Polymers from Renewable Resources. IV. Castor-Oil-Based Interpenetrating Polymer Networks Derived from Isophorone Diisocyanate Poly(Acrylamide) and Poly(Methacrylamide)

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POLYMERS FROM RENEWABLE RESOURCES. IV. CASTOR-OIL-BASED INTERPENETRATING POLYMER NETWORKS DERIVED FROM ISOPHORONE DIISOCYANATE POLY(ACRYLAMIDE) AND POLY(METHACRYLAMIDE)

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ABSTRACT

A number of polyurethanes were synthesized by reacting castor oil with isophorone diisocyanate while varying the NCO/OH ratio. All these polyurethanes were reacted with such acrylic monomers as acrylamide and methacrylamide by using ethylene glycol dimethacrylate as a cross-linker and benzoyl peroxide as the initiator. The physicochemical properties of interpenetrating polymer networks (IPNs) are reported. The durability, solvent absorption, outdoor weathering, and aging properties of IPNs have been studied. Thermogravimetric analysis was used to study the thermal behavior of IPNs and the evaluation of kinetic parameters. A number of equations, such as those of Freeman–Anderson, Broido, Piloyan–Novikova, Horowitz–Mitzger, and Coats–Redfern, have been used to determine the kinetic parameters. The degradation mechanism is discussed.

INTRODUCTION

In 1960 Millar [1] first reported the synthesis of interpenetrating polymer networks (IPNs). During the last three decades a large number of papers and patents have been published by Sperling [2-20], Tan [21], Ayorinde [22], Frisch [23-28], Hourston [29, 30], Mayer [31-33], and Suttar [34-36] on IPN synthesis. Sperling and coworkers [6] reported the synthesis of a large number of IPNs from castor-oil-based polyurethane derived from 2,4-toluene diisocyanate and styrene monomer in the presence of 5% divinyl benzene as a crosslinker. These IPNs showed high strength, good resiliency, and resistance to abrasion and hydrolysis.

Recently, the use of renewable resources has attracted the attention of many researchers because of their possible substitution for petrochemical derivatives. Much attention is focused on the innovation and development of newer materials from renewable resources, i.e., forest products which could be grown again and again. Orissa is one of the states in India crowned with various forest products of oil-bearing wild plants such as castor, tung, *Vernonia*, linseed, *Crambe*, *Lunaria*, cashew nut, *Lipatage benghalensis*, *Wrightia tinctoria*, and *W. tomentosa*. These plants are abundantly grown in the forests of Orissa, and the oils of some of these plants contain the triglyceride of ricinoleic and isoricinoleic acid.

It is planned to utilize some of these oils for the synthesis of some novel IPNs. Among the most interesting wild plant oils are the special functional group triglyceride oils. Although some of the triglyceride oils, such as linseed and tung, have only double bond functionality, a few others have developed such functional groups as hydroxyl and epoxy [6]. One of the most naturally occurring vegetable oils is castor oil [37-43], which has the advantage of possessing relatively high purity and being abundantly available in the forests of Orissa. This oil is extracted from the beans of the plant *Ricinum cummunis*. It is mainly used in Orissa as a burning oil in place of kerosene.

Castor oil is unique in possessing both unsaturation and nonconjugated hydroxyl function. The trifunctional nature of castor oil contributes toughness to the structure, and its long fatty acid chain imparts flexibility. Due to its unusual structure, this oil is very versatile in its applications. Although this oil has been known from primitive times for its medicinal values, it now plays an important role in the field of polymer chemistry. As a polyfunctional alcohol, castor oil reacts with polyfunctional isocyanates to form polyurethanes (PUs) that range from rigid foams to elastomers [38, 44-46]. The hydroxyl function of the oil can also be made an important additive to impart plasticization in many polymer blends.

Castor oil has been used in reaction injection molding (RIM), high pressure impingement mixing (HPIM), and reinforced RIM processes [47-50].

Castor oil also undergoes many familiar organic reactions to form useful derivatives. Epoxidized, hydrogenated, and hydroxylated oils are among the many derivatives. Epoxy derivatives are used to stabilize poly(vinyl chloride) resins, and hydroxylated oil yields quick-drying alkyds [39]. The hydrogenated derivatives are used as greases and vehicle paints. Sebacic acid, a product of alkali fusion of castor oil, is used in the manufacture of nylon [43].

We recently reported [52] the thermal and mechanical properties of some IPNs synthesized by using toluene-2,4-diisocyanate and hexamethylene diisocyanate, and reacting the prepolymers with some acrylic monomers. This communica-

tion reports the preparation of large number of IPNs by using castor oil, isophorone diisocyanate, and acrylamide and methacrylamide as vinyl monomers. The physico-chemical properties and the thermal behaviors of these IPNs have been investigated.

EXPERIMENTAL

Materials

Castor oil (refined) was used without any further purification. It was obtained from the local market. Its characteristic values, including its hydroxyl number, acid number, and isocyanate equivalent, were determined by standard procedures and are listed in Table 1.

The chemicals used in the investigation were analytical grade. Benzoyl peroxide was recrystallized from chloroform, and vinyl monomer was freed from the inhibitor before use. The isocyanate content was determined by titration with standard n-butyl amine.

Polyurethane Synthesis

Castor oil (10.11 g, 0.0108 mol) was reacted with isophorone diisocyanate (IPDI) (4.817 g, 0.0218 mol) to maintain the NCO/OH ratio at 1.6. The reaction was carried out at 45°C with continuous stirring for 2 hours. The prepolymer was isolated as a viscous liquid. Other PUs with varying NCH/OH ratios were prepared by following this procedure.

Synthesis of IPNs

IPNs were synthesized by charging the PU in different proportions into a round-bottomed flask. To this, a mixture of acrylamide, 1% ethylene glycol dimethacrylate (EGDM), and 0.5% benzoyl peroxide was added. The mixture was stirred at room temperature for 15 minutes to form a homogeneous solution. The temperature was then raised to 60°C to initiate acrylamide polymerization. After stirring for 1 hour, 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 hours and at 120°C for 4 hours. The IPN thus formed was cooled slowly and removed from the mold with

TABLE 1.   Properties of Castor Oil

Acid number (mg KOH/g)	1.48
Acid value	2.45
Hydroxyl number (mg KOH/g)	160–162
Hydroxyl value (meq/g)	2.80
Isocyanate equivalent	330
Molecular weight (mean)	930
Water content (wt%)	0.21
Specific gravity at 28°C	0.965

different compositions of the same vinyl monomer and PU. Nine IPNs were synthesized, and a large number of IPNs were also prepared with different monomers.

Characterization

IPNs were characterized according to the standard methods listed in Table 2.

The thermal behavior was assessed on a DuPont 951 Thermal Analyzer at a heating rate of 20°C/min in a nitrogen medium.

RESULTS AND DISCUSSION

The prepolymers were synthesized using castor oil and isopherone diisocyanate to give various NCO/OH ratios. IPNs were synthesized by varying the composition of prepolyurethane (PPU) and acrylic monomers such as acrylamide and methacrylamide. The colors of the IPNs range from white to yellow. The IPNs are almost insoluble in common organic solvents, and their densities are heavier than that of water. The densities and percentage yields of all IPNs were determining, and they are furnished in Table 3 together with data on the feed composition of individual IPNs.

Infrared Spectroscopy

The polyurethanes were characterized from their IR spectral data. It is clear from IR spectra that the prepolymer has the characteristic polyurethane group frequencies. In addition to these, a strong band easily discernible at 2260 cm^{-1} may be assigned to isocyanate groups; in fact, these polyurethanes are isocyanate-terminated polymers. A distinct but broad band was observed around 1750–1730 cm^{-1}, which may be assigned to carbonyl groups. Other bands are $\nu C{=}O$ ester at 1746 cm^{-1} and $\nu C{=}O$ urethane at 1734 cm^{-1}.

Durability

The percentage change in weight loss of some of the IPNs (IPN$_1$, IPN$_3$, IPN$_5$, ..., IPN$_{17}$, and IPN$_{18}$) were determined in NaOH, HNO$_3$, CH$_3$COOH, HCl, 1,4-dioxane, DMF, DMSO, and m-cresol. The results are furnished in Table 3. There is almost no significant change in physical appearance of all IPNs in the solvents

TABLE 2.   Standard Methods Used to Characterize IPNs

Property	ASTM specifications
Resistance to chemical reagents	ASTM D 543 (1978)
Aging	ASTM D 799
Solvent absorption	ASTM D 570
Outdoor weathering	ASTM D 1435

TABLE 3. Data on Feed Composition of Individual IPNs: Percent Yield, Specific Gravity, and Percent Weight Loss on Treatment in Different Chemical Reagents[a]

Sample code	DI/CO used	NCO/OH ratio	Monomer used	PPU content, wt%	Monomer content, wt%	Yield, wt%	Specific gravity, g/mL	5% NaOH	5% HNO$_3$	25% CH$_3$CO$_2$H	15% HCl	1,4-Dioxane	DMF	DMSO	m-Cresol
IPN$_1$	IPDI	1.6	AM	25	75	68.2	1.012	1.1	2.8	13.0	1.5	1.8	1.7	0.9	0.7
IPN$_2$	IPDI	1.6	AM	35	65	57.5	1.056	1.2	1.6	9.8	1.8	1.7	2.6	1.0	1.0
IPN$_3$	IPDI	1.6	AM	45	55	63.3	1.112								
IPN$_4$	IPDI	1.8	AM	25	75	64.2	1.032	1.8	2.8	18.5	1.6	2.4	1.8	1.4	1.4
IPN$_5$	IPDI	1.8	AM	35	65	55.2	1.105	1.2	2.1	13.7	0.8	3.2	1.6	1.2	1.5
IPN$_6$	IPDI	1.8	AM	45	55	73.8	1.073								
IPN$_7$	IPDI	2.0	AM	25	75	67.7	1.052	1.4	1.8	22.5	1.3	3.5	2.0	0.7	0.8
IPN$_8$	IPDI	2.0	AM	35	65	60.2	1.108	2.2	2.7	13.4	2.5	3.5	2.0	1.2	0.9
IPN$_9$	IPDI	2.0	AM	45	55	69.3	1.136								
IPN$_{10}$	IPDI	1.6	MAM	25	75	73.8	1.085	1.7	2.8	9.6	2.2	1.8	2.2	1.6	1.4
IPN$_{11}$	IPDI	1.6	MAM	35	65	58.1	1.026	2.8	2.7	13.1	1.8	2.0	2.1	0.8	0.7
IPN$_{12}$	IPDI	1.6	MAM	45	55	69.4	1.098								
IPN$_{13}$	IPDI	1.8	MAM	25	75	71.8	1.045	1.6	3.3	16.0	3.5	2.5	1.4	2.9	1.2
IPN$_{14}$	IPDI	1.8	MAM	35	65	54.5	1.061	2.0	2.7	18.1	2.3	1.5	2.8	2.5	1.7
IPN$_{15}$	IPDI	1.8	MAM	45	55	68.8	1.015								
IPN$_{16}$	IPDI	2.0	MAM	25	75	69.2	1.036								
IPN$_{17}$	IPDI	2.0	MAM	35	65	55.2	1.041								
IPN$_{18}$	IPDI	2.0	MAM	45	55	74.2	1.110								

[a]The contents of prepolyurethane 45% were discarded due to experimental difficulties. IPDI = Isophorone diisocyanate. AM = Acrylamide. MAM = Methacrylamide. PPU = Prepolyurethane. CO = Castor oil. DI = Diisocyanate.

under investigation. The IPNs have little resistance to alkali but much resistance to acid.

Solvent Absorption

Solvent absorption experiments were carried out as per the procedure given by Sperling et al. [57]. Each sample was weighed and soaked in deionized water until absorption equilibrium was achieved, followed by damp drying with towels and reweighing in the absorbing state. Samples were then redried and reweighed. This procedure was repeated by using toluene as the absorbent. The percentage of absorption was calculated for each IPN according to the formula [57]

% Solvent absorption

$$= \frac{(\text{weight of absorbing polymer}) - (\text{weight of dry polymer})}{\text{weight of dry polymer}} \times 100$$

It is very interesting to study the absorption restrictions of these IPNs. The basis for the absorption restriction experiment is the method of Zapp [58] who employed different solvents to examine interfacial bonding between different elastomeric phases. According to Zapp [58], a differential solvent is defined as one which is a good absorbent for the other phase. In the present context the theory suggests that if two microscopically continuous IPNs exist, the presence of the less absorbing phase will restrict the absorption of the more absorbing phase and vice versa. If one phase is continuous and other discontinuous, absorption will be restricted only when the absorbent is preferential to the discontinuous phase. It is evident from the data that slight or very low absorption occurs in toluene, acetone, and NaCl whereas absorption is more prominent in H_2SO_4, CH_3COOH, HCOOH, benzene, and m-cresol.

Outdoor Weathering

ASTM D 1435 procedure was used for this test. The IPNs were mounted outdoors on racks slanted at a 45° angle and facing south. Weathering conditions were: maximum temperature 31°C, minimum temperature 11°C, maximum humidity 70%, and minimum humidity 50%. There was no noticeable weight gain. Data are furnished in Table 4.

TABLE 4.   Outdoor Weathering: Percentage Weight Gain

	Sample									
	IPN_1	IPN_3	IPN_5	IPN_7	IPN_9	IPN_{11}	IPN_{13}	IPN_{15}	IPN_{17}	IPN_{18}
Percentage weight gain	0.096	0.082	—	0.053	0.087	0.012	0.086	0.112	0.098	0.124

Aging

The IPNs were heated in an aging oven in air to measure the loss of weight for 1 hour at temperatures of 150, 200, 250, and 300°C. There was no considerable weight loss of IPNs up to 300°C. Hence, IPNs may be safely used up to 300°C (Table 5).

Thermal Analysis

Thermograms of seven typical IPNs are presented in Figs. 1 and 2 to give comparative pictures of the thermal stability. The characteristic thermal data and oxidation indices (OI) are presented in Table 6 together with the weight loss at different temperatures and the decomposition ranges. The calculated OI values are based upon the weight of the carbonaceous char as related by the empirical equation [51]

$$OI \times 100 = 17.5 \times 0.4 \, C.R. \tag{1}$$

Kinetic parameters have been evaluated using Freeman–Anderson [53], Broido [54], Piloyan–Novikova [59], Horowitz–Mitzger [60], and Coats–Redfern [61] methods which provide overall kinetic data averaged for the experimental temperature range. A disadvantage is that observations at the extreme end are erratic and inexplicable. Here, for the sake of the calculations and to know the nature of the decomposition, the complete thermogram is divided into three distinct sections because the IPNs under observation do not break down in a simple manner, an individual sigmoid should be 100%, and there is a change in the morphological structure of the IPNs at each and every instant of pyrolysis and that affects the rate of decomposition.

Although the above-cited methods involve much labor for an evaluation of the kinetic data, they were used because of their merit for the single thermogram [55, 56].

The Freeman–Anderson method makes use of the following equation, where a plot of $\Delta \log(-dw/dt)$ vs $\Delta 1/T$ gives the energy of activation E^*:

TABLE 5.   Aging: Percentage Weight Loss of IPNs

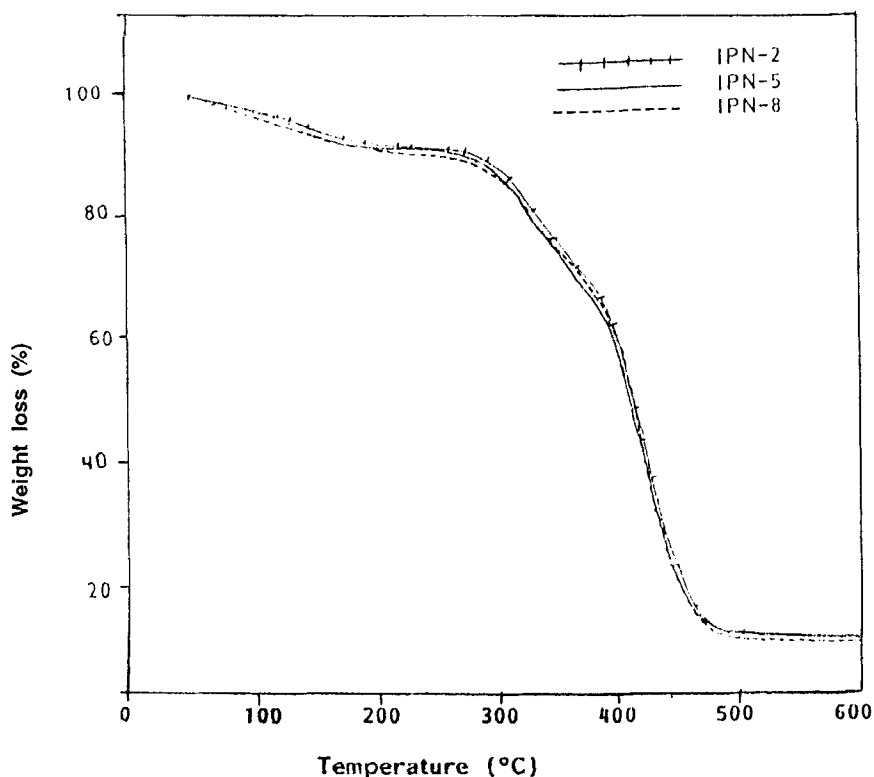| Sample	150°C	200°C	250°C	300°C
IPN$_1$	6.55	7.86	12.17	14.31
IPN$_3$	10.29	12.86	15.85	18.13
IPN$_5$	7.18	14.10	16.82	17.30
IPN$_7$	4.09	9.93	14.11	16.07
IPN$_9$	7.04	10.10	15.27	17.60
IPN$_{11}$	10.57	11.60	13.58	15.24
IPN$_{13}$	10.28	16.71	19.54	21.26
IPN$_{15}$	7.55	12.39	17.10	19.82
IPN$_{17}$	2.58	8.93	11.52	12.35
IPN$_{18}$	11.45	14.28	18.12	21.37

FIG. 1.   Thermogram of interpenetrating polymer networks.

$$\Delta \log(-dw/dt) = n\Delta \log w - (E^*/2.303R)(\Delta 1/T) \tag{2}$$

According to the Broido method for $n = 1$,

$$\ln \log(1/y) = (E^*/R)(1/T + K) \tag{3}$$

where k = any constant, Y = normalized weight (w_t/w_0), and E^* = energy of activation obtained from the slope of the most appropriate plot.

According to the Piloyan–Novikova method,

$$\log(\alpha/T^2) = \log(ZR/\beta E) - E^*/2.303RT \tag{4}$$

where a plot of $\log(\alpha/T^2)$ vs $1/T$ gives the slope for calculation of the activation energy E^*.

According to the Horowitz–Mitzger method,

$$\log[-\ln(1 - \alpha)] = E^*/2.303RT^2 \tag{5}$$

where a plot of log $[-\ln(1 - \alpha)]$ vs $1/T^2$ gives the slope for calculation of the activation energy E^*.
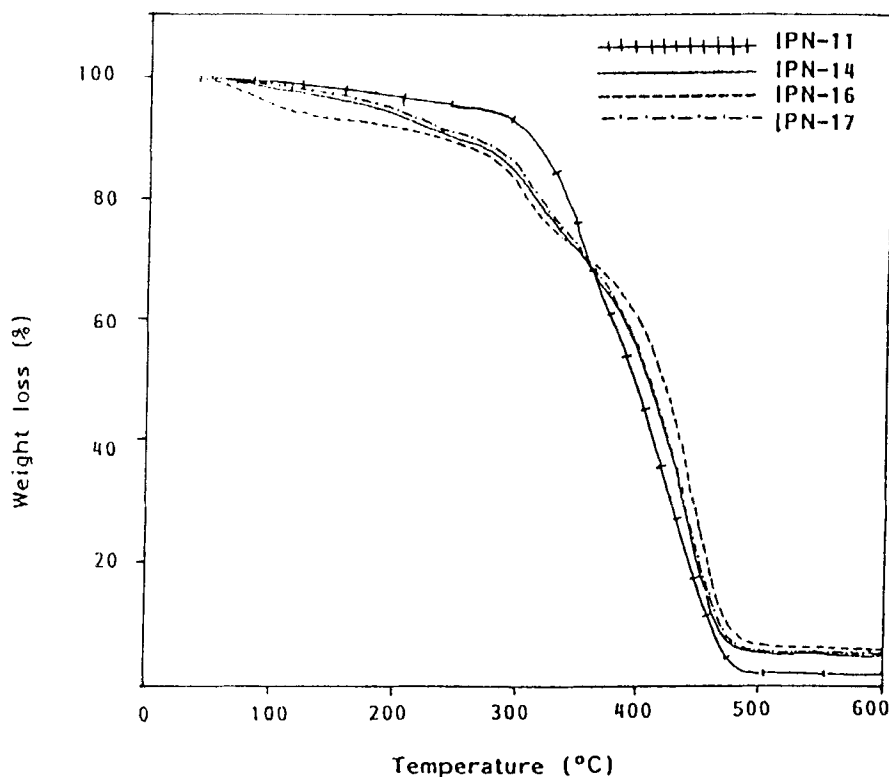
According to the Coats–Redfern method,

FIG. 2. Thermogram of interpenetrating polymer networks.

$$\log[-\ln(1 - \alpha)/T^2] = \log ZR/\beta E^*(1 - 2RT/E^*) - E^*/2.303RT \qquad (6)$$

where a plot of $\log[-\ln(1 - \alpha)/T^2]$ vs $1/T$ gives the slope for evaluation of the activation energy E^* most appropriately.

Freeman–Anderson, Broido, Piloyan–Novikova, Coats–Redfern, and Horwitz–Mitzger plots of the IPNs prepared using IPDI, acrylamide, and methacrylamide are displayed in Figs. 3, 4, and 5, respectively, and the kinetic parameter data are tabulated in Table 7.

Examination of the results indicates that all the IPNs decompose completely at around 600°C. The IPNs prepared by using the prepolymer having an NCO/OH ratio of 1.8 decompose at a higher temperature than do IPNs prepared from the prepolymer having an NCO/OH ratio of 1.6. IPNs prepared from acrylamide and methacrylamide decompose in almost the same temperature range. Based upon the mass of carbonaceous char, it is concluded that IPNs are not good flame retardants as evidenced by their OIs. Table 6 shows that the OI values are almost the same for all the IPNs.

The energy of activation values for IPN-2 and IPN-11 were calculated by Freeman–Anderson, Briodo, Piloyan–Novikova, Horwitz–Mitzger, and Coats–Redfern methods (Table 7). The results indicate that the energy of activation values calculated by the various methods are almost the same for both polymers.

TABLE 6.   Characteristic Thermal Data[a]

Sample	Decomposition ranges (°C)			Percent weight loss ($\pm$ 2%) up to various temperatures (°C)						OI[e]
	First[b]	Second[c]	Third[d]	250	300	350	400	450	500	
IPN$_2$	50–150	328–416	416–595	10	14	27	46.5	83	90	0.1800
IPN$_5$	50–146	290–411	411–640	10.2	14	29	49	84	90	0.1800
IPN$_8$	50–112	377–416	416–600	9	12	24	44	83	91.5	0.1785
IPN$_{11}$	50–180	180–418	418–590	4	8	26	53	86	98	0.1763
IPN$_{14}$	50–215	309–440	440–600	10	17	30	48	82	94	0.1775
IPN$_{16}$	50–82	306–444	444–570	11	18	29	42	78	93.8	0.1777
IPN$_{17}$	50–96	341–444	444–600	9	15	27.5	42	80	94	0.1784

[a]IPNs were analyzed at a heating rate of 20°C/min in nitrogen atmosphere (medium).
[b]Weight loss due to retained moisture.
[c]Major decomposition range.
[d]Secondary decomposition.
[e]OI $\times$ 100 = 17.5 + 0.4 $\times$ C.R.
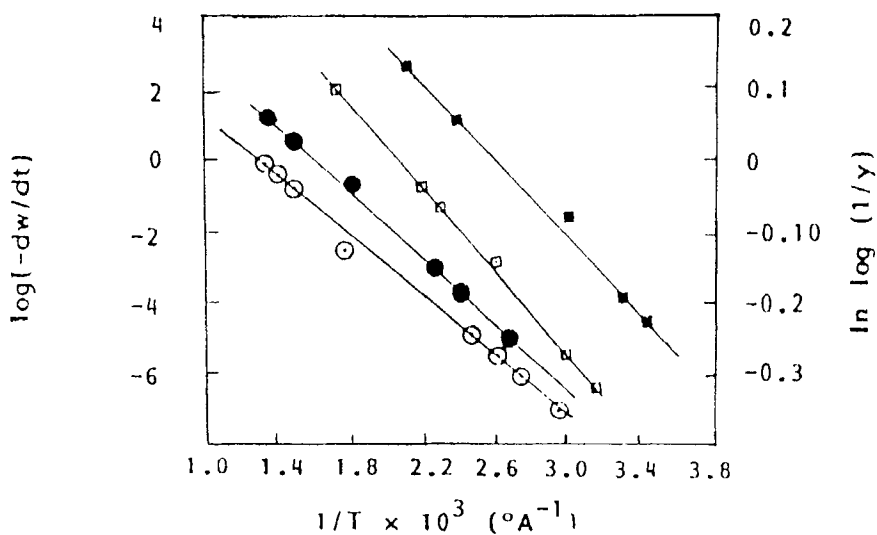
FIG. 3.   Typical Freeman–Anderson and Broido plot for determination of activation energies (E^*) of IPN-2 and IPN-11: ($\bigcirc$, $\bullet$) ln log ($1/y$) vs $1/T$; ($\square$, $\blacksquare$) d log($-dw/dt$) vs $1/T$.
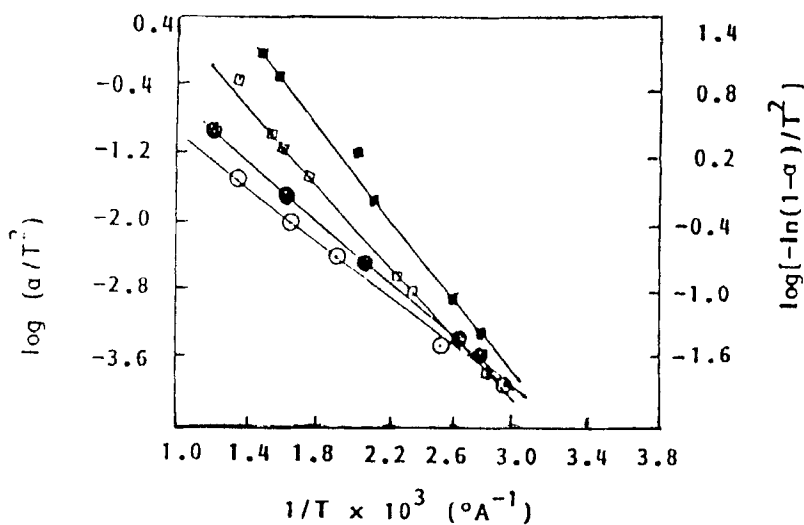

FIG. 4.   Typical Piloyan–Novikova and Coats–Redfern plot for determination of activation energies (E^*) of IPN-2 and IPN-11: ($\bigcirc$, $\bullet$) log(α_2/T^2) vs $1/T$; ($\square$, $\blacksquare$) log[-ln(1 $- \alpha$)/T^2].
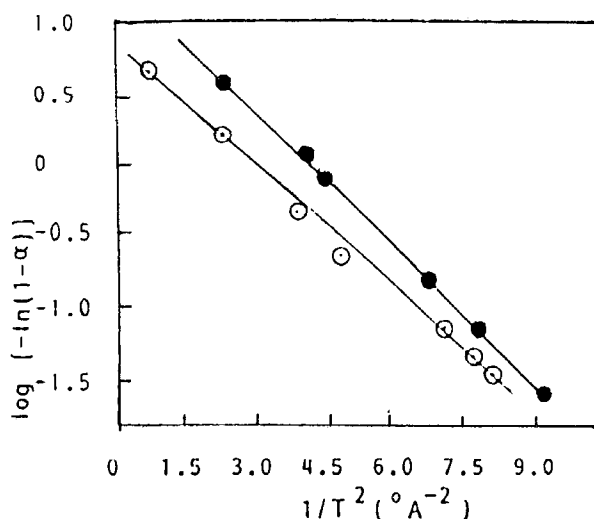
FIG. 5. Typical Horowitz–Mitzger plot for determination of activation energies (E^*) of IPN-2 and IPN-11: ($\bigcirc$, $\bullet$) $\log[-\ln(1 - \alpha)]$ vs $1/T^2$.

Since the structures of IPNs are very complicated, it is difficult to predict the exact mechanism of decomposition of IPNs which decompose in three different steps. The first step is the loss of absorbed moisture, the second step is decrosslinking of the IPN, and the third step is probably the decrosslinking of the vinyl monomer attached to the polyurethane.

TABLE 7.   Kinetic Parameters

Sample	Name of the method	Energy of activation (E^*), kJ/mol
IPN_2	Broido	26.30
	Freeman–Anderson (FA)	5.40
	Piloyan–Novikova (PN)	29.50
	Horowitz–Mitzger (HM)	6.80
	Coats–Redfern (CR)	20.80
IPN_{11}	Broido	33.90
	Freeman–Anderson (FA)	5.30
	Piloyan–Novikova (PN)	33.50
	Horowitz–Mitzger (HM)	5.60
	Coats–Redfern (CR)	24.20

CONCLUSION

Polyurethanes have been synthesized by reacting castor oil with isophorone diisocyanate and acrylamide and methacrylamide monomers, using benzoyl peroxide as the initiator. The physicochemical properties have been studied. From thermal analysis data it is evident that the IPNs decompose around 600°C. The degradation steps of IPNs have been predicted from their kinetic parameters.

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