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Thermal stability of castor oil-based interpenetrating polymer networks

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Abstract

Two-component sequential-interpenetrating polymer networks (IPNs) from castor oil-based polyurethanes and poly(methyl methacrylate) have been prepared. Component I-polyurethane was formed by reacting the hydroxyl functionality of castor oil with different diisocyanates in the stoichiometric NCO/OH ratio of 1.6. These polyurethanes were mixed individually with methyl methacrylate monomer and subsequently an interpenetrating network prepared by free radical polymerization initiated by benzoyl peroxide in the presence of crosslinking agent. The interpenetrating polymer networks, PU/PMMA IPNs, were moulded into tough and transparent films. The thermal stability of these IPNs was assessed by thermogravimetric analysis.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are studied for their unusual properties in multifarious commercial applications and constitute a fast growing field in polymer science. IPNs can be defined as alloys of two crosslinked polymers, catenated physically by two independent and non-interfering polymerization reactions [1–4]. Sperling and co-workers [5, 6] reported a series of IPNs from castor oil-based polyurethanes and polystyrene as well as polyurethane-ester and polystyrene. They reported that the elastomeric and plastic properties of the IPNs depended on the contents of two components in the IPNs.

We have reported a series of IPNs from castor oil-based polyurethanes and vinyl polymers and their ultimate properties [7–12]. The present work was undertaken with a view to establishing a structure–property relationship. In this paper, we report on the thermal stabilities of a series of IPNs from castor oil-based polyurethanes and poly(methyl methacrylate).

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EXPERIMENTAL

Materials

All the chemicals used were of analytical grade purity. Castor oil was obtained from the local marketplace (the hydroxyl value was found to be 165.3, corresponding to 2.75 -OH groups per mole of castor oil). Methyl methacrylate and ethylene glycol dimethacrylate (Schuchardt M, Munich) were freed from stabilizer prior to use. Benzoyl peroxide was recrystallized from chloroform. The different diisocyanates, namely, toluene-2,4-diisocyanate (TDI), diphenyl methane diisocyanate (MDI), isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HMDI) were purchased from Fluka, Switzerland.

The detailed synthesis of interpenetrating polymer networks have been described elsewhere [7-12]. A typical synthesis comprises two steps; firstly formation of the polyurethane, and secondly copolymerization of vinyl monomer, e.g. to produce poly(methyl methacrylate).

Synthesis of polyurethanes

A mixture of castor oil (10.00 g, 0.0107 mole) and toluene-2,4-diisocyanate (4.1106, 0.0236 mole) containing stoichiometric NCO/OH ratio 1.6, was stirred continuously for 2 h at 45°C. The isocyanate-terminated polyurethane was isolated as a thick syrup and abbreviated as PU_T. The other polyurethanes were prepared from the other diisocyanates (MDI, IPDI and HMDI) following the above procedure (Table 1).

Synthesis of IPNs

Polyurethane (PU) was placed in different proportions by weight into a round-bottomed flask. To this a mixture of methyl methacrylate, ethylene glycol dimethacrylate (1% based on MMA), 1,3-propane diamine (1% based on PU), and benzoyl peroxide (0.5%) was added. The mixture was stirred at room temperature for 5 min to form a homogeneous mixture. The temperature was then raised to 60°C to initiate the polymerization along with the added cross-linking agent. After stirring for 1 h, the solution was poured into a glass mould in a preheated air circulating oven maintained at 60°C. It was held at this temperature for 24 h and subsequently at 120°C for 4 h. The film formed, was cooled slowly and removed from the mould. A series of IPNs (IPN-1 to IPN-3) of different compositions was obtained following the above procedure. Each series is abbreviated as PU_T/PMMA, PU_M/PMMA, PU_I/PMMA and PU_H/PMMA IPNs respectively (Table 1).

The homopolymer component networks of polyurethanes (PU_T, PU_M,

TABLE 1

Data on feed composition (individual polyurethane and methyl methacrylate) for PU/PMMA IPN synthesis

Polymer	Code	Amount of polyurethane in parts	Amount of methyl methacrylate in parts	Specific gravity/ $g\,cm^{-3}$
PU_T/PMMA	IPN-1	20	80	1.18
PU_T/PMMA	IPN-2	40	60	1.13
PU_T/PMMA	IPN-3	60	40	1.15
PU_M/PMMA	IPN-1	20	80	1.16
PU_M/PMMA	IPN-2	40	60	1.14
PU_M/PMMA	IPN-3	60	40	1.10
PU_I/PMMA	IPN-1	20	80	1.17
PU_I/PMMA	IPN-2	40	60	1.15
PU_I/PMMA	IPN-3	60	40	1.13
PU_H/PMMA	IPN-1	20	80	1.15
PU_H/PMMA	IPN-2	40	60	1.14
PU_H/PMMA	IPN-3	60	40	1.12
PU_T		100	–	1.06
PU_M		100	–	1.07
PU_I		100	–	1.03
PU_H		100	–	1.05
PMMA		–	100	1.14

PU_I, PU_H) and poly(methyl methacrylate) (PPMA) were prepared under identical conditions to compare with PU/PMMA IPNs.

Characterization

The infrared spectra were measured directly on the films using a Perkin-Elmer 983 spectrophotometer. The thermal stability was measured with a Du Pont 951 thermogravimetric analyser at a heating rate of $10\,K\,min^{-1}$.

RESULTS AND DISCUSSION

The hydroxyl groups of castor oil were reacted with different diisocyanates in the stoichiometric NCO/OH ratio of 1.6. The resulting polyurethanes were thick liquid. The IR spectra of polyurethanes show the characteristic polyurethane group frequencies. In addition to these, a strong band easily discernible at $2270\,cm^{-1}$ can be assigned to the isocyanate group; in fact, these polyurethanes are isocyanate-terminated polymers. A distinct but broad band was observed in the region $1750–1730\,cm^{-1}$, which can be assigned to carbonyl groups: ν(C=O) ester at 1746 cm^{-1} and ν(C=O) urethane at 1734 cm^{-1}. Freshly prepared polyurethanes were soluble in organic solvents like acetone, dioxane, toluene, dimethyl formamide, but upon standing at room temperature, they continued to crosslink, resulting in a product that was insoluble in common organic solvents. Thus, the polyurethanes were used immediately for making interpenetrating networks with methyl methacrylate. Two component sequential interpenetrating polymer networks of PU/PMMA and individual component networks (PUs and PMMA) were obtained by transfer moulding technique. These IPNs were semi-transparent films and insoluble in all common organic solvents such as alcohols, aromatic hydrocarbons, chloroform, carbon tetrachloride, dioxane, pyridine, dimethyl formamide and dimethyl acetamide.

Thermal behaviour

Table 2 lists the thermal stabilities of the individual component networks and the two-component PU/PMMA IPNs. The thermal behaviour is

TABLE 2

Data on thermal stabilities of PU/PMMA IPNs

Polymer	Code	Percentage weight loss (±2%) at different temperatures								Activation energy/kJ mol^{-1}
		250^{a}	300^{a}	350^{a}	400^{a}	450^{a}	500^{a}	550^{a}	600^{a}	
PU_T/PMMA	IPN-1	3	10	24	52	79	93	–	–	59.3
PU_T/PMMA	IPN-2	3	9	23	40	63	79	93	96	65.6
PU_T/PMMA	IPN-3	4	5	20	42	67	83	87	90	40.4
PU_M/PMMA	IPN-1	6	9	21	40	55	79	88	94	63.6
PU_M/PMMA	IPN-2	3	5	15	29	57	81	88	93	74.2
PU_M/PMMA	IPN-3	3	5	18	35	50	70	81	84	67.8
PU_I/PMMA	IPN-1	2	7	18	42	65	89	93	96	78.5
PU_I/PMMA	IPN-2	–	–	10	30	63	84	92	95	101.9
PU_I/PMMA	IPN-3	–	–	3	22	67	85	92	94	116.9
PU_H/PMMA	IPN-1	4	8	21	42	65	90	93	96	73.8
PU_H/PMMA	IPN-2	2	5	20	40	63	89	92	97	82.2
PU_H/PMMA	IPN-3	–	4	15	44	66	88	93	95	91.3
PU_T		3	8	34	60	76	89	93	–	72.7
PU_M		–	3	19	30	40	66	93	–	70.6
PU_I		11	52	88	94	–	–	–	–	81.9
PU_H		–	2	14	42	61	82	90	–	84.3
PMMA		7	35	80	97	–	–	–	–	61.8

[a] Temperature in °C.

examined on the basis of percentage weight loss at different temperatures. The thermograms of all these IPNs and homopolymers were analysed by the method proposed by Broido [13] to estimate the kinetic parameters of their degradation reactions.

Examination of the thermograms reveal that all the IPNs are stable up to 280°C. However the thermal stability changed in the series depending upon structural variation within the IPNs. Thus, the thermal stability of these IPNs were assigned on the basis of the variation in composition of the individual component network as well as the compositional change of the component networks in the IPNs. Examination of the data of these IPNs revealed that IPNs containing polyurethane derived from castor oil and 4,4′-diphenyl methane diisocyanate are found to be more stable than those IPNs containing polyurethane in which isophorone diisocyanate and hexamethylene diisocyanate were reacted with castor oil. This can be explained by the IPNs incorporating aromatic moieties usually being more stable than those containing aliphatic moieties. All these IPNs have TG thermograms almost identical in shape indicating that there is a similar decomposition pattern for them all. The major step of decomposition occurs around 400–500°C with loss in weight varying from 30% to 70% in the case of IPNs from MDI and TDI; in case of IPNs from IPDI and HMDI, a loss in weight occurred around 50–90%. The final complete decomposition was observed around 500–600°C but the IPNs derived from MDI and TDI indicated some amount of weight residue even at the final decomposition temperature around 500–600°C. This may further be evidence that thermal stability among these IPNs depends upon the structural variation in the compounds studied here.

Comparison of the thermal stability of three IPNs in each series indicated that higher polyurethane content in IPN increases the thermal stability. This can be explained on the basis of the theory proposed by Kim and co-workers [14, 15], who observed that the increased thermal stability in the IPNs indicates increased physical crosslinking due to higher polyurethane interpenetration. They further proposed that vinyl polymers unzipped during thermal degradation of IPNs act as free radical scavengers for PU degradation products, thus delaying the further reaction of radicals into volatile products.

The thermal behaviour of IPNs at different temperatures is compared with homopolymer networks: polyurethanes (PU_T, PU_M, PU_I, PU_H) and poly(methyl methacrylate). These networks exhibited one step degradation around 250°C, lost their weight rapidly around 350°C and decomposed completely beyond 400°C. This means thermal stability of the individual component network is very poor. Interpenetration of both the component networks in the IPNs results in higher thermal stability and slower rate of their decomposition over a wide range of temperatures. It is evident that these observations further support the view that additional enhancement of the stability is to be expected due to the increased miscibility of the two component networks in the IPNs during their interpenetration and thereby synergism in the thermal stability is observed.

The Broido treatment indicates that there is enough justification of the assumption made in the derivation of the Broido relation. TG thermograms of all the IPNs show that the degradation reaction appears to run through a single step and it is contemplated that the order of degradation is unity. The activation energies of degradation of IPNs are shown in Table 2.

CONCLUSIONS

The thermal behaviour of these IPNs indicates that the PU/PMMA IPNs are thermally more stable than their individual component networks which may be due to a synergistic effect in IPN formation. In addition, the thermal stability is enhanced due to inclusion of aromatic moieties and also to an increase in the content of polyurethane component in IPNs.

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