

Poly (vinyl toluene) and Poly (arsenic acrylate) based interpenetrating Polymer Network : Synthesis and Characterization

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Abstract

A series of IPN based on poly (vinyl toluene) and poly (arsenicacrylate) have been synthesized by sequential mode of synthesis, using benzoyl peroxide as initiator, in dimethyl formamide and divinylbenzene as crosslinking agent. The values of coefficient of interaction (k_{AB}) between the two polymers in different solvents such as DMSO, DMF, dioxane reflect contraction of the polymer coils in the order DMSO, DMF, dioxane. The scanning electron microscopy reveals a dual phase morphology of poly (vinyl toluene)(PVT) and arsenic acrylate. The IR spectrum indicates characteristic frequency of ester group of acrylate between 1680cm^{-1} - 1735cm^{-1} . The band at 3030cm^{-1} of aromatic ring predicts that both the components are mutually entangled with each other. The properties like percentage swelling, average molecular weight between crosslinks (M_c), increases with concentration of poly(vinyl toluene) and benzoyl peroxide. However, these properties decreases with increase in concentration of arsenic acrylate and divinyl benzene. The value of activation energy, calculated from thermogravimetric analysis, is 20 KJ/mol.

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 much more complex combination of different polymer structures, structural states in composite materials are Interpenetrating polymer networks (IPNs). IPNs are composed of two (or more) chemically distinct networks held together predominantly with the help of crosslinker by their trapped mutual entanglements rather than by covalent bond grafting. Millar¹, Sperling²⁻⁴, Frisch⁵⁻⁶, Liptov⁷ and coworkers are pioneers in the field of IPN. There is voluminous scientific literature concerning IPN's based on polyurethanes⁸, methylene bis acrylamide and vinylterrocene⁹. A search of literature reveals that reports on synthesis of IPN using d-block elements (such as Zn, Cu, Cr) in the form of acrylates with vinyl monomer(acrylonitrile)¹⁰⁻¹² and two metal acrylate IPNs¹³⁻¹⁴ have appearance in various polymer journals. However, IPN formation using p-block elements such as arsenic in the form of metal acrylate with novel vinyl monomer p-vinyl toluene has yet not been reported.

The present communication, therefore, highlights synthesis and characterization of mechanically strong novel IPNs of poly(vinyl toluene) crosslinked with arsenic acrylate.

Experimental :

Purified solvents, monomer and divinyl benzene have been used. Benzoyl peroxide (BPO) (M.P=103°C) is recrystallised in chloroform.

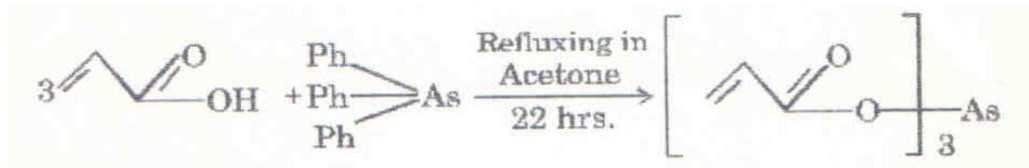
Synthesis of poly(vinyl toluene) :

A solution containing vinyl toluene (Fluka no. 90965) and BPO as initiator in dimethylformamide (DMF) were kept for two hours at $65^{\circ}\text{C} \pm 1^{\circ}\text{C}$ under an inert atmosphere of nitrogen. The polymer, was precipitated with methanol and dried to constant weight.

Synthesis of metal acrylate :

- (a) **Arsenic acrylate:** The arsenic acrylate, was synthesized by the reported method's, by refluxing a suspension of acrylic acid and triphenylarsine (Merck no. Art. 821199) (30 wt% stoichiometric excess), using acetone as solvent for 22 hrs. The evaporation of excess solvent yielded arsenic acrylate.

Synthesis of IPN



A

series of 18 IPN's have been synthesized by systematic variation of concentration of poly (vinyl toluene) (IPN1-5, Table II); arsenic acrylate (IPN 6-10, Table III); BPO (IPN 11-14, Table IV) and DVB (IPN 15-18, Table V), in DMF for 90 min. at $85^{\circ}\text{C} \pm 1^{\circ}\text{C}$ under a blanket of nitrogen. Finally IPN's were vacuum dried until a constant weight was obtained.

Characterisation of IPN

The soluble or uncrosslinked component of IPN was removed with the help of soxhlet extractor. The percentage extractable material has been calculated according to the following equation.

$$\% \text{ extractable material} = \frac{W_b - W_a}{W_a} \times 100$$

W_b = weight of IPN before extraction
 W_a = weight of IPN after extraction

Swelling properties :

Swelling data has been calculated by soaking the above sample in different protic and aprotic solvents such as dimethyl formamide; dimethylsulphoxide, dioxane, benzene,

until an equilibrium weight was achieved (- 24hrs). The swelling solvent was then removed by heating the samples to 60°C under vacuum, until an equilibrium weight was achieved. The percentage swelling has been calculated according to the following relationship¹⁶.

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

W_s = weight of swollen IPN.

W_d = weight of dry IPN.

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 equation¹⁷⁻¹⁸.

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

Where,

M_c = average mol wt. of network 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 by the following expression".

$$X_{12} = B + \frac{V_1}{RT} (\delta_p - \delta_s)^2$$

Where δ_p and δ_s = solubility parameters of polymer and swelling solvent.

B = lattice constant, the value of which is taken as 0.34

The crosslink density further paves path for determining young's modulus or stress,-strain relationship by the following equation¹⁹.

$$E = 3n RT (V_p)^{1/3}$$

V_p = vol. fraction of polymer in swollen gel.

n = crosslink density

R, T are constant.

Complex formation

The ability of the 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.

Solutions used in viscosity measurements were prepared in the following way²⁰⁻²¹. The Poly(vinyl toluene) solution, in dioxane, was used as the solvent and dissolved to give a series of solutions having concentrations ranging from 2.5×10^{-4} to 10×10^{-4} g/cm³. After dissolution and filtration, the second polymer poly(arsenic acrylate) (conc. 10×10^{-4} g/cm³) was dissolved in these solutions. According to this method, the intrinsic viscosity of the polymer A, $([\eta_A])_B$ poly(arsenicacrylate) is determined in a number of solutions of different concentration of polymer B (PVT) which serves as a series of solvents. For $([\eta_A])_B$ we have²⁰

$$[\eta_A]_B = [\eta_A] / [\eta_r]_B [1 + 2k_{AB} (\eta_B) C_B + \dots]$$

where $[\eta_r]_B$ is the relative viscosity of the copolymer at concentration (C_B).

$[\eta_A]$, $[\eta_B]$ are intrinsic viscosities of the poly (arsenicacrylate) and copolymer.

The plot of f vs the reduced concentration C gives the value of k_{AB} from the intercept on the y axis (Fig.2) where

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

$$C = [\eta_B] C_B$$

SEM Morphology:

The morphology of the IPN's has been studied by the scanning electron microscopy (SEM) which has a resolution of 50 \AA and depth of field 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 840 A scanning electron microscope.

Thermo Gravimetric Analysis (TGA)

Thermogravimetric analysis was carried on TGA V5 1A Dupont 2100 at heating range of $20^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The activation energy (E_a) and order of a reaction was calculated from Coats and Redfem equation²².

$$\log g (\alpha)/T^2 = \frac{E_a}{2.3RT} + \log_{10} \frac{Z A}{B E} (1 - \frac{2RT}{E_a})$$

$$g = -\log [(1-\alpha)^{1/n}]$$

where Z = pre exponential factor

T = temperature

B = linear heating rate.

R = gas constant

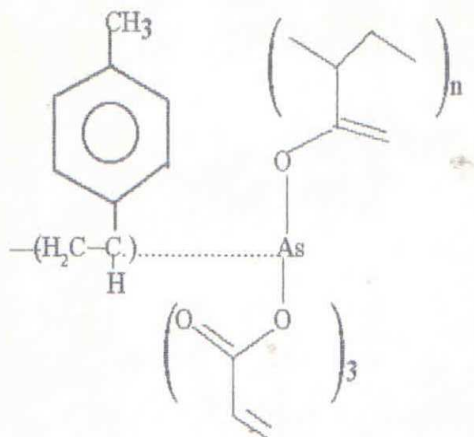
The plot of $\log [g \alpha/T^2]$ versus $1/T \times 10^3$ gives a linear curve, whose slope is equal to $-E_a/2.3RT$ and its intercept corresponds to $\log_{10} \frac{Z A}{B E} (1 - \frac{2RT}{E_a})$.

RESULTS AND DISCUSSION

The structure of IPN is evidenced from IR spectrum (Fig.1) indicating characteristic frequencies of ester group of acrylate between 1680 cm^{-1} - 1735 cm^{-1} ; around 3030 cm^{-1} of aromatic ring. The -CH stretching and bending band of -CH₂ group of PVT at 2962 cm^{-1} and 1470 cm^{-1} . The presence of arsenic was confirmed by spot analysis curve (obtained by computer) (Fig.2), SEM (Fig.3) and qualitative analysis²³, in which the ash obtained by burning the polymer was dissolved in ammonium molybdate and nitric acid solution. The formation of yellow precipitate of ammonium arsenomolybdate, was obtained on boiling, which was insoluble in nitric acid, confirmed the presence of arsenic in polymer.

Complex Formation:

The determination of k_{AB} values, which are 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 has been calculated. 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 intermolecular excluded volume effect which results in contraction of the coil. The k_{AB} values characterise the intensity of complexation in different solvents namely DMSO, DMF, dioxane. The results are summarised in Table I. The value of mutual interaction coefficient k_{AB} for the given system A = PAsA and B = PVT was determined by extrapolating these lines. The common intercept was obtained on the y axis (Fig.4) and $k_{AB} = 0.29$ (DMSO); 0.17 (DMF); 0.11 (dioxane). These values indicate that the interaction between PVT and PAsA involves vander waal's forces. The higher value of k_{AB} in DMSO ($k_{AB} = 0.29$) in comparison to DMF ($k_{AB} = 0.17$) and dioxane ($k_{AB} = 0.11$), show that the strength of complexation is stronger in DMSO, than DMF and dioxane (weaker) and is related to the dielectric constant of the solvents.



After the formation of complex, emphasis is laid on the effect of concentration of PVT, PAsA, DVB, BPO on properties such as swelling, crosslink density, young's modulus, phase behaviour.

Effect of Composition :

The effect of composition of poly(vinyl toluene) purports that an increase in $[PVT]_{(base\ M)}$ (0.042 -0.155 mole/lit.) results in increased swelling(76 - 99%) and M_c value (2252-3683) in DMF (Table II). This implies that the presence of poly (vinyl toluene) restricts crosslinking of arsenic acrylate. This restriction is due to overall decrease in concentration of crosslinking sites of arsenic acrylate with increase of poly(vinyl toluene). As the $[PVT]$ increases, it produces some degree of crosslinking in PAsA to some extent. A similar explanation can be given for percentage swelling and M_c , which, are inverse function of $[AsA]$ (Table III),It is also observed from the data of Table III, that, with increase in concentration of arsenic acrylate the value of young's modulus also increases(1.65 - 6.22 dynes/cm²) in DMF, thereby increasing mechanical strength of the polymer.

Effect of Initiator [BYO]:

Table IV presents data on the effect of [benzoyl peroxide] on swelling and M_c of IPN. The data shows that both swelling (38-72%) and M_c values (992-2068) in DMF increases with increase of $[BP0](0.068- 2.75 \times 10^{-2})$ mol/lit.

Effect of Crosslinker (DVB):

Table V represents that as $[DVB]$ increases, the percentage extractable material increases. The reason for this is that higher concentration of crosslinking agent increases crosslinking and consequently percentage yield. The percentage swelling of IPN in different solvents and M_c are inverse function of $[DVB]$. This shows that increase of $[DVB](0.011- 4.61)$ mol/lit. increases crosslinking level which results in decrease of swelling (71-50^o/o) and M_c value (2077-1161) in DMF.

Morphology and Thermal property:

The scanning electron microscope is an ideal tool for the examination of surface morphology. The SEM study (Fig. 3) reveals that IPN exhibit a characteristic morphology at a magnification of 2500 times; where the PVT constitutes the continuous phase and the second component PAsA constitutes the dark phase, thus showing complex structure.

Thermogravimetric analysis:

IPN sample containing (PVT— PAsA) is stable upto 232°C(Fig.5) and started losing weight above this temperature. Rapid decomposition is observed at 439°C - 470°C and almost volatilisation of polymer occurred above 590°C.

The activation energy, calculated from the slope of Linear graph plotted between $-\log [1 - \alpha]/T^2$ Vs $1/T \times 10^3$ (Fig.6), is 20 KJ/ mol.

Conclusions:

The conclusions are as follows

- 1) Complex formation occurs between the two polymer coils.
- 2) M_c is a direct function of [PVT], [BPO] where as inverse function of [Ask' and [DVB].
- 3) IPN's show phase separation and high thermal stability.

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Table 1.

Intrinsic viscosity in polymer solvent (PAsA/PVT)

Temperature = 306C±1

Solution in DMSO	
[PVT]x10 ⁴ gm cm ⁻³ k _{AB}	(\square) _A _B
2.5	0.33
5.0	0.37
0.29	
7.5	0.40
10.0	0.45
Solution in DMF	
2.5	0.16
5.0	0.18
0.17	
7.5	0.19
10.0	0.20
Solution in Dioxane	
2.5	0.13
5.0	0.16
0.11	
7.5	0.17
10.0	0.22

A = PAsA
B = PVT

Table II**Effect of Polyvinyl toluene)_(base M) on IPN properties**

S.No.	[PVT] _(base M) x10 ² mol/lit	% yield	% swelling in DMF	Mc in DMF
IPN-1	4.23	21	76	2252
IPN-2	7.06	24	84	2712
IPN-3	9.88	32	88	2908
IPN-4	12.7	38	96	3320
IPN-5	15.5	42	99	3683

$$[\text{AsA}] = 1.01 \times 10^{-2} \text{ mol/lit}$$

$$[\text{BP0}] = 1.37 \times 10^{-2} \text{ mol/lit.}$$

$$[\text{DVB}] = 2.30 \text{ mol/lit.}$$

$$\text{Temperature} = 85^{\circ}\text{C} \pm 1$$

$$\text{Time} = 90 \text{ min.}$$

Table III**Effect of variation of arsenic acrylate on IPN**

S.No.	[AsA] x10 ² mol/lit	% yield	% swelling in DMF	M _c in DMF	Young modulus (dynes/cm ²)
IPN-6	1.01	59	82	2822	1.65
IPN-7	2.71	55	79	2541	1.87
IPN-8	4.06	23	60	1588	2.98
IPN-9	5.42	22	46	1064	4.97
IPN-10	6.77	20	41	867	6.22

$$[\text{PVT}]_{(\text{base M})} = 4.23 \times 10^{-2} \text{ mol/lit}$$

$$[\text{BP0}] = 1.37 \times 10^{-2} \text{ mol/lit.}$$

$$[\text{DVB}] = 2.30 \text{ mol/lit.}$$

$$\text{Temperature} = 85^{\circ}\text{C} \pm 1$$

$$\text{Time} = 90 \text{ min.}$$

Table IV
Effect of [BPO] on IPN properties

S.No.	[BPO] $\times 10^2$ mol/lit	% yield	% swelling in DMF	M_c in DMF
IPN-11	0.068	21	38	2252
IPN-12	1.37	41	47	2712
IPN-13	2.06	48	60	1588
IPN-14	2.75	52	72	3683

$$[\text{PVT}]_{(\text{base M})} = 4.23 \times 10^{-2} \text{ mol/lit}$$

$$[\text{AsA}] = 1.01 \times 10^{-2} \text{ mol/lit}$$

$$[\text{DVB}] = 2.30 \text{ mol/lit.}$$

$$\text{Temperature} = 85^\circ\text{C} \pm 1$$

$$\text{Time} = 90 \text{ min.}$$

Table V
Effect of [DVB] on IPN properties

S.No.	[DVB] mol/lit	% yield	% swelling in DMF	M_c in DMF
IPN-15	0.01	30	71	2207
IPN-16	2.30	48	60	1588
IPN-17	3.46	52	54	1360
IPN-18	4.61	63	50	1161

$$[\text{PVT}]_{(\text{base M})} = 4.23 \times 10^{-2} \text{ mol/lit}$$

$$[\text{AsA}] = 1.01 \times 10^{-2} \text{ mol/lit}$$

$$[\text{DVB}] = 2.30 \text{ mol/lit.}$$

$$\text{Temperature} = 85^\circ\text{C} \pm 1$$

$$\text{Time} = 90 \text{ min.}$$

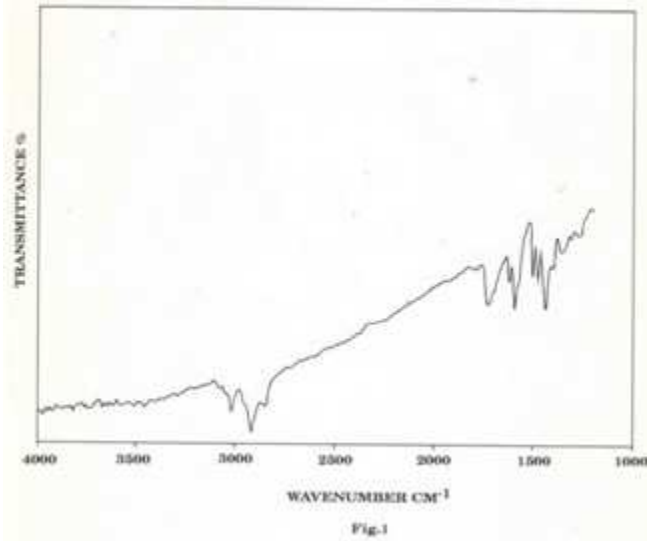
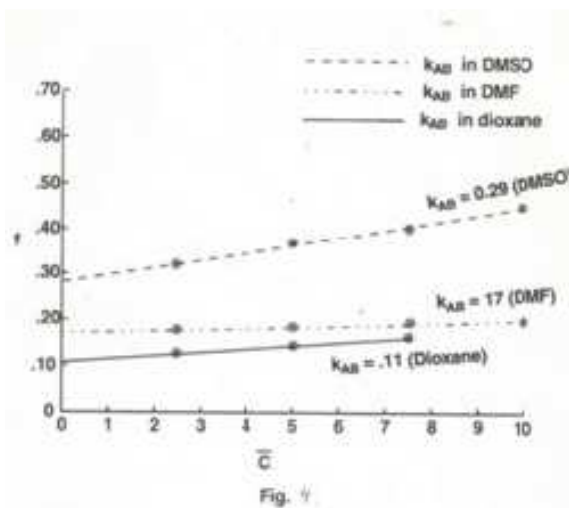


Fig.3



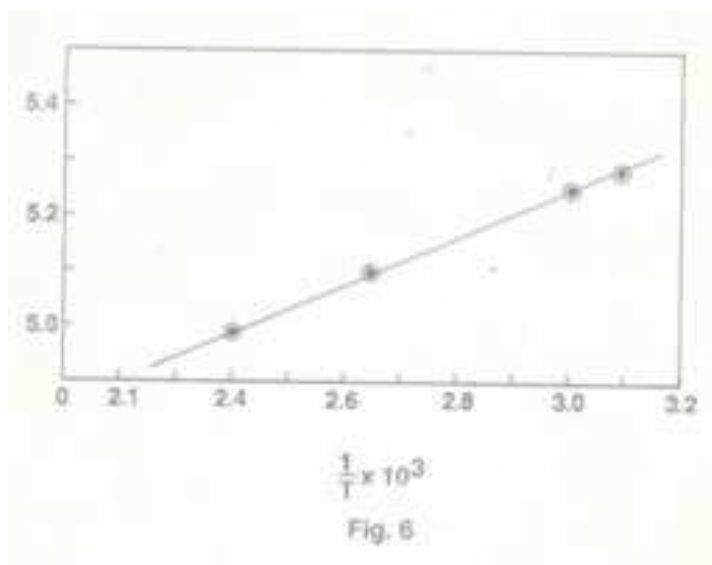
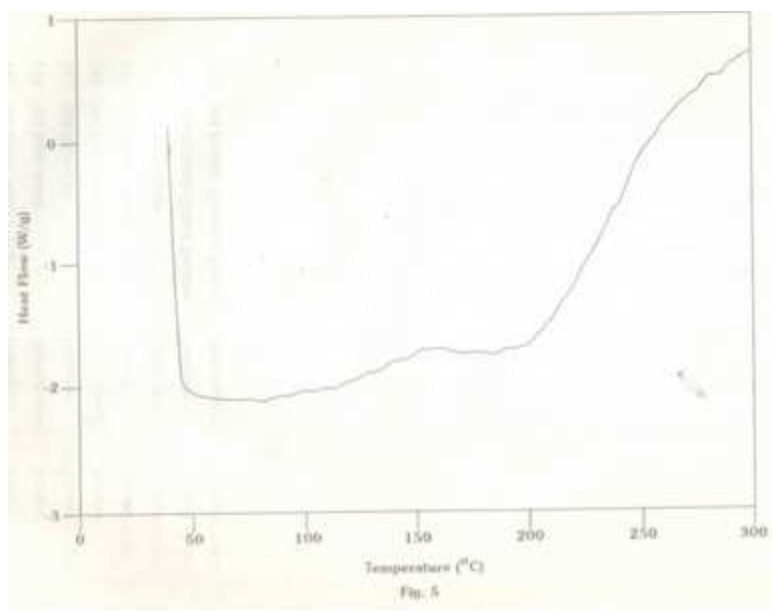


TABLE CAPTION

1. Intrinsic viscosity in polymer solvent (PAsA/PVT)
2. Effect of Polyvinyl toluene)(base M) on IPN properties
3. Effect of variation of arsenic acrylate on IPN
4. Effect of [BPO] on IPN properties
5. Effect of [DVB] on IPN properties

FIGURE CAPTION

1. Fig.1: IR spectrum of IPN-6.
2. Fig. 3: SEM photograph of IPN-6 at magnification 250 times.
3. Fig. 4: A graph plotted between f Vs C.
4. Fig. 5: TGA curve of IPN-3.
5. Fig. 6: Graph plotted between— $\log [\log(1-\alpha)/T^2]$ Vs $1/T \times 10^3$