Correlation of Mechanical Property, Crosslink Density and Thermogravimetric Behavior of Castor Oil Polyurethane–Polystyrene divinyl benzene Simultaneous IPN Networks

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Synopsis

Several simultaneous interpenetrating networks (IPN) of castor oil polyurethane (COPUN) and polystyrene divinyl benzene (PSN) were synthesized under conditions where the free radical polymerization of styrene and the crosslinking reaction of castor oil and toluene diisocyanate progress at comparable rates. Comparison of the mech nical properties and crosslink density of the COPUN and COPUN/PSN-IPNs indicates a marginal increase in tensile strength and crosslink density from COPUN to 60COPUN/40 PSN IPN. IPN samples prepared with further increased PSN content show steady decrease in the above properties. This reversal of the expected trend was attributed to the possible greater molecular interpenetration achieved due to similar gelation times with resultant extension of chains and increase in free volume between crosslinks. This was further confirmed from thermogravimetric data on the initial stages of decomposition of the IPNs.

INTRODUCTION

Cosynthesis and interpenetration of two different polymer networks present a promising tool for achieving certain desired properties which are otherwise difficult to achieve by structural and chemical variations on polymer chains. There are several factors which govern the ultimate property of the interpenetrating networks. This includes the nature and compatability of the interpenetrating networks, their mutual solubility, method of synthesis, rate of polymerization, and crosslinking reactions etc.[1] The extent of interpenetration is governed by many of these parameters and total mutual solubility is required for molecular interpenetration. Most of the IPNs that are synthesized phase separate to varying extents and many authors consider the IPNs as polymer/polymer composites where one of the networks functions as a filler to the already formed polymer network.[2,3]

Mutual dispersion of the phases provides synergestic and useful improvement in the properties of a polymeric system on interpenetration with another. This is achieved by selecting the proper combination of the polymeric systems and arriving at actual reaction conditions. Incorporation of a compatible elastomeric component into a plastic network is shown to improve the toughness and impact resistance of the plastic component. The elastomeric

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particles in the system help to absorb the energy without breakdown and by stress distribution and relief and act also as craze termination points. Similarly, interpenetration of a plastic network into an elastomeric network increases the strength of the material, often retaining the elastic property to a great extent.

Sperling et al. have carried out extensive investigations on several IPN systems based on castor oil polyurethane and castor oil polyester networks in an attempt to develop toughened plastics and reinforced elastomers from castor oil.[4-8] As was expected, incorporation of plastic components into the castor oil polyurethane and polyester networks have resulted in increased strength and toughness. The polymer networks in these cases were allowed to grow one in the immediate presence of the other monomer. The resultant product was described as being composed of one continuous network and the other dispersed in it. At any time during the synthesis, the rate of formation of one of the networks was relatively high compared to that of the other. Separation and further inversion of phases were reported during the synthesis.

Better interpenetration can be expected to be if the two chains are allowed to grow at comparable rates. This could be because the restrictions of placing two polymer chains in juxtaposition do not exist in cases of mutually soluble monomers and when they independently consume their monomers at almost equal rate, improved interpenetration could result in a system comparable to one where one polymer chain is almost completely grown and the second monomer polymerizes at a slower rate. In the present study, an attempt is made to progress the formation of castor oil polyurethane and polystyrene networks at comparable rates and to evaluate the mechanical properties in comparison to the case reported by Sperling et al., where the castor oil polyurethane is formed at a much faster rate than the polystyrene. The trend in the variation in mechanical properties is rationalized by suggesting improved interpenetration and thereby stretching of the chain segments. This observation is further supported by the results on crosslink density studies and the thermogravimetric evaluations.

EXPERIMENTAL

Materials

Castor oil: Commercial quality, dried under vacuum for 16 h.
Toluene diisocyanate: 99% pure.
Styrene: AR quality, freshly distilled and dried over anhydrous sodium sulfate.
Divinyl benzene: AR quality; as 50% solution in ethyl benzene; distilled and dried over anhydrous sodium sulfate.
Benzoyl peroxide: AR quality
N,N-Dimethyl aniline: AR quality

Synthesis of Castor Oil Polyurethane (COPUN)

First, 100 g of castor oil and 28 g of TDI are stirred vigorously in a current of dry nitrogen for 5 minutes. The resulting mixture is subjected to vacuum for a few minutes until it is bubble free and the viscous liquid is poured into a mould and kept in dessicator for 18 hours at room temperature. This is

TABLE I

Sample	Castor oil g	TDI g	Styrene g	Benzoyl peroxide g	N,N-di-methyl aniline g	Divinyl benzene g
II	30	8.38	20	0.4	0.14	0.28
III	30	8.38	30	0.6	0.21	0.42
IV	30	8.38	40	0.8	0.29	0.57
V	30	8.38	60	1.2	0.43	0.85

further heated at 100°C for 64 hours (Sample I). The TDI content was varied and samples 1A, 1B, 1C, 1D, and 1E were synthesized for thermal studies.

Synthesis of Castor Oil Polyurethane / Polystyrene Divinyl Benzene Simultaneous IPN (COPUN / PSN)

Styrene, benzoyl peroxide, divinyl benzene, and N,N-dimethyl aniline are stirred for 4 h at 50°C under dry nitrogen atmosphere. Castor oil and toluene diisocyanate are introduced into it. The mixture is further stirred for 30 minutes and the viscous liquid is subjected to vacuum until it is bubble free. This is transferred into a mould and kept at room temperature under vacuum for 18 hours. The samples are heated at 100°C for 64 hours for completion of the curing. The reaction was carried out for four different compositions of COPUN/PSN and amounts of the reactants are given in Table I.

The crosslink densities of the samples are determined by swelling measurements in benzene as per More and Thomas.[9] The mechanical properties are determined using an INSTRON-1121 Universal Testing Machine. Thermogravimetric and differential scanning calorimetric (DSC) studies were carried out in a Dupont-990 Thermal Analyzer.

RESULTS AND DISCUSSION

The castor oil polyurethane (COPUN) and the polystyrene divinyl benzene (PSN) networks are allowed to form in situ through independent condensation and radical polymerization techniques, respectively. The isocyanate castor oil reaction can take place relatively fast even at room temperature and the free radical polymerization of styrene and divinyl benzene with benzoyl peroxide initiator requires temperatures of the order of 60–80°C. This reaction is also made to proceed at room temperature by incorporating N,N-dimethylaniline which facilitates the easy decomposition of the peroxide. Ultimately both reactions are run into completion after transferring the reaction mixture near the gelation point into a mold and heating it further at 100°C. Simultaneous polymerization is claimed on a qualitative basis. However, the absence of phase separation and phase inversion in comparison with many reported SIN syntheses suggest a simultaneous type of polymerization. The mechanical properties of the polymer blocks are determined and the results are tabulated in Table II. The variation of tensile strength (TS) and elongation (%E) with respect to the plastic component (polystyrene) in the product is plotted in Figures 1 and 2, respectively.

TABLE II

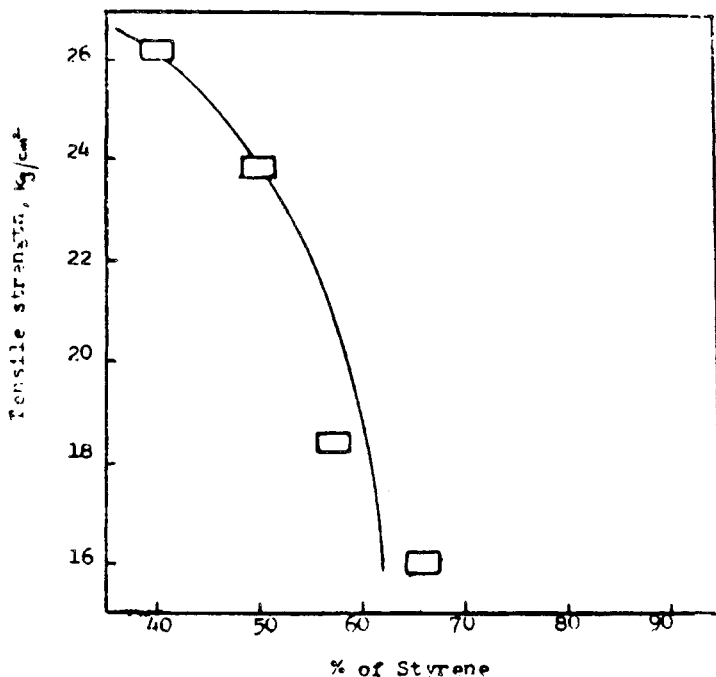| Sample	Composition COPUN PSN		Tensile Strength kg/cm²	Elonga- tion %	Initial modulus kg/cm²
I	100	0	13.6	105	—
II	60	40	26.2	155	20.0
III	50	50	23.9	145	19.3
IV	43	57	18.4	115	17.9
V	34	66	16.0	57	—

Fig. 1. Tensile strength versus percentage PSN content for COPUN/PSN simultaneous IPNs.

It is evident from the table that incorporation of 40% of polystyrene into COPUN by simultaneous interpenetration has helped to impart modest improvements in the tensile strength from a value of 13.6 kg/cm² to 26.2 kg/cm². This trend of marginal improvement in the TS is observed to reverse on further incorporation of PSN. Simultaneous IPNs of COPUN/PSN reported by Sperling et al.[7,8,10] have entirely different mechanical properties and the improvement in tensile strength by incorporation of PSN into COPUN has been marked. Simultaneous IPN with 60% PSN is reported to have tensile strength of 241 kg/cm² and increasing the PSN content to 90% has increased the tensile strength to 375 kg/cm². The present set of experiments indicate only a minor increase in the tensile strength by incorporation of the plastic component up to 40% and further indicating a decrease in the property.

This anomalous behavior is attributed to the variation in the method of synthesis. The comparatively improved simultaneous growth of both the polymer chains could impart increased interpenetration. This is also suggested by the absence of the phase separation and phase inversion steps observed in
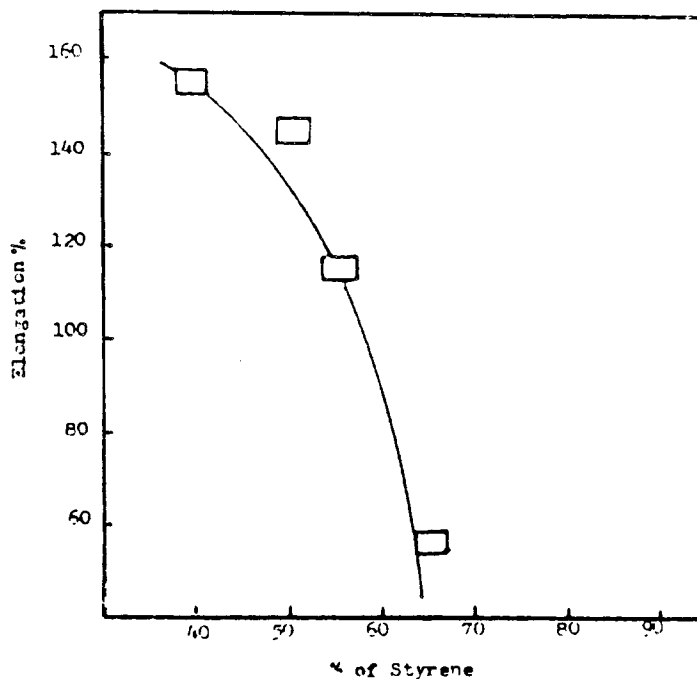
Fig. 2.   Percentage elongations versus percentage PSN content for COPUN/PSN simultaneous IPNs.

earlier synthesis of COPUN/PSN simultaneous IPNs. As described by many authors, the IPNs are polymer/polymer composites and one of the polymers would be behaving as a filler to the other.[1-3] The phase separation and further phase inversions observed during the synthesis and the electron microscopic studies validate the presence of one continuous phase with the other behaving as a sort of compatible filler to it. Interpenetration at molecular level could not lead to phase separation even to this extent. It is suggested that the experimental conditions of the present set of experiments did not give rise to phase separation and this indicates an improved interpenetration.

Mixing of two different polymers is not expected to impart any mutual strain. But placing two polymers in juxtaposition and restricting their mobilities by crosslinking them independently at different points could lead to strain of the chain segments between the crosslinks and subsequent bending and uncoiling of the chain segments. The potential situation could be schematically represented as in Scheme 1. Thus, proper molecular interpenetration could lead to stress points in the chains and this could naturally lead to deterioration of the mechanical properties. The decrease of tensile strength with increasing plastic component interpenetration as against the reported trend is attributed to the weakening of the chains imparted by mutual steric hindrance on molecular interpenetration. In fact, a similar observation has been reported earlier in the case of epoxy/poly(n-butyl acrylate) simultaneous IPN. Weakest materials were yielded on simultaneous gelation of the two polymers and the subsequent formation of fine phase domain structure.[11, 12] Whereas, when one polymer or the other was allowed to polymerize faster, providing nonsimultaneous gelation conditions, the phase domains were larger
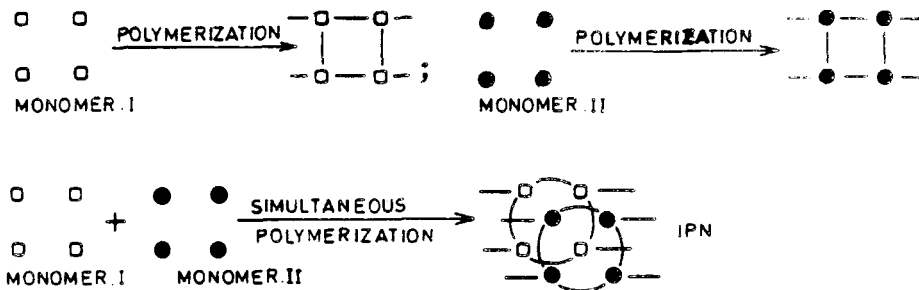
Scheme 1

TABLE III

Sample no.	Crosslink density mol/cm$^3 \times 10^{-4}$
I	3.392
II	3.748
III	3.493
IV	3.169
V	2.254

and the products stronger. This particular observation validates the viewpoint attributed to the weakening of the COPUN/PSN simultaneous IPN products on improved interpenetration.

The crosslink densities of these samples were determined and are given in Table III. The variation of crosslink densities with the amount of plastic component PSN is shown in Figure 3. There exists a similarity between the
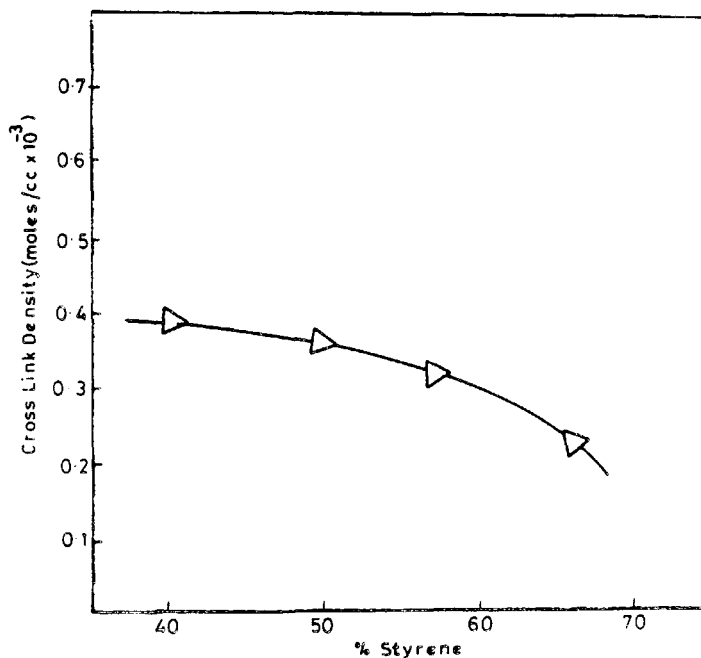

Fig. 3. Crosslink density versus percentage PSN content for COPUN/PSN simultaneous IPNs.

variation of crosslink density and the tensile strength with the amount of plastic content as is evident from the comparison of Figure 3 with Figure 1. In both cases, the parameters decrease with increasing styrene concentration. Assuming the absence of any extra effect involved in interpenetration which increases or decreases the crosslink density of the IPN, the crosslink density of the IPN should have an additive value of the fractional crosslink densities of the individual polymer networks. Although any conclusive and self-standing implications on the chain stretching effects arising due to interpenetration are not possible based on the crosslink density data, the close similarity of the trend in variation of the crosslink density with that of mechanical property is interesting. Incorporation of 40% of PSN increases the crosslink density of COPUN, though to a very small extent, and further increases of PSN decreases the crosslink density. The data could be rationalized on the same grounds as for the anomalous mechanical property by suggesting uncoiling on chain segments and further stretching, resulting in increased free volume between the chains in juxtaposition. This permits increased swelling and results in apparent decrease in crosslink densities. The high crosslink density of PSN compared to COPUN would have resulted in a much higher value for Sample II, but for the apparent decrease effected due to chain stretching due to interpenetration. The latter effect is more pronounced on further increase of PSN content and the crosslink density decreases steadily. In fact, it is reported for many other IPNs that the theoretical crosslink densities have been found to have higher values compared to the experimental values determined by swelling measurements, and the divergence between the experimental and theoretical values were found to increase with increasing levels of interpenetration.[13, 15]
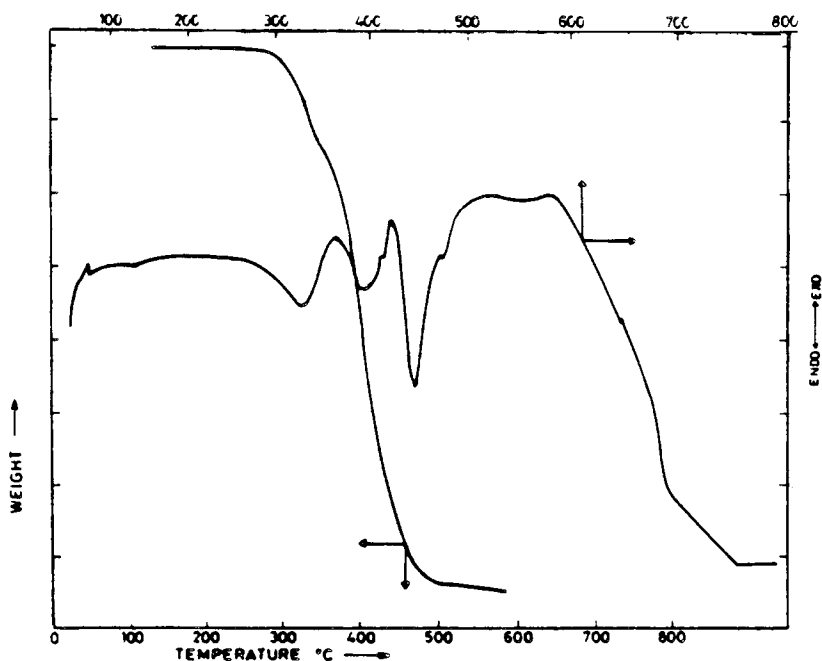

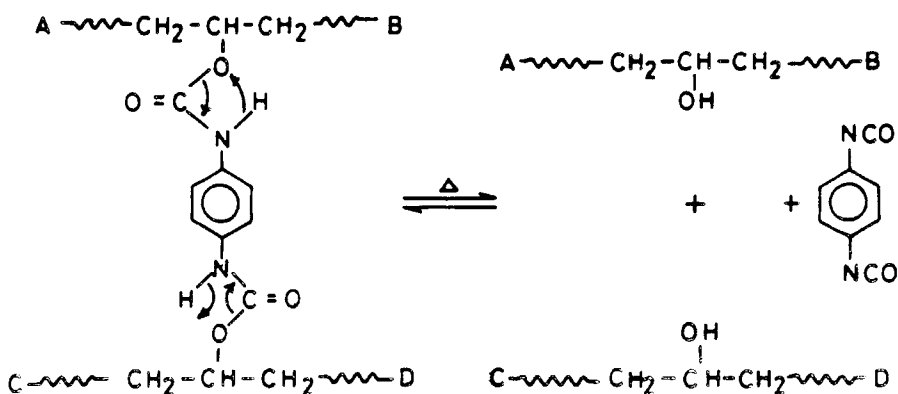Fig. 4. Typical TGA and DTA plot of COPUN.

Thermogravimetric Studies

Thermogravimetric studies on COPUN and COPUN/PSN polymers were carried out in dry nitrogen at a heating rate of 20°C per minute. Figure 4 shows a typical thermogram of COPUN and Figure 5 shows the thermograms of COPUN/PSN simultaneous IPNs.
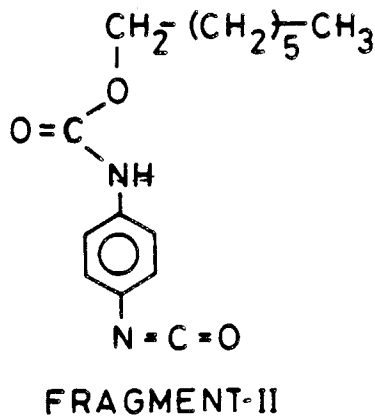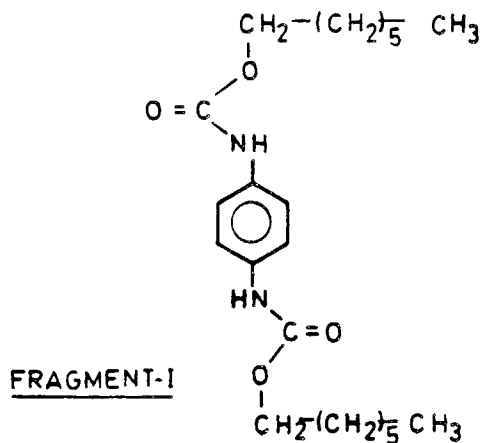
The thermograms of COPUN show three distinct stages of decomposition. This was further confirmed by the DSC as shown in Figure 6. The first stage of decomposition is from 270° to 350°C; second stage from 350° to 410°C and the third stage from 410° to 500°C. The weight loss in the first stage up to 350°C is found to increase linearly with the increasing content of the cross-linking agent TDI. Figure 6 plots the weight loss in stage 1 of the thermal decomposition of COPUNs versus the TDI content of each polymer network. The weight loss in the first stage of decomposition of the COPUNs and the TDI content of each one is tabulated in Table IV. The obvious conclusion from the table of results is that the TDI content of the particular COPUN and the weight loss at the first stage of thermal decomposition are almost equal. This, together with the reported suggestions on the thermal decomposition of polyurethanes[16] indicate the first stage of decomposition to involve the breakdown of the polymer by depolymerization at TDI points resulting in the loss of TDI moieties. A plausible mechanism may be suggested as in Scheme 2.

As polystyrene is relatively thermally stable up to 350°C, the first stage of the thermograms of COPUN/PSN simultaneous IPNs is expected to behave in a similar manner. However, the COPUN content varies with different samples and subsequent change in the first stage weight loss is anticipated. As expected, the weight loss decreases with increasing polystyrene content. This is evident from the plot of first stage weight loss versus PSN content in the IPNs. The actual values of fractional weight loss for each of these samples and the expected weight loss due to TDI is tabulated in Table V.

Unlike COPUN, the fractional weight loss accounts for the loss of a relatively larger moiety than TDI, or the loss of TDI along with some other fragment. The result could be rationalized by assuming strain points developed in the COPUN polymer by interpenetration with PSN. This is very well accountable by assuming that chain stretching developed during interpenetra-

Scheme 2

Fig. 5. TGA plots of COPUN/PSN simultaneous IPNs for Samples II, III, IV, and V.

tion and that cleavage at these sites competes with the depolymerization of TDI. The possible thermal cleavage sites at this stage are indicated in the following scheme: The loss of TDI moiety requires cleavage at two points of the crosslinking chain, and this is competes with the cleavage at two points of the crosslinks on interpenetration. When the former cleavage is more facile,

Scheme 3

$$CH_2-(CH_2)_5 \quad CH_3$$

$$O$$

$$O=C$$

$$NH$$

FRAGMENT-I

$$HN$$

$$C=O$$

$$O$$

$$CH_2-(CH_2)_5 \ CH_3$$

$$CH_2-(CH_2)_5-CH_3$$

$$O$$

$$O=C$$

$$NH$$

$$N=C=O$$

FRAGMENT-II

the moiety eliminated would be largely TDI and when the latter cleavage predominates, fragment I would be eliminated. An almost equally facile cleavage could lead to fragment II.

In fact, weight loss up to 350°C for the COPUN/PSN simultaneous IPNs almost matches with the computed values, assuming a loss of fragment II. This is indicated in Table VI. Furthermore, the activation energy for the first stage of decomposition is calculated using the Coats-Redfern method.[17] Good fits are observed from the reaction order parameter, n, equal to 1 and the plots are shown in Figure 7. The activation energies calculated from the slopes are 28.3, 24.1, and 18.0 kcal/mole, respectively, for COPUN, 60 COPUN/40 PSN, and 50 COPUN/50 PSN samples. The decrease in the activation energy with the increase in PSN content also implies a weakening of the COPUN crosslinkages and is in agreement with the mechanical properties and swelling data.
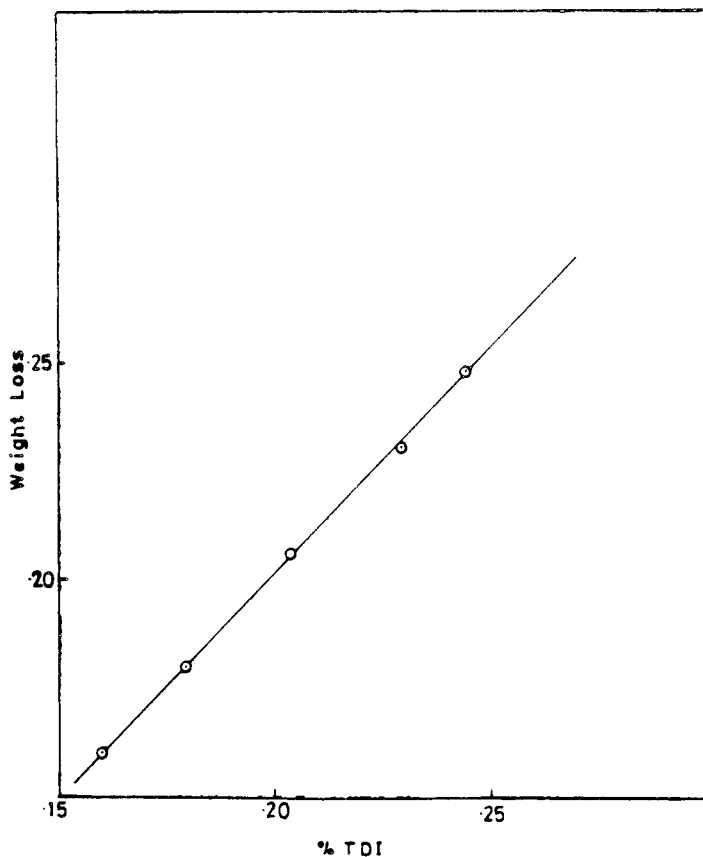
Fig. 6.   Weight loss in stage I (270–350°C) deduced from TGA plots of COPUNs plotted versus percentage TDI content.

TABLE IV

Sample	% TDI content	% Weight loss up to 350°C
I_A	24.4	24.8
I_B	22.4	23.1
I_C	20.4	20.6
I_D	17.9	18.0
I_E	15.9	16.0

TABLE V

Sample	% Weight of TDI	% Weight loss up to 350°C
II	14.2	24.9
III	12.1	21.9
IV	10.5	20.4
V	8.4	14.9
VI	6.4	12.4

TABLE VI

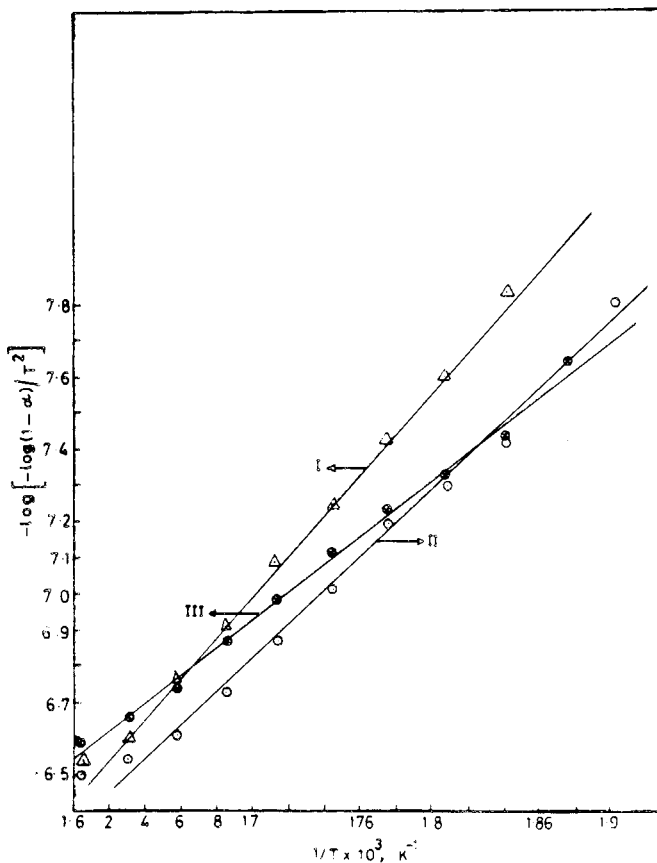| Sample	% Weight loss due to fragment II	% Observed weight Loss
II	23.07	24.9
III	19.67	21.9
IV	17.06	20.4
V	13.65	14.9
VI	10.4	12.4

Fig. 7. Coats-Redfern plots for Samples I, II, and III. $-\log[-\log(1-\alpha)/T^2]$ is plotted versus $\frac{1}{T} \times 10^3$. α is the extent of decomposition calculated from the thermograms and T is the temperature.

CONCLUSIONS

The method of synthesis and the nature of interpenetration is indicated to have a marked effect on the properties of simultaneous IPN networks. The crosslink density, mechanical properties, and thermogravimetric analysis of castor oil polyurethane-polystyrene divinyl benzene simultaneous IPNs suggest detrimental effects on tensile strength and thermal stability when the

two interpenetrating network formations were qualitatively attempted to proceed at comparable rates.

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