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Photo Polymerized Interpenetrating Polymer Network of Poly(antimony acrylate) and Poly(arsenic acrylate): Synthesis and Characterization

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Photo Polymerized Interpenetrating Polymer Network of Poly(antimony acrylate) and Poly(arsenic acrylate): Synthesis and Characterization

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A series of IPN based on poly(antimony acrylate) and poly(arsenic acrylate) have been synthesized by a sequential mode of synthesis. Formation of complex based on "polymer solvent" method reflects the contraction of the polymer coils by determining the value of mutual interaction constant (k_{AB}) in different solvents such as dimethylsulphoxide (DMSO) ($k_{AB} = 0.60$); dimethylformamide (DMF) ($k_{AB} = 0.42$); dioxane ($k_{AB} = 0.26$) predicting weak Vander Waal interaction. The scanning electron microscopy reveals dual phase morphology of both metal acrylates. The infrared spectrum indicates characteristic frequencies of ($>$C=O) at 1730 cm^{-1},thus giving structural evidence for IPN. The properties namely percentage swelling, average molecular weight between crosslinks(M_c),Young's modulus, increases with concentrations of linear polymer(polyantimony acrylate) and initiator (benzoyl peroxide). However, it decreases with concentrations of monomer (arsenic acrylate) and crosslinker (divinyl benzene).The value of activation energy calculated from thermo gravimetric analysis is 15 KJ/mol.

Keywords: polymers; scanning electron microscopy (SEM); thermogravimetric analysis (TGA)

1 Introduction

The dynamic mechanical properties of a macromolecular system may be improved significantly by intermolecular complexation caused through crosslinking. Such a typical representation of hybrid binders, whose use makes it possible to achieve a much more complex combination of different polymer structures, structural states in composite materials, are interpenetrating polymer networks (IPN's). IPN's are composed of two (or more) chemically distinct networks held together predominantly with the help of a crosslinker by their trapped mutual entanglements rather than by covalent bond grafting. Crosslinked polymers are found in many and varied applications throughout the chemical industry including rubbers, latexes, polyurethanes, epoxies, aqueous fluid absorbers and ion exchange resins.

The field of IPN was laid down by Millar (1) and persuaded by Sperling et al. (2–4) and Frisch (5, 6). There is a splendid scientific literature concerning IPN's based on polyurethanes (7, 8), epoxy resins (9), PVC/poly(butadiene-co-AN) based latex IPN4, phenol formaldehyde resins (10). Reza et al. (11) have reported the synthesis and morphology of IPN containing copolymers of methylene-bis-acrylamide and vinyl ferrocene. The synthesis of IPN's containing poly(acrlamide-co-acrylic) and poly(vinyl alcohols) (12) have been studied. Kevi et al. (13, 14) studied the swelling behavior of IPN hydrogels composed of poly(vinyl alcohol) and chilosers. Synthesis and characterization of IPN from poly-carbonate and cellulose acetate butyrate were studied by Laskar et al. (15). Studies on the synthesis of conducting semi-IPN of poly pyrrole with poly esteramide urethane from a sustainable resource was also carried by Ashraf and Alam (16). Besides these applications of IPN's, Song and Nemoto (17) performed the microscopic infrared dichroism, mesoscale deformation and macroscopic stress measurements on the microcrystalline region of isotactic polypropylene (iPP) thin films, subjected to uniaxial stretching at room temperature. Their results reveal that volume dilatation might occur during stretching. Recently, the studies on IPN (18) based on starch and polyacrylatamide co-methylacrylate and their diffusion characteristics evaluation have been carried out. The literature is enriched with IPN formation using only one metal acrylate such as Zn, Cu, Cr with vinyl

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Table 1. The intrinsic viscosity in polymer solvent (PAsA)/PSbA at a temperature of 30°C

Intrinsic viscosity in polymer solvent (PAsA/PSbA) (A = PAsA; B = PSbA)		
Solution in DMSO		
$[PSbA] \times 10^{-4}$	$(\eta_A)_B$	k_{AB}
2.5	0.15	0.60
5.0	0.17	
7.5	0.19	
10.0	0.22	
Solution in DMF		
$[PSbA] \times 10^{-4}$	$(\eta_A)_B$	k_{AB}
2.5	0.09	0.42
5.0	0.11	
7.5	0.14	
10.0	0.17	
Solution in Dioxane		
$PSbA] \times 10^{-4}$	$(\eta_A)_B$	k_{AB}
2.5	0.06	0.26
5.0	0.08	
7.5	0.12	
10.0	0.15	

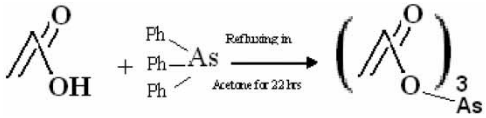
monomers (19–21). However, IPN formation using two metal acrylates via photo polymerization process is still scarce. The main aim of this work is therefore to synthesize and characterize photopolymerized IPN containing poly(antimony acrylate) and poly(arsenic acrylate).

2 Experimental

Purified solvent and divinyl benzene were used as received. Benzoyl peroxide was recrytallized in chloroform (M.P. = 103°C).

2.1 Synthesis of Metal Acrylate

The metal acrylates were synthesized by refluxing a suspension of acrylic acid triphenyl metal (M = As, Sb) in acetone with constant stirring for 22 h, at 25°C. The evaporation of excess solvent yielded the corresponding metal acrylate. For e.g., Arsenic acrylate (22). The reaction is as shown below:



(1)

2.2 Synthesis of IPN

Polymerization runs were carried out in a borosilicate glass which was irradiated with a high pressure mercury lamp (Philips 125 W) at a distance of 25 cm, 440 nm radiation. The light intensity was measured using a Lutron LX-101 LUXMETER and it was found to be 2.53×10^2 Lux. A series of IPN's were synthesized by a systematic variation of concentration of poly(antimony acrylate) (base M) (Table 2); arsenic acrylate (Table 3); arsenic DVB (Table 4); and BPO (Table 5) in DMF for 12 h at a light intensity of 2.5×10^2 Lux.

2.3 Characterization of IPN

2.3.1 Gel Percent

The soluble or uncrosslinked component was removed with the help of a soxhlet extractor using DMF as solvent. The percentage extractable material is calculated according to the following relationship:

$$\%\text{Extractable material} = \frac{W_b - W_a}{W_a} \times 100 \qquad (2)$$

Where, W_b = weight of IPN before extraction; W_a = weight of IPN after extraction.

Table 2. The effect of [PSbA] (base M) on IPN properties

Effect of [PSbA](base M) on IPN properties $[AsA] = 3.48 \times 10^{-3}$ mol/100 ml; $[DVB] = 2.30 \times 10^{-4}$mol/100 ml; $[BPO] = 1.37 \times 10^{-3}$mol/100 ml. Time = 12 h; Light Intensity = 2.52×10^2Lux					
IPN	$[PSbA](baseM) \times 10^{-3}$ (mol/100 ml)	% Yield	% Swelling in DMF	Mc In DMF	Youngs Modulus$\times 10^{-1}$ (dynes/cm^2)
IPN-1	1.49	34	97	119	2006655
IPN-2	2.49	36	102	124	2066547
IPN-3	3.49	40	113	133	2163156
IPN-4	4.49	44	117	136	2193802
IPN-5	5.49	46	121	140	2240359

Table 3. Showing the effect of [AsA] on IPN properties

IPN	[AsA] $\times 10^{-3}$ (mol/100 ml)	Yield %	% Swelling in DMF	M_c in DMF
IPN-6	1.16	22	112	132
IPN-7	2.49	28	105	126
IPN-8	3.49	34	97	119
IPN-9	4.49	38	82	106
IPN-10	5.49	43	79	103

[PSbA] (base M) = 1.49×10^{-3} mol/100 ml; [DVB] = 2.30×10^{-4} mol/100 ml; [BPO] = 1.37×10^{-3} mol/100 ml. Time = 12 h; Light intensity = 2.52×10^2 Lux.

2.4 *Swelling Properties*

Swelling data were calculated by soaking the sample in different polar and non-polar solvents such as DMF, DMSO, dioxane, benzene, toluene until an equilibrium weight was achieved (~24 h).Weight measurements were made by blotting the sample dry and immediately weighing them. The swelling solvent was then removed by heating the samples to 60°C under vacuum, until an equilibrium weight was achieved. The percentage swelling is calculated according to the following relationship (23):

$$\%\text{Swelling} = \frac{W_s - W_d}{W_d} \times 100 \tag{3}$$

Where, W_s = weight of swelled IPN; W_d = weight of dry IPN.

The degree of crosslinking is defined as the number of crosslinks per unit volume of polymer. The following relation is used for calculation of degree of crosslinking (24).

$$C = \frac{n}{2} = \frac{d}{2M_c} \tag{4}$$

where, C = degree of crosslinking; d = density of network; M_c = average molecular weight between crosslinks.

Table 4. Showing the effect of [DVB] on IPN properties

IPN	[DVB] $\times 10^{-4}$ (mol/100 ml)	Yield %	% Swelling in DMF	M_c in DMF
IPN-11	1.15	19	103	125
IPN-12	2.30	22	97	118
IPN-13	3.46	28	90	113
IPN-14	4.61	32	83	107

[PSbA] (base M) = 1.49×10^{-3} mol/100 ml; [AsA] = 3.48×10^{-3} mol/100 ml; [BPO] = 1.37×10^{-3} mol/100 ml. Time = 12 h; Light intensity 2.52×10^2 Lux.

Table 5. The effect of [BPO] on IPN properties

IPN	[BPO] $\times 10^{-3}$ (mol/100 ml)	% Yield	% Swelling in DMF	M_c In DMF
IPN-15	1.37	22	85	108
IPN-16	2.75	26	92	115
IPN-17	4.13	31	97	119
IPN-18	5.50	36	101	122

[PSbA](base M) = 1.49×10^{-3} mol/100 ml; [DVB] = 2.30×10^{-4} mol/100 ml; [AsA] = 3.48×10^{-3} mol/100 ml. Time = 12 h; Light intensity = 2.52×10^2 Lux.

2.5 *Crosslink Density*

The crosslink density of the network was determined by using the swelling data of IPN in DMF with the help of Flory Rehner equation (25, 26) given as:

$$\frac{1}{M_c} = \frac{-\ln(1 - V_p) + V_p + X_{12}V_p^2}{\rho V_1(V_p^{1/3} - V_p/2)} \tag{5}$$

Where, M_c = average molecular weight of networks between crosslinks; ρ = density of network; V_1 = molar volume of solvent; V_p = volume fraction of polymer in swollen gel; X_{12} = polymer solvent interaction parameter, calculated as 0.342 by the following expression (27):

$$X_{12} = B + \frac{V_1}{RT}(\delta_p - \delta_s) \tag{6}$$

Where, δ_p and δ_s are solubility parameters of the polymer and the swelling solvent. B = lattice constant. The value of which is taken as 0.34 (27):

The crosslink density further paves a path for determining Young's modulus or stress –strain relationship by the following Equation (24):

$$E = 3nRT(V_p)^{1/3} \tag{7}$$

Where, V_p = volume fraction of polymer in swollen gel; n = crosslink density; R, T are constants.

2.6 *Complex Formation*

The ability of two polymers to form a complex depends upon the solvent, on the concentration ratio of polymers in the mixture, on their total concentration and on time. Preparation of polymer samples, their characterization, procedure used in measurement has been reported in earlier papers (29–31).

To find out the strength of interaction between polymers, the interaction constant k_{AB} of a mixture of stereo complex polymers of poly(antimony acrylate) and poly(arsenic acrylate) is evaluated. In this study we describe the determination of viscometeric parameter k_{AB} at 30°C, which characterizes mutual interaction between two polymers at this temperature as an analogy of a solution of binary mixture of compatible polymers in a common solvent. For this purpose, the method of polymer solvent was employed (28–33). According to this method, the intrinsic viscosity of the polymer A $(\eta_A)_B$ (polyarsenic acrylate) is determined

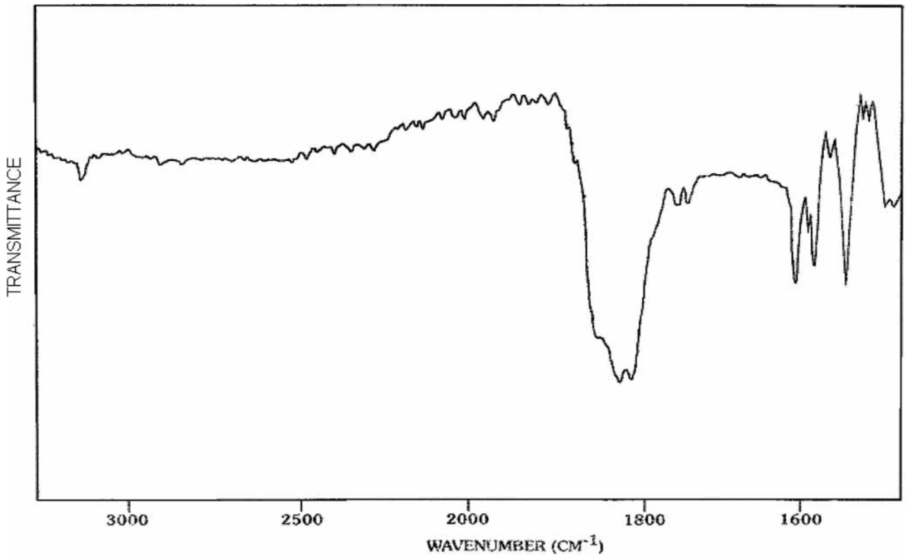


Fig. 1. IR spectrum of IPN.

in a number of various concentrated solutions of polymer B(polyantimony acrylate) in DMF which serves as a series of solvents and vice versa. For $(\eta_A)_B$ we have (29),

$$(\eta_A)_B = \frac{(\eta_A)}{(\eta_r)B}[1 + 2k_{AB}(\eta_B)C_B + \cdots] \tag{8}$$

Where $(\eta_r)_B$ is the relative viscosity of the polymer B at concentration C_B and (η_A), (η_B) are intrinsic viscosities of the polymer A and B. The constant k_{AB} is a criterion of interaction. It may be obtained from the graph of f vs. reduced concentration (η_A) C_B giving directly k_{AB} from the intercept on the y axis (Fig. 3), where

$$f = \frac{[\eta_A]_B[\eta_r]_B}{[\eta_A]} - \frac{1}{2} \tag{9}$$

$$C = [\eta_A]C_B \tag{10}$$

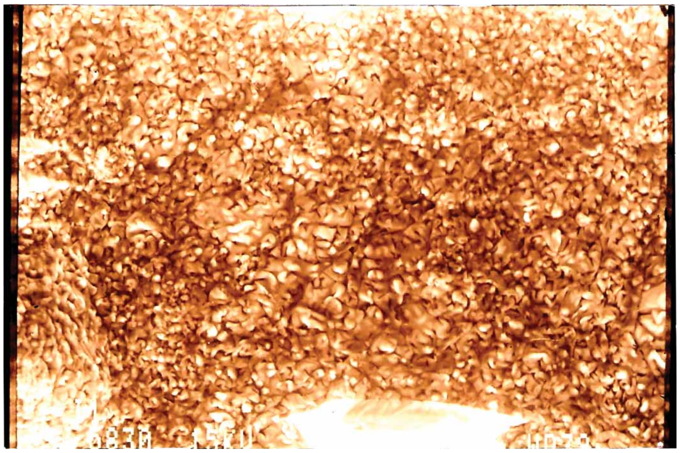


Fig. 2. SEM photograph of IPN-3 at magnification of 1500 times.

2.7 *SEM Morphology*

The morphology of IPN's was studied by scanning electron microscopy (SEM), which had the resolution of 50 A° and depth of field was 30μ. Samples were mounted on a SEM stub by graphite adhesive paste and coated with gold in a SEM coating unit. The samples were then scanned in a JEOL JSM 840A electron microscope.SEM also helps to estimate the percentage of metals present in the sample.

2.8 *Thermogravimetric Analysis*

Thermogravimetric analysis was carried out using a TGA V5 1A Dupont2100 at a heating range of 10°C/min under a nitrogen atmosphere. The activation energy (Ea) and order of the reaction was calculated from the Coats and Redfern equation (34, 35) given as:

$$\log g\frac{(\alpha)}{T^2} = \frac{E_a}{2.3RT} + \log\frac{ZA}{BE(1-(2RT/E_a))} \tag{11}$$

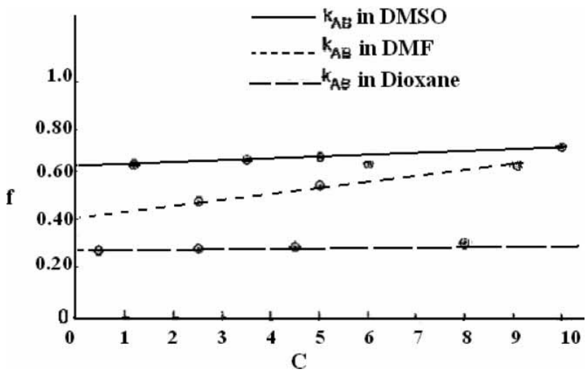
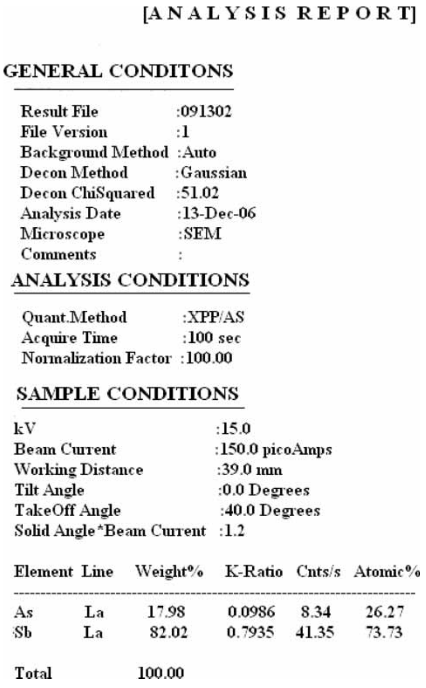


Fig. 3. Graph between f v/s C, where C is reduced concentration.



[ANALYSIS REPORT]

GENERAL CONDITONS

Result File :091302
File Version :1
Background Method :Auto
Decon Method :Gaussian
Decon ChiSquared :51.02
Analysis Date :13-Dec-06
Microscope :SEM
Comments :

ANALYSIS CONDITIONS

Quant.Method :XPP/AS
Acquire Time :100 sec
Normalization Factor :100.00

SAMPLE CONDITIONS

kV :15.0
Beam Current :150.0 picoAmps
Working Distance :39.0 mm
Tilt Angle :0.0 Degrees
TakeOff Angle :40.0 Degrees
Solid Angle*Beam Current :1.2

Element	Line	Weight%	K-Ratio	Cnts/s	Atomic%
As	La	17.98	0.0986	8.34	26.27
Sb	La	82.02	0.7935	41.35	73.73
Total		100.00			

Fig. 4. Spot analysis of IPN.

Where g = $-\log[(1-\alpha)\,1/n]$; Z = pre-exponential factor; T = Temperature; B = linear heating rate; R = Gas constant.

The plot of $\log[g\ \alpha/T^2]$ vs. $(1/T) \times 10^3$ gives a linear curve, whose slope is equal to $-Ea/2.3RT$ and its intercept corresponds to $\log_{10} 2A/(B\Delta E)(1-2RT/E_a)$.

3 Results and Discussion

Structural evidence for IPN comes from IR spectrum (Fig. 1) indicating characteristic frequencies of carbonyl groups ($>C{=}O$) at 1730–1740 cm^{-1}, and at 3020 cm^{-1} of aromatic ring of DVB.Antimony and Arsenic was confirmed by spot analysis (Fig. 4) and also through SEM (Fig. 2).

3.1 Complex Formation

The determination of k_{AB} values which is associated with the interaction of unlike polymer molecules in the field of shear forces and is similar to the Huggins coefficient k_A and k_B. In general, the Huggins coefficient originates from a superposition of several types of interactions, hydrodynamic and thermodynamic interactions being the most important. The thermodynamic contribution includes, the intramolecular excluded volume effect, resulting in an expansion of the coil and, the intermolecular excluded volume effect, which results in contraction of the coil. The k_{AB} values characterizes the intensity of complexation in different solvents namely DMSO, DMF, dioxane. The results are summarized in Table 1. The value of mutual interaction coefficient k_{AB} for the given system A = PAsA and B = PSbA can be determined by extrapolating these lines. The common intercept was obtained on the y-axis (Fig. 3), and k_{AB} = 0.60(DMSO); 0.42(DMF); 0.26 (dioxane). The k_{AB} values are low in comparison to those reported earlier. These values indicate that the interaction between PSbA and PAsA is weak and involves Vander

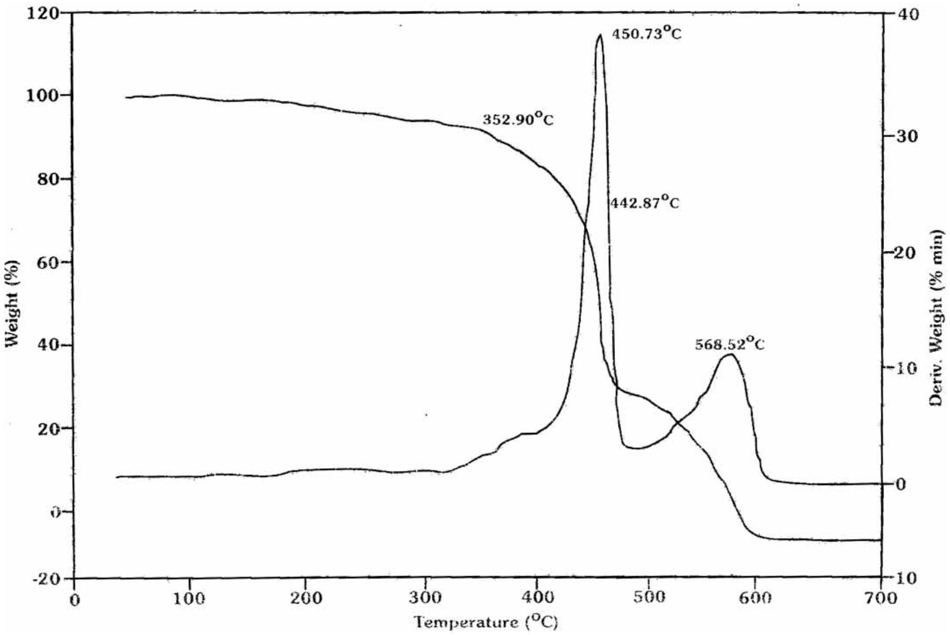


Fig. 5. Thermo gravimetric analysis curves IPN sample containing PSbA and PAsA.

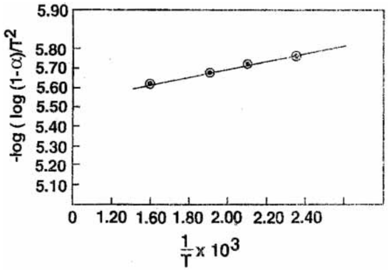
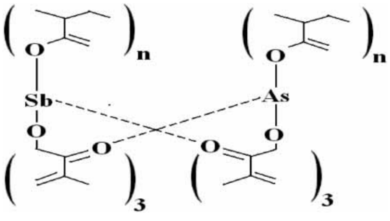


Fig. 6. Graph between –log [log $(1 - \alpha)/T^2$] vs. $1/T \times 10^3$.

Waals forces. The higher value of k_{AB} in DMSO ($k_{AB} = 0.60$) in comparison to DMF ($k_{AB} = 0.42$) and dioxane ($k_{AB} = 0.26$), shows that the strength of complexation is stronger in DMSO, than in DMF and dioxane (weaker) and is related to the dielectric constant of the solvents. The reaction involving complex formation is shown below



(12)

3.2 Effect of Crosslinker (DVB)

The increase in concentration of DVB increases the percentage extractable material (Table 4). The reason behind is that, due to increase in crosslinking agent, crosslinking and consequently percentage yield increases. The percentage swelling of IPN in different solvent and Mc are inverse function of [DVB]. This shows that increase of [DVB] increases crosslinking level which result in decrease of swelling and Mc.

3.3 Effect of Composition

The effect of composition of PSbA follows a logical trend since an increase in [PSbA] results in increased swelling and Mc (Table 2). This implies that the presence of PSbA restricts crosslinking of PAsA.This restriction is due to overall decrease in concentration of crosslinking sites of AsA. As the poly(antimony acrylate) increases, the probability of grafting by AsA also increases, which produces some degree of crosslinking between the two polymers. Also, it is observed that an increase in concentration of PSbA increases the value of Young's modulus (Table 2).This result predicts that the increase in [PSbA] increases the modulus value and, therefore mechanical strength of the polymer. A similar explanation is given for the percentage swellings and Mc, which are inverse function of [AsA] (Table 3).

3.4 Effect of Initiator

Table 5 presents the data of the effect of the concentration of benzoyl peroxide on swelling and Mc of these IPN's. The data shows that both swelling and Mc increases with an increase of BPO concentration.

3.5 Morphology

The scanning electron microscopy is an excellent tool for the determination of surface morphology. The SEM study (Fig. 2) reveals that IPN exhibit characteristic dual phase morphology at a magnification of 1500 times, indicating crosslinking between the two polymers, thus showing complex structure.

3.6 Thermogravimetric Analysis

IPN sample containing PSbA and PAsA was stable up to 352°C and started loosing weight above this temperature (Fig. 5). Rapid decomposition of the sample was observed between 442°C–460°C and almost complete volatization of the polymer occurred around 590°C. Initial weight loss of 25% was observed around 442°C. The activation energy, calculated, from the slope of linear graph plotted between –log[log$(1 - \alpha)/T^2$] vs. $1/T \times 10^3$ (Fig. 6), is 15 KJ/mol.

4 Conclusions

The first conclusion obtained is, that the complex formation occurring between the two polymer coils, undergoes contraction, involving weak Vander Waals forces. Secondly, we found that M_c is directly proportional to the concentrations of linear polymer and initiator. Furthermore, Mc was also found to be inversely proportional to concentrations of monomer and the crosslinker. Finally we found that the phase separation also varies directly with the concentration of linear polymer.

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