleimide unit is in the range of 24–48 mol%, as shown in *Figures 3a, b* and *c*.

Polymer–polymer miscibility can be enhanced by a minor modification in chemical structure[8,9]. Since the maleimide unit is able to have various kinds of side groups, we varied the *para*-position of the phenylmaleimide unit in SMI to investigate the substituent effect on miscibility.

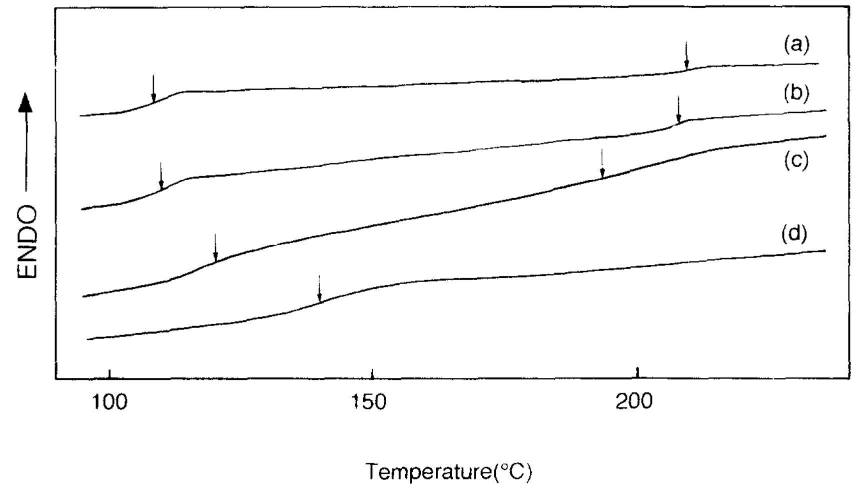


Figure 2 D.s.c. thermograms of blends (50/50 by weight) of (a) SAN 6/SMI-T48, (b) SAN 10/SMI-T48, (c) SAN 16/SMI-T48, (d) SAN 20/SMI-T48

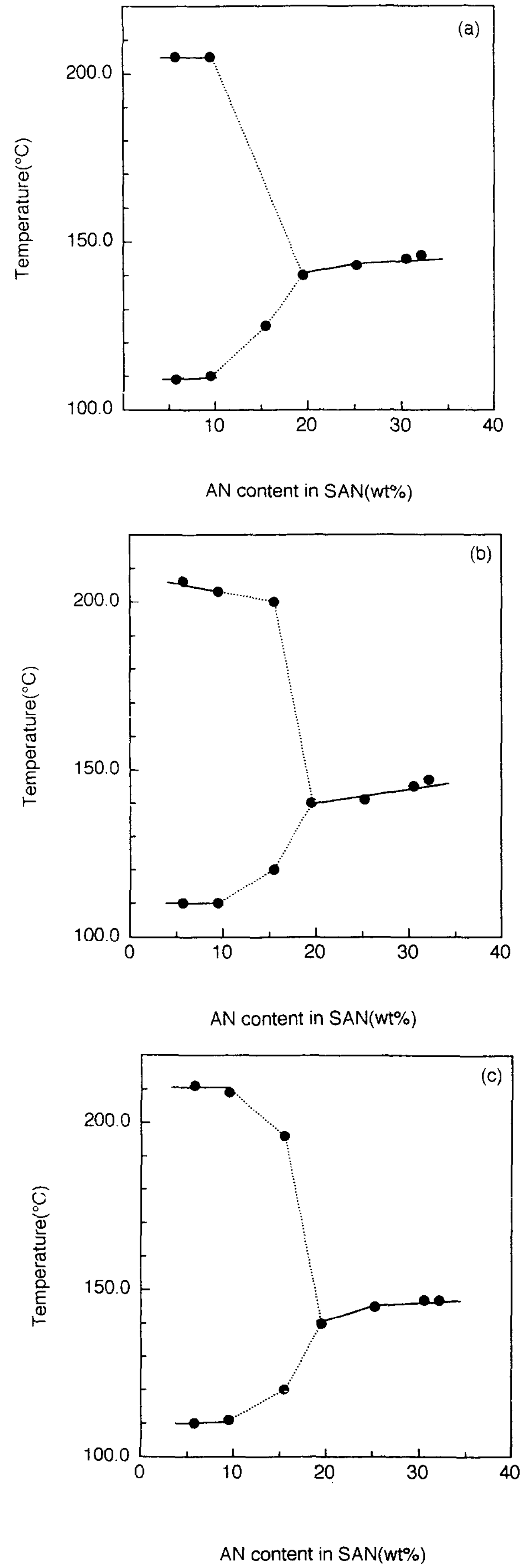


Figure 3 T_g behaviours of SAN/SMI-T (50/50 by weight) blends: (a) SAN/SMI-T24 blends; (b) SAN/SMI-T40 blends; (c) SAN/SMI-T48 blends

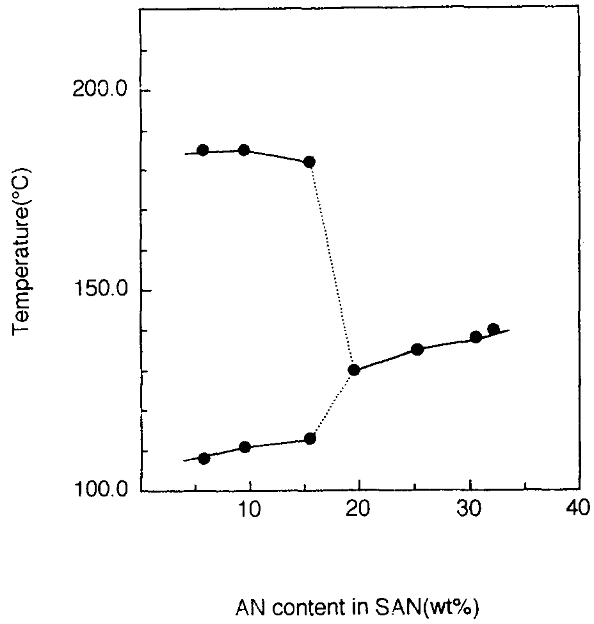


Figure 4 T_g behaviours of SAN/SMI-A (50/50 by weight) blends

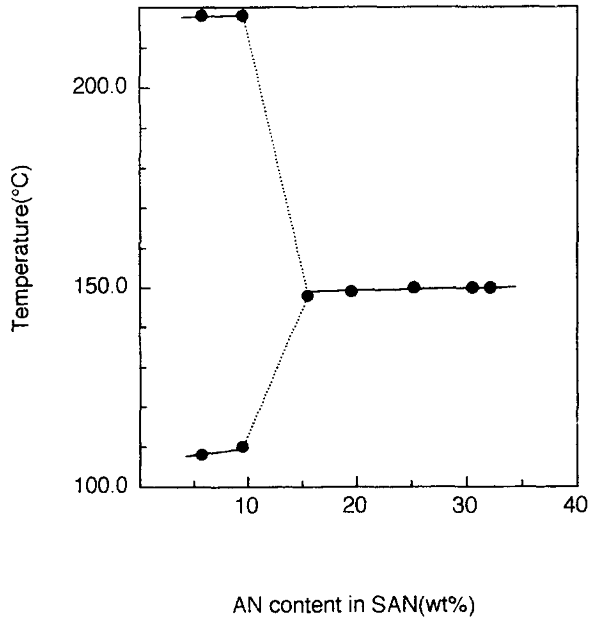


Figure 5 T_g behaviours of SAN/SMI-C (50/50 by weight) blends

As shown in *Figures 4* and *5*, the overall miscibility behaviours of SMI-A and SMI-C are similar to those of SMI-T in *Figure 3*. In the miscibility boundary region, however, some differences are found. Compared with SAN/SMI-T blends, the transition regions of two T_gs to one T_g for the SAN/SMI-C and SAN/SMI-A blends are narrower and the transition regions differ according to the type of substituent: 10–15 wt% AN for SAN/SMI-C blend and 15–20 wt% AN for SAN/SMI-A blend. Although the imide content of SMI-C is smaller than those of SMI-A and SMI-T48, the T_g value in the miscible region is higher for the SAN/SMI-C blends than for the SAN/SMI-T48 and SAN/SMI-A blends, showing that the type of substituent has a greater effect than the copolymer composition on the T_g behaviour of blends.

This information will be usefully applied for the improvement of thermal resistance of SAN by the blending method.

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