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Poly(2,6-dimethyl-1,4-phenylene oxide)–Poly(methyl methacrylate) Interpenetrating Polymer Networks[†]

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ABSTRACT: We prepared two component simultaneous interpenetrating polymer networks (SIN's) of brominated poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) cross-linked with ethylenediamine (EDA) and poly(methyl methacrylate) (PMMA) cross-linked with ethylene glycol dimethacrylate (EGDMA). The estimated molecular weights between cross-links (M_e) from the stoichiometry of the PPO and PMMA networks were 6000 and 7900, respectively. Differential scanning calorimetry (DSC) measurements show that the IPN's have a single glass transition (T_g) intermediate in temperature to the T_g's of the component networks. Transmission electron micrographs also are consistent with a single-phase morphology. A maximum in tensile strength significantly higher than the tensile strengths of a component network occurred at an intermediate composition just as has been observed for the PPO/polystyrene IPN's.

1. Introduction

Recently we have become interested in studying simultaneous[1–4] IPN's of PPO and various other network components made from glassy, plastic to elastomeric polymers. The first such IPN that has been studied by us involved the highly compatible PPO and polystyrene (PS) (a typical glassy amorphous) polymer, whose linear blends are also compatible over all compositions. In this paper we investigate IPN's and pseudo interpenetrating polymer networks of PPO and poly(methyl methacrylate) (PMMA) cross-linked via ethylene glycol dimethacrylate, whose linear blends are not compatible. These full IPN's show no microphase separation over the full composition range and possess improved ultimate mechanical properties.

2. Experimental Section

A. Materials. The names and descriptions of the raw materials used are shown in Table I. Poly(2,6-dimethyl-1,4-phenylene oxide) was supplied by the General Electric Co. It had an intrinsic viscosity of 0.50 dL/g and molecular weights of $\bar{M}_w$ = 43 560 determined by light scattering and $\bar{M}_n$ = 13 390 by vapor-phase osmometry.

PPO was purified by dissolving it in chloroform at 50 °C for 3–4 h, was then precipitated with methanol, and dried in an oven at 50 °C for 24 h. The dried PPO is a pale yellow solid. Ethylenediamine was distilled before use and dried over molecular sieves.

Methyl methacrylate (MMA) monomer was washed with 5% aqueous potassium hydroxide (KOH) solution, followed by a washing with distilled water. It was then dried over molecular sieves and distilled at 40 °C under 2-mm vacuum to remove the stabilizer (hydroquinone monomethyl ether, bp 243 °C). Ethylene glycol dimethacrylate (EGDMA) was also distilled at 40 °C under 2-mm vacuum to remove stabilizer (hydroquinone, bp 205 °C). Benzoyl peroxide (BPO) was used without further purification.

B. Synthesis. I. Preparation of Cross-Linked Poly(2,6-dimethyl-1,4-phenylene oxide). The poly(2,6-dimethyl-1,4-phenylene oxide) was cross-linked by a two-step procedure, the first of which is the methyl bromination of PPO by Price's method.[5] Under free radical conditions, i.e. *N*-bromosuccinimide (0.050 NBS/repeating chain unit) and light, bromination occurs exclusively at the methyl groups. ^{1}H NMR, ^{13}C NMR, and bromine elemental analysis were performed on the methyl-brominated polymer. The analysis showed that the polymer contained 0.043 Br/repeating unit.

The subsequent reaction was the cross-linking reaction.[1] The methyl-brominated PPO was dissolved in dry toluene to form a 30% by weight solution. The solution was stirred and heated at 60 °C until a clear and transparent yellow solution was obtained. To the solution was added 0.0233 mol of ethylenediamine/mol of repeating chain unit of the PPO. The solution was stirred for 15 min and poured into Petri dishes, placed in an oven for 24 h at 80 °C, and then heated for four additional hours under vacuum at 110 °C to remove excess solvent. Samples were 2.5 in. in diameter and 0.026 in. thick. The dried sample was relatively stiff, transparent, and light yellow in color.

The cross-link density of the network was determined by a swelling experiment by immersing a polymer sample (weighing 2–2.5 g) into chloroform.[3] The samples swelled to about 5 times their initial volume. This allowed us to determine the average molecular weight between the cross-links, M_e = 5500, which agreed with M_e = 6000 expected from stoichiometry.

II. Cross-Linking of Poly(methyl methacrylate). The stoichiometric composition of 100 g of distilled MMA monomer, 2.5 g of distilled ethylene glycol dimethacrylate (EGDMA), and 2.0 g of benzoyl peroxide was weighed out and dissolved in toluene to produce a 30% by weight solution. This solution was heated at 60 °C for 15 min. When the solution started to become viscous, it was poured into Petri dishes and cured at 80 °C for 48 h and 110 °C for 4 h to remove additional solvent. The sample was transparent, colorless, and very brittle.

III. Preparation of PPO–PMMA Full IPN's. Six sets, each weighing 4 g, of brominated PPO were dissolved in dry toluene to produce 30% by weight in toluene solution. The six sets were designated as A, B, C, D, E, and F. To the first set, A, 10% by weight of methyl methacrylate monomer was added, and the solution was mixed thoroughly for about 10 h. The solution was heated at 60 °C under a nitrogen atmosphere until it turned clear and yellow. Cross-linking agents for both polymers were subsequently added with their initiators, ethylenediamine (EDA), ethylene glycol dimethacrylate (EGDMA), and benzoyl peroxide (BPO), and the solution was further heated for 25 min. When the solution started to become viscous, it was poured into Petri dishes and put into a vacuum oven for

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[†] Taken from M.S. thesis submitted to Department of Chemistry by S. Singh.

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Table I
Starting Materials

designatn	name and descriptn	source
PPO	poly(2,6-dimethyl-1,4-phenylene oxide) ($\bar{M}_w$ = 43 560)	General Electric Co.
EDA	ethylenediamine (98%) (MW = 60)	Aldrich Chemical Co.
toluene	toluene (solvent grade)	Aldrich Chemical Co.
chloroform	chloroform (solvent grade)	Aldrich Chemical Co.
NBS	*N*-bromosuccinimide (99%) (MW = 177.99)	Aldrich Chemical Co.
methanol	methanol (solvent grade)	Aldrich Chemical Co.
BPO	benzoyl peroxide (MW = 242.23; mp 104–106 °C dec)	Aldrich Chemical Co.
MMA	methyl methacrylate (99%) inhibited with 5–10 ppm of MHQ (hydroquinone monomethyl ether) (MW = 100.12)	Aldrich Chemical Co.
EGDMA	ethylene glycol dimethacrylate inhibited with 40–150 ppm of HQ (hydroquinone) (MW = 198.22)	Aldrich Chemical Co.

Table II
Thermal and Mechanical Data on Full IPN's

sample	compositn PPO–PMMA, wt %	type of PPO (L, C)[a]	type of MMA (L, C)[a]	tensile strength, psi	% elongation to break	T_g,[b] °C
control	100–0	C		6200	5.3	199
A	90–10	C	C	8300	5.6	187
B	80–20	C	C	9530	6.7	190
C	60–40	C	C	8091	5.7	186
D	50–50	C	C	7500	5.5	183
E	40–60	C	C	6830	5.2	179
F	20–80	C	C	3740	2.5	162
control	0–100		C	4106[c]	4.9[c]	155

[a] Where L = linear and C = cross-linked. [b] The T_g's mentioned are obtained with the help of DSC over the temperature range of 80–250 °C. [c] Reference 8.

Table III
Thermal and Mechanical Data on Semi-IPN's (PDIPN-1)

sample	compositn PPO–PMMA, wt %	type of PPO (L, C)[a]	type of MMA (L, C)[a]	tensile strength, psi	% elongation to break	T_g,[b] °C
control	100–0	C		6200	5.30	199
G	90–10	C	L	6300	6.07	112, 193
H	80–20	C	L	8900	5.10	..., 191
I	60–40	C	L	6910	8.80	128, 188
J	50–50	C	L	6510	8.70	115, 183
K	40–60	C	L	6800	3.90	..., 189
L	20–80	C	L	5890	3.00	..., 178
control	0–100		L			98

[a] Where L = linear and C = cross-linked. [b] The T_g's mentioned are obtained with the help of DSC over the temperature range of 80–250 °C.

Table IV
Thermal and Mechanical Data on Semi-IPN's (PDIPN-2)

sample	compositn PPO–PMMA, wt %	type of PPO (L, C)[a]	type of MMA (L, C)[a]	tensile strength, psi	% elongation to break	T_g,[b] °C
control	100–0	L				189
M	90–10	L	C			147, 202
N	80–20	L	C	7500	4.90	141, 181
O	60–40	L	C			135, 177
P	50–50	L	C			146, 178
Q	40–60	L	C			164, 215
R	20–80	L	C			170, 187
control	0–100		C	4106[c]	4.9[c]	155

[a] Where L = linear and C = cross-linked. [b] The T_g's mentioned are obtained with the help of DSC over the temperature range of 80–250 °C. [c] Reference 8.

24 h at 80 °C and for 4 h at 110 °C. The same procedure was used in preparing IPN's of 20, 40, 50, 60, and 80 wt % of PMMA. The color of all the samples was yellow. They were all transparent solids and hard to break. Above 50 wt % of PMMA, the IPN samples are a little darker (somewhat brown) in color.

IV. Preparation of Pseudo- or Semi-IPN's. Six sets of the two types of pseudo-IPN's were prepared, one from cross-linked PPO(CPPO)/linear MMA (LMMA) (PDIPN-1) and the other from a linear PPO (LPPO)/cross-linked MMA (CMMA) (PDIPN-2). The curing conditions and compositions were the same as those for the full IPN's. The color of all the samples was yellow.

V. Preparation of Linear Blends. Six sets of linear blends were prepared from the solutions of PPO and MMA monomer with BPO initiator. The curing conditions and compositions were the same as those for the full IPN's. The color of all the samples was yellow.

3. Physical Measurements

A. Electron Micrographs. The samples were stained with osmium tetroxide, embedded in Spurr resin,[7] and sectioned by a two-step sectioning method. The electron micrographs were taken at magnifications of 95 000–33 000 by using a Philips 300 transmitting electron microscope.

B. Differential Scanning Calorimetry. The glass transition temperature (T_g's) were determined on a DSC V2.2A Du Pont 9900 differential scanning calorimeter. Measurements on 10-mg samples were carried out from 80 to 260 °C under nitrogen at a scanning rate of 20 °C/min.

C. Ultimate Tensile Strength. The tensile strength (TS) and elongation to break were determined on an INSTRON tester (ASTM Method 4208) at room temperature at a crosshead speed of 1 in./min using dumbbell-shaped specimens (0.021 in. × 0.25 in. × 1.5 in.).

4. Results and Discussion

The results of the DSC measurements on the full IPN, PDIPN-1, PDIPN-2, and linear blends are listed in Tables II, III, IV, and V, respectively, and DSC thermograms are shown in Figure 1 at 60:40 PPO/PMMA composition. The full IPN's show only a single glass transition temperature that is in between the values of the pure cross-linked polymer components. The electron micrographs of the full IPN also show no indication of phase separation up to magnification of 33 000–42 000 even though the solubility parameters of the two components are different. This suggests complete segmental mixing of the two polymers which is in agreement with the electron microscopy. It should be noted that the linear blends of PPO/PMMA are completely incompatible although the full IPN's show no microphase separation over the full composition range. On the basis of solubility parameter considerations PPO (like polystyrene) would not be miscible with linear PMMA. Presumably the catenation of the network in the full IPN's prevents phase separation. In the case of PDIPN-1 (cross-linked PPO and linear PMMA), PDIPN-2 (linear PPO and cross-linked PMMA), and linear blends (linear PPO and linear PMMA), one observed two T_g's, which confirms at least some phase separation of the components, although electron micrographs do not show any indications of phase separation up to magnifications of 33 000–42 000.

Formation of permanent entanglements in the full IPN's occurs sufficiently rapidly and extensively to prevent phase separation of the components, which is apparently not

Table V
Thermal and Mechanical Data on Linear Blends

sample	compositn PPO–PMMA, wt %	type of PPO (L, C)[a]	type of MMA (L, C)[a]	tensile strength, psi	% elongation to break	T_g,[b] °C
control	100–0	L				189
S	90–10	L	L	7040	5.00	150, 212
T	80–20	L	L	8250	4.70	149, 182
U	60–40	L	L			166, 200
V	50–50	L	L			151, 206
W	40–60	L	L			179, ...
X	20–80	L	L			153, 205
control	0–100		L			98

[a] Where L = linear and C = cross-linked. [b] The G_g's mentioned are obtained with the help of DSC over the temperature range of 80–250 °C.

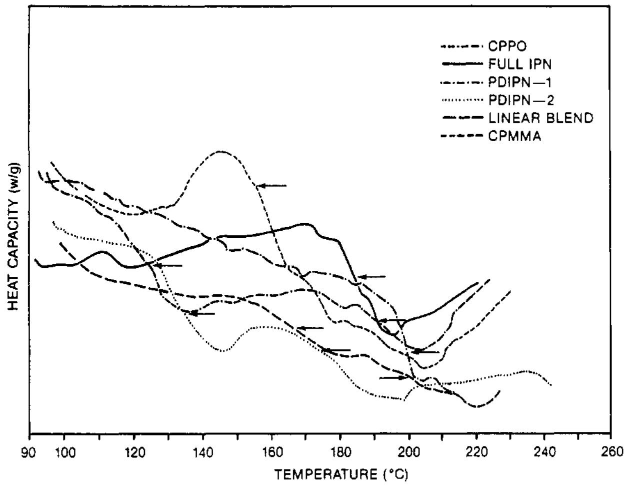

Figure 1. Comparison of DSC thermograms of CPPO, full IPN, PDIPN-I, PDIPN-2, the linear blend, and CPMMA at 60:40 PPO/PMMA wt % composition. Arrows indicate the T_g's.

the case for the PDIPN-1, PDIPN-2, and the linear blends. There are no topological constraints (i.e. permanent entanglements); hence the components can phase separate without breaking covalent bonds.

We see from Table II that like the PPO/PS (polystyrene)[2] IPN, the PPO/PMMA IPN exhibits a "maximum"[6] in the tensile stress to break behavior at or near 20% by weight of PMMA (80% brominated PPO) resulting from permanent entanglements of the chains. The PDIPN's (cf. Tables III and IV) and the linear blends (Table V) of the brominated PPO and PMMA do not exhibit any maximum. The elongation, as shown in Table II, shows a slight increase at or near 20% by weight of PMMA, indicating the exceptional toughness of this IPN. The tensile strength of the pure PMMA and cross-linked PMMA could not be obtained because of the brittleness of those specimens. In Table II we have quoted from the literature (ref 8) the tensile strength of cross-linked PMMA, which is quite low because of the brittleness of the PMMA. The tensile strength of full IPN's are higher than those of the PDIPN's and linear blends at the same composition. There is generally no significant difference in tensile strength between the PDIPN's and linear blends. The enhancement in the tensile strength of the full IPN's may be due to the absence of weak interfaces. The tensile strength of PDIPN-2 and linear blends are unfortunately available only up to 20 wt % of PMMA because of the extreme brittleness of the samples.

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Registry No. (EGDMA)(MMA) (copolymer), 25777-71-3; ethylenediamine, 107-15-3.

References and Notes

(1) Frisch, H. L.; Klempner, D.; Yoon, H. K.; Frisch, K. C. *Macromolecules* **1980**, *13*, 1016.
(2) Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, 1981.
(3) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979.
(4) Frisch, K. C.; Klempner, D.; Xiao, H. X.; Cassidy, E.; Frisch, H. L. *Polym. Eng. Sci.* **1985**, *12*, 25.
(5) Staffin, C. C.; Price, C. C. *J. Am. Chem. Soc.* **1960**, *82*, 3632.
(6) Frisch, H. L.; Frisch, K. C.; Klempner, D. *Polym. Eng. Sci.* **1974**, *14*, 646.
(7) Spurr, A. *J. Ultrastruct. Res.* **1969**, *26*, 31.
(8) Kim, S. C.; Klempner, D.; Frisch, K. C. *J. Appl. Polym. Sci.* **1977**, *21*, 1209.