Polymers from Renewable Resources. XIII. Interpenetrating Polymer Networks Derived from Castor Oil–Hexamethylene Diisocyanate and Polymethacrylamide

P. NAYAK, D. K. MISHRA, K. C. SAHOO, N. C. PATI, P. K. JENA, S. LENKA, P. L. NAYAK

Laboratory of Polymers & Fibres, Department of Chemistry, Ravenshaw College, Cuttack-753 003, Orissa, India

ABSTRACT: Several castor oil-based polyurethanes (PUs) samples were synthesized using various diisocyanates such as hexamethylene diisocyanate (HMDI) with varying NCO/OH ratios. All the PUs were reacted with methacrylamide (MAM) using an ethylene glycol dimethacrylate (EGDM) crosslinker and benzoyl peroxide as an initiator. Thermogravimetric analysis of the polymers was followed using a computer analysis method for assigning the kinetic mechanism. The degradation steps are discussed in the light of kinetic parameters. The scanning electronic microscopy of some of the interpenetrating polymer networks (IPNs) were studied and the morphology was examined. The samples were subjected to wide-angle X-ray diffraction analysis. Ruland and Vonk's method was used to calculate the degree of crystallinity. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1349–1353, 2001

Key words: interpenetrating polymer networks; polyurethanes; castor oil; hexamethylene diisocyanate; polymethacrylamide

INTRODUCTION

The synthesis and characterization of interpenetrating polymer networks (IPNs) from natural products have attracted the attention of many research groups. An IPN is defined as a combination of two polymers in network form, at least one of which has been synthesized and/or crosslinked in the immediate presence of the others. The IPN component networks may be synthesized sequentially or simultaneously. Since both polymers are covalently crosslinked at the end of the reaction sequence, these IPNs are thermosets.

Three classes of polymers are recognized as having noncovalent or physical crosslinks:

multiblock copolymers, which phase separate, semicrystalline polymers, and polymers possessing ionic charges. In all cases, such materials have separated regions of polymer chains, which impart physical crosslink properties to the polymer. Combinations of two such physically crosslinked polymers, especially where both polymers have some degree of dual-phase continuity, belong in a relatively new class of IPNs, designated as thermoplastic IPNs. Thus, thermoplastic IPNs are hybrid polymeric materials possessing physical crosslinking capabilities and frequently possessing interpenetration of phases. These materials flow at elevated temperatures, yet behave as thermosets at the used temperatures. Research work involving IPNs using naturally occurring triglyceride oils, which was initiated by Sperling and coworkers[1–5] at Leigh University, has gained momentum in recent years. Over the years, a large number of articles have been pub-

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Table I   Chemical Composition and Thermal Decomposition Data of IPNs

Sample Code	System	PU (NCO/OH) Ratio	PU/MAM Composition	% Wt Loss to Various Temperatures (°C)		
				100–300	300–400	400–500
IPN-1	CO + HMDI + MAM	1.6	25 : 75	8	54	95
IPN-2	CO + HMDI + MAM	1.6	35 : 65	13	53	94
IPN-3	CO + HMDI + MAM	1.6	45 : 55	16	48	96
IPN-4	CO + HMDI + MAM	1.8	25 : 75	11	46	90
IPN-5	CO + HMDI + MAM	1.8	35 : 65	16	44	89
IPN-6	CO + HMDI + MAM	1.8	45 : 55	14	46	91

CO, castor oil.

lished in this area using biomonomers as the base materials. These oils are generally synthesized naturally with multiple chemical functionality. The oils which have attracted attention for the preparation of IPNs are castor, vernonia, lesequrella palmeri, etc. Of these oils, castor oil has received attention in recent years because of its availability on a large commercial scale. Orissa is one of the States in India with various forest products of oil-bearing wild plants such as castor, tung, vernonia, linseed, crambe, cashew nut, w. tomentosa, and apocyanaceace. These plants are abundantly grown in the forests of Orissa and the oils of some of these plants contain the triglyceride of ricinoleic acid. Our laboratory has taken up a program for the synthesis and characterization of IPNs and semi-IPNs from the oils available in the forests of Orissa.

Recently, we reported the synthesis and characterization of some IPNs from castor oil using a multitude of vinyl monomers.[6–10] This communication presents the thermal properties of IPNs prepared from castor oil–hexamethylene diisocyante (HMDI) and methacrylamide (MAM) as the monomer. The thermal properties of IPNs were studied using a novel LOTUS package method developed by Rao and Mohanty.[11] The samples were subjected to wide-angle X-ray diffraction analysis. Ruland and Vonk's[12,13] method was used to calculate the degree of crystallinity.

EXPERIMENTAL

Materials

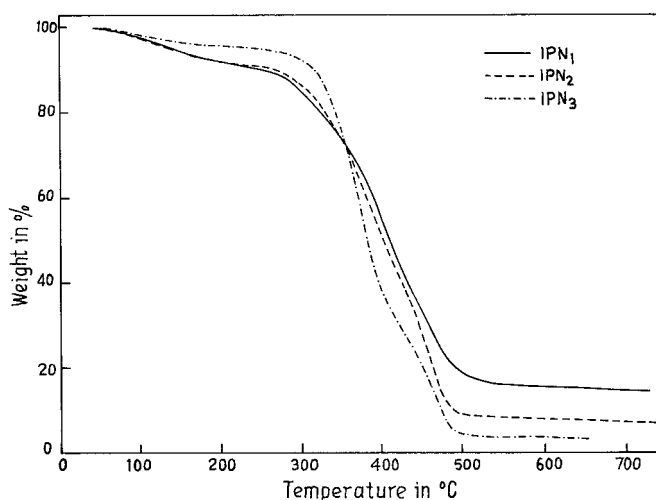Refined castor oil was used without any purification. Its characteristic values such as hydroxyl

Figure 1   Weight loss curves of the IPNs: (——) CO + HDMDI + MAM (NCO : OH, 1.6), (PU : MAM, 25 : 75); (- - - - -) CO + HMDI + MAM (NCO : OH, 1.6), (PU : MAM, 35 : 65); (··········) CO + HMDI + MAM (NCO : OH, 1.6), (PU : MAM, 45 : 55).

Table II Values of Activation Energy of Different IPNs Prepared from Castor Oil-Based PU–PolyMAM

Sample Code	$g(\alpha)$ Employed	Temperature Range in °C	E (kJ/mol)	R^2
IPN-1	D_2	300–400	111.58	0.99043
	D_1	410–500	44.03	0.99034
IPN-2	D_1	300–400	88.03	0.98825
	D_1	410–490	44.59	0.96978
IPN-3	D_4	300–400	81.37	0.99366
IPN-4	D_2	300–490	61.67	0.99076
IPN-5	D_1	300–400	69.13	0.99195
	D_1	410–490	45.88	0.99447
IPN-6	D_3	300–400	144.17	0.99204
	D_1	410–490	27.91	0.99797

number, acid number, and isocyanate equivalent were determined by standard procedures.[6] The chemicals used in the investigation were analytical grade. Benzoyl peroxide was recrystallized from chloroform and the vinyl monomer was freed from the inhibitor before use. The isocyanates used were of analytical grade.

Polyurethane Synthesis

Castor oil (9.32, 0.01 mol) was reacted with HMDI (4.2 g, 0.025 mol) to maintain the NCO/OH ratio at 1.6. The reaction was carried out at 45°C with continuous stirring for 2 h. The prepolymer was isolated as a viscous liquid. Following this procedure, other polyurethanes (PUs) with varying NCO/OH ratios were prepared.

Synthesis of IPNs

The isolated PUs were taken in a round-bottomed flask and a mixture of MAM, 1% EGDM, and 0.5% of benzoyl peroxide was added. The mixture was stirred at room temperature for 15 min to form a homogeneous solution. Then, it was stirred at room temperature for 1 h and the solution was poured into a glass mold kept in a preheated oven maintained at 60°C. It was kept at this temperature for 24 h. Following this procedure, a number of IPNs were prepared. The feed composition and thermal decomposition data of the IPNs are furnished in Table I.

Samples of IPN films of about 1-mm thick were investigated. All samples were crystallized isothermally for 1 h at 380 K and then quenched in ice. Measurement was carried out using the symmetrical reflection technique with a Phillips vertical power diffractometer and Ni-filtered CuKα radiation produced at 30 kV, 20 MA, by a highly stabilized generator. Intensity measurements were taken using a Geiger–Muller counter employing fixed-count step-scanning. The CuKα radiation was monochromatized by employing a curved quartz crystal on the diffracted beam.

For the SEM studies, samples were first coated with an ultrafilm of gold by an ion sputterer JFC-1100 (JEOL Ltd., Tokyo, Japan) and then exposed under a JEOL electronic microscope (JSM 35 CF). For this purpose, the working height was kept at
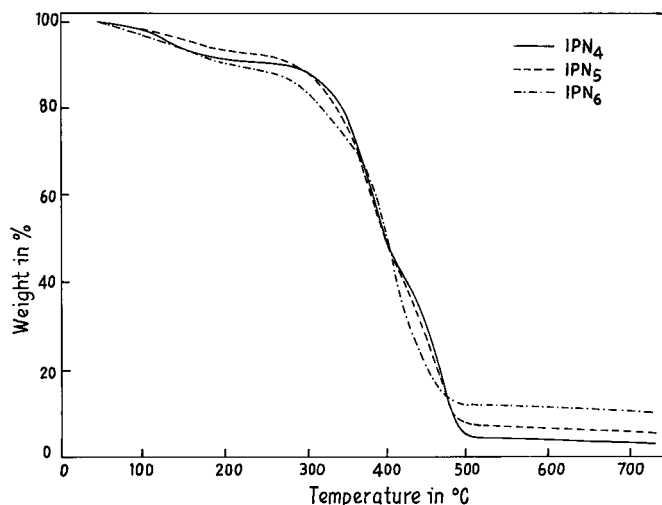

Figure 2   (a) I versus 2θ for IPN$_1$; (b) I versus 2θ for IPN$_2$; (c) I versus 2θ for IPN$_3$.

Table III   Degree of Crystallinity (X_{cr}) of IPNs Samples

Sample Code	Conventional Graphical Method	Ruland–Vonk Computer Method
IPN-1	0.5643	0.592932
IPN-2	0.6071	0.669900
IPN-3	0.6803	0.688615
IPN-4	0.5531	0.612979
IPN-5	0.6062	0.622752
IPN-6	0.5708	0.636537

15 mm with a working voltage ranging between 10 and 25 kV. The absorbed secondary and back-scattered electron images of the area of the IPN sample under investigation and X-ray image mapping were directly photographed from the oscilloscope with the help of the built-in camera.

RESULTS AND DISCUSSION

Thermal Studies

A perusal of Figure 1 indicates that all the IPNs prepared decompose by 12 wt % in the temperature range 0–300°C. All the IPNs decompose by about 50 wt % in the temperature range 300–400°C and 95 wt % in the temperature range 400–500°C. The initial slow weight loss in the range 0–300°C is attributed to the moisture retained in the sample. The weight loss to about 50% in the temperature range 300–400°C may be due to the decrosslinking of IPNs. Further, the third weight loss occurring in the range 400–500°C indicates complete decomposition of the IPNs around 500°C. The final weight loss occurs because of the breakage of bonds in the polymer consisting of polymethacrylamide attached to the ricinoleic acid backbones.

Since there are two breaks in the TG Curves around 300–400 and 410–500°C, the activation energies were calculated using different mechanisms, taking into account the highest correlation coefficient value as furnished in Table II.

A perusal of the results indicates that for all the polymers, the values of the activation energy (E) are higher in the temperature range 300–400°C and considerably lower in the range 410–500°C. This clearly indicates that the degradation process is slower in the temperature range 300–400°C and faster in the temperature range 410–500°C. This is quite evident considering the structure of IPNs. As decrosslinking occurs in the temperature range 300–400°C, this process is bound to be slower, but in the temperature range 410–500°C, the polymethacrylamide attached to the backbone of ricinoleic acid decomposes at a faster rate; hence, the activation energy is low.
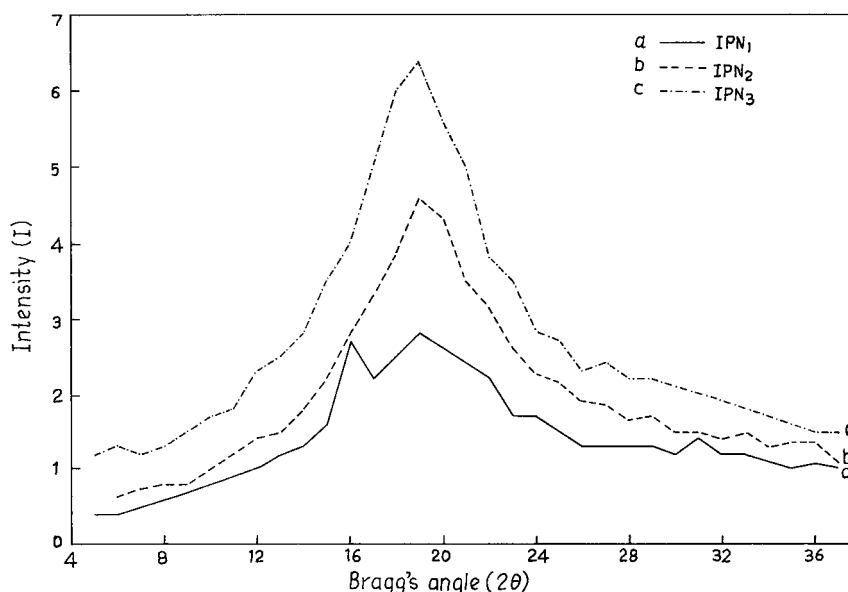

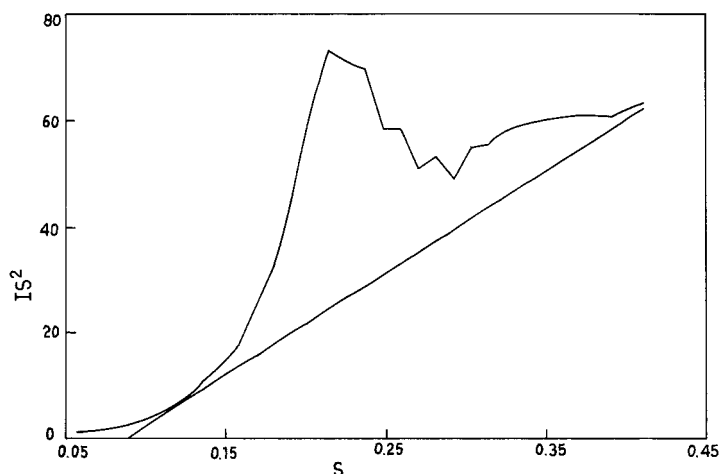**Figure 3**   SEM micrograph; (a) IPN-2; (b) IPN-3; (c) IPN-5; (d) IPN-6.

Figure 4 IS^2 versus S graph of IPN_3.

XRD Studies

Figure 2 (a–c) represents the diagrams of X-ray diffraction intensity distribution curves of IPN-1, IPN-2, and IPN-3, respectively, showing intensity (I) versus the Bragg's angle ($2\ \theta$). It is observed that the intensity peaks gradually rise with increase of the prepolymer content, that is, 25–45% as compared to the monomer content. Table III represents the values of X_{cr} of the IPNs calculated by a conventional graphical method and Ruland–Vonk's computer method.

It is observed that the degree of crystallinity increases with increase of the prepolymer content. Hence, in this case, the X_{cr} depends on the PPU/monomer ratio rather than on the NCO/OH ratio in the PU.

Morphological Study by SEM

The morphology of the IPNs derived from castor oil–HMDI-based PU and polyMAM was studied by SEM. Figure 3 (a,b) shows SEM micrographs of IPN-2 and IPN-3, respectively. It is observed that, when the prepolymer (PPU) content increases from 35 to 45%, the heterogeneity gradually decreases and the morphology changes from a discontinuous to a continuous phase. Figure 3 (c,d) shows SEM micrographs of IPN-5 and IPN-6, respectively. Similar phase change observations are also noted in this case.

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