

Impact Modification of Imide Containing Copolymers

Numerous studies have demonstrated that elastomers can be functionalized so that monomers are polymerized to form random grafts useful for toughening polymer glasses.¹ Of comparable effectiveness for impact modification but often more difficult to obtain from a synthetic point of view are well defined A-B-A triblock copolymers,²⁻⁴ where the hard block segments are identical in composition to or miscible with the glassy polymer matrix to be toughened.

In this paper poly(2-ethyl-2-oxazoline)-*b*-polyisobutylene-*b*-poly(2-ethyl-2-oxazoline) A-B-A triblock copolymers are employed as impact modifiers for poly(styrene-*alt*-maleimide) copolymer.⁵ In a previous paper⁶ the miscibility between styrene/maleimide copolymers and poly(2-ethyl-2-oxazoline) was demonstrated. Thus, the poly(2-ethyl-2-oxazoline) end blocks would serve as the anchoring points for the elastomeric polyisobutylene midblock to the S/MI copolymer matrix. The poly(styrene-*alt*-maleimide) copolymer was selected for this study because (1) styrene monomer and maleimide monomer exhibit the propensity toward alternating copolymerization under free radical polymerization conditions; (2) effective interaction (miscibility) with poly(2-ethyl-2-oxazoline) is achieved via hydrogen bonding,⁶ and (3) the maximum in glass transition temperature is achieved with the alternating S/MI copolymer. This last point allows for heat distortion temperature performance which far exceeds any styrenic resin commercially available today.

The poly(styrene-*alt*-maleimide) copolymer was prepared by solution polymerization in *N,N*-dimethylacetamide by a technique previously described.⁶ The S/MI (50/50 mol %) copolymer exhibited a glass transition temperature of 259°C by differential scanning calorimetry, a number average molecular weight (M_n) by gel permeation chromatography (vs. monodisperse PS standards) of 245,400 ($M_w/M_n = 2.6$), and weight percent maleimide content equal to 48.2 as determined via elemental nitrogen analysis.

The poly(2-ethyl-2-oxazoline)-*b*-polyisobutylene-*b*-poly(2-ethyl-2-oxazoline) A-B-A triblock copolymer was prepared based on the inifer technology pioneered and developed by Kennedy.⁷ Tosyl-telechelic polyisobutylenes have been used as macroinitiators for the block polymerization of 2-methyl-2-oxazoline.⁸

A 0.5 pint pressure vessel was charged with 150 g of dichloromethane, 0.20 g (0.87×10^{-3} mol) of *p*-bis(α,α -dimethylchloromethyl)benzene, and 168 g (3.0 mol) of isobutylene. The reactor contents were cooled to -50°C followed by the addition of 0.22 g (1.87×10^{-3} mol) of boron trichloride in dichloromethane. The stirred reaction mass became hazy and inhomogeneous after 10 min at -50°C . The reaction was terminated by the addition of 5 mL of methanol after a total reaction time of 15 min at -50°C . The α,α -di(*tert*-chloro)polyisobutylene was dissolved in tetrahydrofuran (20% solids) and filtered through a boric acid canister. The tetrahydrofuran was removed under vacuum to yield α,α -di(*tert*-chloro)polyisobutylene (35% conversion based on charged isobutylene) exhibiting an M_n (GPC vs. known polyisobutylene standards) of 61,700.

The α,α -di(*tert*-chloro)polyisobutylene (58.8 g) was dissolved in a 60/40 w/w 1,2-dichloroethane/toluene solvent system and cooled to 0°C , wherein diethylaluminum chloride catalyst was added. After 10 min at 0°C , dry 2-ethyl-2-oxazoline was added, and the reaction temperature was set and held for 18 h. The polymer reaction was cooled to room temperature, and methanol was added to quench the reaction. The polymer solution was coagulated into diethyl ether, which left a polymer powder. This polymer powder was redissolved in tetrahydrofuran and coagulated into hexane, resulting in a swollen polymer mass, which was then dried under vacuum 24 h/ 40°C and then over phosphorous pentoxide 48 h/ 25°C . The specifics of the A-B-A triblock synthesis and characterization are detailed in Table I.

The PEOx-*b*-PIB-*b*-PEOx A-B-A triblock copolymers were prepared with moderate variations in the molecular weight of the PEOx hard block segment by varying reaction temperature.⁹ The molecular weight of the PEOx A blocks were determined based on diethyl aluminum chloride/*t*-butylchloride catalyzed polymerizations of 2-ethyl-2-oxazoline monomer under identical conditions to those employed in the preparation of the A-B-A triblock copolymers.

TABLE I
PEOx-*b*-PIB-*b*-PEOx A-B-A Triblock Copolymer Characterization^a

A-B-A triblock copolymer	Rxn temp (°C)	Conversion to PEOx (%)	PEOx/PIB (w/w %) in A-B-A	M_n (MWD) ^b A-B-A copolymer	M_n (MWD) PEOx blocks	% PEOx formed ^c as A blocks
1	60	86	29/71	102,100 (1.3)	22,400 (2.0)	99
2	70	87	29/71	129,300 (1.3)	37,400 (1.6)	99
3	80	90	30/70	149,700 (1.4)	45,200 (1.7)	98

^aEt₂AlCl = 1.77(×10³ mol); 2-ethyl-2-oxazoline = 0.275 mol.

^b M_n determined by GPC vs. known polyisobutylene standards.

^cBased on extraction of A-B-A block polymers with water at 25°C/145 h (water is a good solvent for PEOx). A blend of PEOx homopolymer (M_n = 45,200) and A-B-A-3 triblock copolymer was extracted with water 25°C/145 h, resulting in total recovery of homopolymer.

TABLE II
Glass Transition Temperature Analysis of S/MI//A-B-A Triblock Copolymer Blends

S/MI	100	78	78	78
A-B-A-1 ^a	—	22	—	—
A-B-A-2 ^a	—	—	22	—
A-B-A-3 ^a	—	—	—	22
S/MI//PEOx end block ratio (w/w)	—	92.5/7.5	92.5/7.5	92.2/7.8
T_g (°C, DSC)	259	232	232	234

^a T_g = 58°C for PEOx end blocks in A-B-A triblocks.

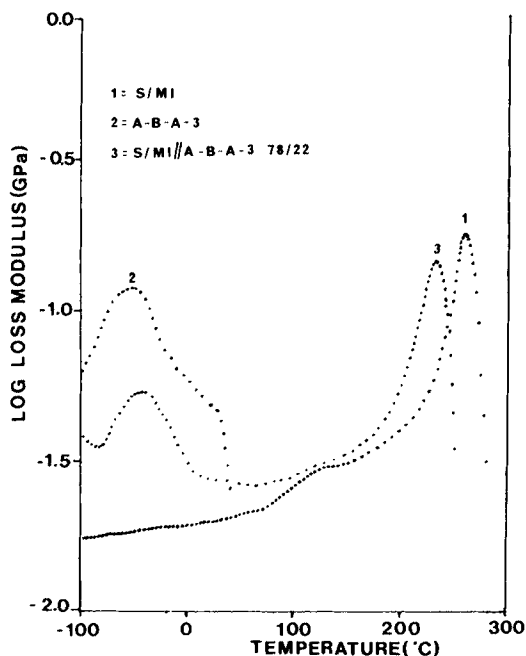


Fig. 1. DMA analysis: (1) S/MI; (2) A-B-A-3; (3) S/MI//A-B-A-3, 78/22.

TABLE III
 Impact Modified S/MI Copolymers

S/MI	100	89	84	78	78	78
A-B-A-1	—	11	16	22	—	—
A-B-A-2	—	—	—	—	22	—
A-B-A-3	—	—	—	—	—	22
Extrusion temp (°C)	325	320	320	310	310	310
Molding temp (°C)	330	325	325	315	315	315
T_g (°C, DSC)	259	245	239	232	232	234
HDT (1/8 in., unannealed, °C)	234	220	209	201	201	204
Tensile impact (ft-lb/in. ²)	21	43	57	197	205	181
Notched Izod (ft lb/in.)	0.8	1.2	1.2	4.4	5.1	5.2
Total PIB content (wt %)	—	7.9	11.4	15	15	15

The initial study of S/MI//PEOx polymer blend miscibility employed a PEOx homopolymer of significantly higher molecular weight than PEOx hard blocks in the A-B-A copolymers of the current study. This fact coupled with the known restriction based on polymer molecular weight for solubilization of a polymer into a domain of a block polymer where mixing is either athermal or where an exothermic heat of mixing (miscibility) exists⁴ warranted an evaluation of the miscibility between the poly(styrene-*alt*-maleimide) copolymer and the end blocks of the PEOx-*b*-PIB-*b*-PEOx triblock copolymers. Polymer blends of the S/MI copolymer and the A-B-A triblock copolymers (Table II) were prepared in the melt and subsequently molded into test specimens. Dynamic mechanical analysis and differential scanning calorimetry both support miscibility between the S/MI copolymer and the PEOx hard blocks (Fig. 1; Table II). Therefore, the molecular size limitation for polymer-block polymer component molecular level mixing has not been exceeded in the case of the PEOx hard block, and coupling of the elastomeric polyisobutylene midblock to the S/MI copolymer should be efficient.

The effectiveness of the PEOx-*b*-PIB-*b*-PEOx triblock copolymers as impact modifiers for the poly(styrene-*alt*-maleimide) copolymer was found not to be influenced by changes in the PEOx hard block molecular weight (within the scope of this study, $M_n = 22,800$). Significant improvements in the impact performance of the S/MI copolymer were realized with a minimum PIB content of 15% by weight (Table III). Impact modification of any glassy matrix is dependent on both (1) efficient coupling of the elastomer to the matrix and (2) particle size of the dispersed elastomer. Transmission electron microscopy of a microtomed specimen (S/MI//A-B-A-3, 78/22 w/w) which had been immersed in 2,4-octadiene showed a PIB particle size of 0.5–2.5. The

 TABLE IV
 S/MI//A-B-A-3 Polymer Blend Aqueous Environment Exposure

	Tensile impact (ft lb/in.)
S/MI//A-B-A-3 (78/22)	181
Boiling water, 24 h	162
Equilibrium moisture (0.85%), 100°C, 24 h, circulating air oven	172
20% K ₂ CO ₃ aqueous, 100°C, 24 h	62

2,4-octadiene was employed to provide osmium tetroxide active functionality exclusively partitioned in the PIB midblock.

Given the water solubility of poly(2-ethyl-2-oxazoline) and the equilibrium moisture absorption of the S/MI (52/48 wt %) copolymer of 0.85%, a study of the impact-modified S/MI copolymer after aqueous environment exposure shows some interesting performance characteristics (Table IV). Whereas both the S/MI//PEOx interaction⁶ and the imide functionality appear stable to hydrolysis under the cited conditions, the carbonate instability of the imide was manifested in the 20% K₂CO₃ aqueous environment exposure.¹⁰ Thus, PEOx-*b*-PIB-*b*-PEOx A-B-A triblock copolymers are effective impact modifiers for the poly(styrene-*alt*-maleimide) copolymer.

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Received January 12, 1988

Accepted February 29, 1988

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