Sequential-Interpenetrating Polymer Networks from Castor Oil-Based Polyesters. XXVI.

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SYNOPSIS

Polyesters were obtained from castor oil and dibasic acids for example, malonic, succinic, glutaric, adipic, suberic, and sebacic acids. These prepolyesters were characterized by infrared spectrometry, viscosimetric measurements, and molecular weight determinations (GPC). These prepolyesters were mixed with methyl methacrylate and were subsequently polymerized by free radical polymerization by benzoyl peroxide in the presence of the crosslinker ethylene glycol dimethacrylate. Polyester/poly(methyl methacrylate)-interpenetrating polymer networks, PPE/PMMA IPNs, were obtained as soft and opaque elastomers by the transfer molding technique. These IPNs were characterized by static mechanical properties, differential scanning calorimetry (DSC), and thermogravimetry. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are known for their synergistic properties in multitudes of industrial applications, and they constitute a fast-growing field in polymer science. Interpenetrating polymer networks can be defined as unique alloys of two crosslinked polymers, catenated physically by two independent and noninterfering polymerization reactions.[1,2] Castor oil has been used extensively in IPN research, beginning in 1977, with sulfur-crosslinked castor oil, which was then swelled with styrene and divinylbenzene and polymerized.[3] Subsequently, an enormous amount of work on IPNs from castor oil has been published.[4-9] Castor oil is a triglyceride of glycerol and ricinoleic acid-containing hydroxyl functionality, ester groups, and double bonds. The hydroxyl groups are important in the present work, where esterification can play an important role in establishing the structure–property relationship. The synthesis of sequential-interpenetrating polymer networks (IPNs), based

on castor oil–polyurethane, was reported to yield toughened plastics and reinforced elastomers. When castor oil reacts with difunctional acids, a three dimensional esterification reaction occurs, forming a network. The hydroxyl group of castor oil reacts to form crosslinked polyesters with dibasic acids. Simultaneous to the formation of ester groups, free hydroxyl groups are formed. Given favorable reaction conditions, these OH groups constitute a new locus for further reactions. The reaction between castor oil and individual dibasic acids forms a regular polyester, constituting different methylene units. This contributes to the low glass transition temperature of the final products. This aspect attains importance in the development of novel elastomers for impact-resistant plastics and tough leathery products. The present work involves the synthesis of polyesters from castor oil and dibasic acids, including oxalic, malonic, succinic, glutaric, adipic, suberic, and sebacic acids. These polyesters were subsequently interpenetrated by radical polymerization of methyl methacrylate in the presence of benzoyl peroxide and a crosslinker, ethylene glycol dimethacrylate (1%). These polyester/poly(methyl methacrylate)-interpenetrating polymer networks, PPE/PMMA IPNs, were characterized by the conventional methods.

EXPERIMENTAL

Materials

Castor oil, from a local market, was found to have a hydroxyl value of 165.3, corresponding to 2.75 —OH groups per molecule of castor oil.[10] Methyl methacrylate and ethylene glycol dimethacrylate (EGDM), from Fluka AG, Switzerland, and benzoyl peroxide, from Aldrich (USA), were purchased. The other chemicals used were of analytical grade purity.

Synthesis of Polyester

Castor oil (9.32 g, 0.0275 mol of hydroxyl groups) was mixed with adipic acid (2.0075 g, 0.0275 mol of carboxyl group) and p-toluene sulfonic acid (0.2 g) in a flask and was heated in an oil bath at 180°C with stirring for 8 h. After this period, the reaction mixture was cooled and was treated with a large amount of methanol (500 mL) to remove unreacted castor oil and adipic acid. The resulting mass was a thick, syrupy, castor oil–adipic polyester (PPE-A). The other polyesters were prepared from oxalic, malonic, succinic, glutaric, suberic, and sebacic acids and are abbreviated as PPE-O, PPE-M, PPE-S, PPE-G, PPE-Su, and PPE-Sc, respectively (Table I).

Synthesis of IPNs

A series of IPNs (IPN 1–7) of 50/50 PPE/PMMA compositions were obtained (Table II). Sequential-IPNs were synthesized from castor oil-polyesters, respectively, and methyl methacrylate by radical polymerization, using benzoyl peroxide as initiator. A typical procedure is described below:

PPE-A (5 g) and stabilizer-free methyl methacrylate (5 g) were mixed in minimum acetone (5 mL). To this solution, benzoyl peroxide (25 mg), cross-linker, EGDM (1%, based on MMA), stannous octoate (~ 25 mg; 1%, based on PPE) were added. The mixture was stirred at room temperature for 5 min to form a homogeneous mixture. The reaction mixture was heated at 60°C for 1 h to initiate polymerization of methyl methacrylate. The reaction mixture was poured onto a glass plate-mold, kept at 60°C, in a preheated air circulating oven. It was kept at this temperature for 24 h and then kept at 120°C for another 24 h. Thus, formed film was removed slowly from the mold and the film was designated as PPE-A/PMMA IPN. Similarly, six other IPNs of 50/50 compositions were prepared.

A series of IPNs, obtained from castor oil-based polyesters and poly(methyl methacrylate), was postcured at room temperature for 24 h prior to characterization.

Measurements

The IR spectra of these liquid polyesters were scanned on a Perkin–Elmer 983 Spectrophotometer, using a KBr disc. Dilute solution viscosities of these polyesters were measured at 30°C in an Ubbelohde suspended-level viscometer. Kinetic corrections were applied and were found to be less than 1% of the limiting viscosity number. The limiting viscosity number was estimated from the Huggins relationship.[11] The GPC (Gel Permeation Chromatography) measurements were performed on a Waters Maxima 820 GPC/HPLC system, equipped with an NEC PowerMate 386/25 data station. Mechanical properties were measured on a Table Model Instron

Table I   Characterization of Polyesters from Castor Oil

Polymer Code	Dibasic Acid	Carbonyl $\diagdown$C$=$O$\diagup$ in cm^{-1}[a]	Limiting Viscosity Number[b] $[n]$ dL g^{-1}	GPC Data[c] $\bar{M}_n$	$\bar{M}_w$	Polydispersity $\bar{M}_w/\bar{M}_n$
PPE-O	Oxalic	1742	0.18	300	1094	3.65
PPE-M	Malonic	1743	0.21	1058	1323	1.25
PPE-S	Succinic	1746	0.24	2200	7104	3.23
PPE-G	Glutaric	1745	0.20	413	1031	2.49
PPE-A	Adipic	1746	0.23	3328	3673	1.10
PPE-Su	Suberic	1745	0.19	4884	6113	1.25
PPE-Sc	Sebacic	1746	0.20	3161	4793	1.52

[a] IR was scanned in neat liquid on a KBr disc.

[b] Limiting viscosity number was estimated in toluene at 30°C.

[c] GPC measurements were obtained in toluene at 30°C.

Table II   Data on Castor Oil-Based Polyester/Poly(Methyl Methacrylate) IPNs

Polymer Code	PPE/ PMMA Composition	Mechanical Properties[a]				Glass Transition Temperature[b] (°C)	
		Tensile Strength (KPa)	Young's Modulus (KPa)	Elongation at Break (%)	Hardness Shore A	T_{g1}	T_{g2}
IPN-1	50/50	140	860	53	28	−71	32
IPN-2	50/50	180	740	56	31	−72	30
IPN-3	50/50	170	800	57	27	−75	34
IPN-4	50/50	180	730	54	33	−70	33
IPN-5	50/50	220	980	50	42	−76	28
IPN-6	50/50	230	970	51	40	−75	30
IPN-7	50/50	280	1200	41	43	−70	25
Poly(methyl methacrylate)	0/100	2100	154,000	12	98	—	41

[a] The mechanical data on the control polyesters (100% PPEs) are not obtained. The films are rubbery and brittle. This specimen size could not be cut.

[b] From DSC at a heating rate of 10°C per min in air.

Testing Machine. The thermal stability was measured on a DuPont 951 thermal analyzer at a heating rate of 10°C min^{-1}. The glass transition temperatures were obtained on a Du Pont 9900 differential scanning calorimeter at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

The reaction of the hydroxyl group of castor oil with dibasic acids, *viz.* oxalic, malonic, succinic, glutaric, adipic, suberic, and sebacic acids, respectively, yielded liquid prepolyesters. These prepolyesters (PPEs) are highly viscous and glassy liquids. They are soluble in common organic solvents, except alcohols. Thus, all PPEs could be isolated by repeated washings with large amounts of methanol. Table I indicates the different prepolyesters from dibasic acids and their characterization. The structural evidence comes from the IR spectral study. IR spectra of all the PPEs indicate characteristic group frequencies. An intense and clearly discernible band around 1740–1750 cm^{-1} was observed in all PPEs. This band was assigned to the carbonyl group of the ester linkage.[12] The characteristic ester carbonyl group frequency of each PPE is shown in Table I. In addition, stretching and bending vibrations were observed, due to alkyl groupings around 2900–2800 and 1400–1300 cm^{-1}, respectively. The limiting viscosity numbers (n) of all the PPEs were estimated in toluene at 30°C. Their values ranged from 0.18 to 0.24 dL g^{-1}. The molecular weight parameters

($\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$) of all the PPEs were estimated from gel permeation chromatography. Table I indicates the number- and weight-average molecular weights of the PPEs. Low $\bar{M}_n$ and $\bar{M}_w$ values for the PPE-O, PPE-M, PPE-S, and PPE-G may be assumed, due to the low reactivity of the dibasic acids namely, oxalic, malonic, succinic, and glutaric acids. During polyesterification, it may also lead to the decomposition, as well as some side reactions, resulting in low molecular weight. The higher homologues of dibasic acids (adipic, suberic, and sebacic acids), in the present work, are reasonably good monomers in the polyesterification reactions of castor oil, resulting in higher molecular weight prepolyesters. In fact, these prepolyesters are of low molecular weight and thick liquid, however, they are referred to as polyesters throughout this article.

Table II indicates the feed composition [each polyester (PPE) and methyl methacrylate] for the IPN synthesis. A series of PPE/PMMA IPNs (IPN-1–IPN-7) of 50/50 compositions of PPE and PMMA, and also control homopolymer poly(methyl methacrylate), were prepared in identical experimental conditions. The controls homopolymers of individual polyesters, were prepared as films, but these films were extremely soft, rubbery, and brittle, and did not permit us to use them as specimen size for their characterization. Unfortunately, no data on the characterization of individual homopolymers of all the PPEs were reported. These PPE/PMMA IPNs were opaque and rubbery films, insoluble in all common organic solvents, including DMF,

DMSO, and DMAc. This probably reflects the entanglement of polymer chains, resulting in the interpenetrating polymer networks.

Mechanical Properties

Sperling and his coworkers[3-5,13] reported the synergistic behavior of IPNs from the polyesters (castor oil or Lesquerella palmeri oil and sebacic acid) and polystyrene (PS) component networks. They observed interesting properties, as the resulting material is a rubber-toughened plastic or a reinforced elastomer, depending upon the level of polystyrene component in the formation of IPNs. Midrange compositions of these IPNs have moduli in the leathery range.[3-5,13] The mechanical properties of PPE/PMMA IPNs in the present investigation were studied in terms of tensile strength, Young's modulus, elongation at break (%), and hardness Shore A. The data among IPN-1–IPN-7, presented in Table II, show the variation in the mechanical properties to the homopolymer, poly(methyl methacrylate) networks. It is observed from the mechanical properties of these IPNs that incorporation of the plastic phase–poly(methyl methacrylate) component into viscoelastomeric polyesters has provided modest improvement in the elongation at break (%), while also providing much reduction in the tensile strength of these IPNs. Thus, it may be concluded that, in the present set of IPNs, toughness in the viscoelastomeric PPE increases with the increase in the PMMA content of IPNs.
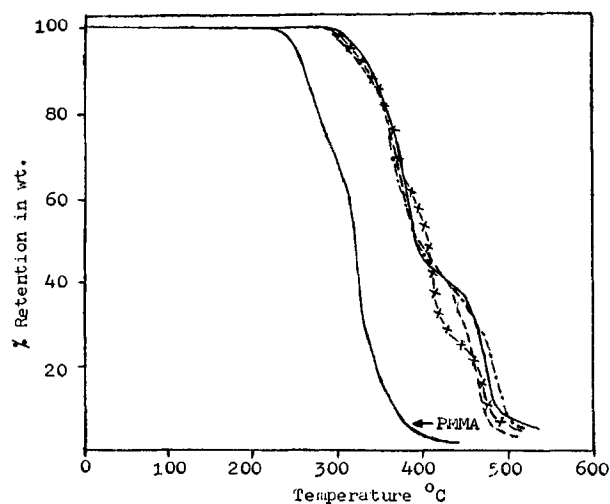

Figure 1   TG Curves of PPE/PMMA IPNs and homopolymer PMMA. (——) PMMA, (——) IPN-1, (– – –) IPN-2, (-x-x-) IPN-3, (– · – · –) IPN-4.

Table III   Thermogravimetric Data of PPE/PMMA IPNs

| Polymer Code | Percent Weight Loss (±2%) at Differing Temperatures (°C) | | | | | |
	250	300	350	400	450	500
IPN-1	—	2	18	55	68	93
IPN-2	—	4	19	52	70	97
IPN-3	—	3	18	48	76	94
IPN-4	—	3	22	53	65	92
IPN-5	—	—	24	48	66	95
IPN-6	—	—	26	53	69	93
IPN-7	—	—	23	45	64	92
Control : PMMA	7.5	35	80	97	—	—

Thermal Behavior

The thermal behavior of these PPE/PMMA IPNs was studied from DSC measurements and thermogravimetric analysis. The DSC thermograms of these IPNs were obtained at a heating rate of 10°C/min in air. As shown in Table II, each IPN shows two distinct glass transition temperatures (T_{g1} and T_{g2}), corresponding to those of individual component networks. This observation confirms that the phase domain interfaces become more distinct and phase separation results. Similar behavior has been reported by Sperling and his coworkers.[5,13] Sperling and his coworkers,[5,13,14] and Klempner and his coworkers,[15-16] have established that the component of network I dominates the properties of the IPNs, through its greater continuity in space.

TG thermograms of all PPE/PMMA IPNs indicate a characteristic behavior of thermal degradation (Fig. 1). The weight loss in all the IPNs is not uniform and does not show any trend of thermal stability in the series (Table III). Therefore, it is difficult to arrive at any conclusion regarding the structural variations in the PPEs component. It is observed that the thermal stability of the individual component prepolyester a liquid—decomposes rapidly around 400°C and poly(methyl methacrylate)-depolymerization is poor. Thus, a minimal increase in thermal stability in this series of PPE/PMMA IPNs may be due to the synergism of two component networks during interpenetration. This observation is supported by other workers[17-20] and is presumably related to the presence of the unzipped vinyl monomer. The unzipped vinyl monomers may act as radical scavengers for the radicals produced from the IPN degradation, thus delaying the further reaction of the radicals into volatile materials.[17]

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