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Interpenetrating Polymer Networks as Binders for Solid Composite Propellants

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ABSTRACT

A new family of polymeric binders for solid composite propellants is proposed, based on two component interpenetrating polymer networks (IPNs). These networks comprise two different polyurethanes based on hydroxy terminated polybutadiene and ISRO polyol interpenetrated with two different vinyl polymers, viz poly methyl methacrylate and polystyrene. The networks synthesised by the simultaneous interpenetrating technique have been characterised for their properties, such as stress-strain, density, viscosity, thermal degradation, and heat of combustion. Phase morphologies have been determined using electron microscopy. Suitable explanations have been adduced to rationalise the properties of IPNs in terms of their structures and chain interactions. A study of the mechanical properties and burning rates of the ammonium perchlorate (AP)-based solid propellant using the newly synthesised IPNs as binders, has been carried out. The results show that both mechanical strength and burning rate of solid propellants could be suitably modified by simply changing the nature and/or the ratio of the two interpenetrating polymer components.

INTRODUCTION

Solid propellant rocket motors draw the attention of investigators because of their operational simplicity. Both combustion and mechanical properties of these motors are much influenced by the nature of the oxidiser and elastomeric binder used therein[1,2]. Modifications in composition are continuously being made to alter the properties of existing propellants in an attempt to increase the structural integrity and/or specific impulse, modify the burning rate and decrease the incidence of combustion instability of the rocket engine. Keeping pace with the growth, the polymeric binders have undergone profound technological improvement[3]. In the last decade, the relatively poor economics of new polymer production in relation to the need for new cost-effective materials for specific applications, has generated wide interest in multicomponent polymer systems. A right combination of the components, often available readily, may result in desired properties of the final product, without invoking new synthesis. The new multicomponent materials may be obtained in the form of blends, block and graft copolymers, or interpenetrating networks, all of which are usually characterised by the presence of two or more polymeric phases in the solid stage[4]. Of the various methods of mixing two kinds of polymer materials, the use of interpenetrating polymer networks (IPNs) has been considered in the present study.

The purpose of selecting the IPNs used in the present investigation is severalfold; blended polymers often experience phase stability problems due to lack of permanent chemical bonding between the two polymer phases. The graft and block copolymers are more expensive than simple blends and certainly more restricted in their range of composition[5]. IPNs are a relatively novel and special type of chemical combination of different polymer networks in which permanent entanglements are formed with simultaneous or sequential cross-linking of the component networks[6,7]. It is generally believed that the interpenetrated and entangled chains of the two polymers network can increase the phase stability and

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therefore enhance the mechanical properties of the final product. Moreover, this seems to be the only way to blend two cross-linked polymers.

In this article, the synthesis and characterisation of two components, viz IPNs comprising polyurethane (PU) and poly methyl methacrylate (PMMA) and PU-polystyrene (PS) synthesised by the simultaneous polymerisation technique have been discussed. The characterisation of IPNs include morphology, physical properties, thermal behaviour and heat of combustion of unfilled IPN systems, and mechanical properties and burning rates of propellant systems using the newly synthesised IPNs as binders.

2. EXPERIMENTAL

2.1 Materials

Hydroxy terminated polybutadiene (HTPB) and ISRO polyol (ISPO) were obtained from VSSC, Thiruvananthapuram. They were kept in an oven at 80 °C for 1 hr to evaporate the moisture before use. Methyl methacrylate (MMA) (Merck Germany) and styrene (Burgoyne Urgidges and Co, India) were used after purification and distillation under reduced pressure. 2,4-toluene diisocyanate (TDI), dibutyl tin dilaurate (DBTDL), divinyl benzene (DVB) (Aldrich, USA), and glycerol (E. Merck (India) Limited) were used without further purification. The commercially available (Analar or equivalent grade) benzoyl peroxide (BPO), benzoic acid, ammonium perchlorate (AP) and sodium hydroxide, were used as such.

2.2 Synthesis

2.2.1 Polyurethane

A resin kettle equipped with a nitrogen inlet, magnetic stirrer and thermometer was charged with 1 equivalent HTPB, to which 1.5 equivalent TDI (*NCO/OH* = 1.5) was added slowly with constant stirring. DBTDL was used as a catalyst. The reaction was carried out under nitrogen at 70 °C. The PU prepolymer was then homogeneously mixed with 0.1 equivalent glycerol for 5 min. The air entrapped during mixing was removed by applying vacuum for 5-10 min. The mixture was then cast in a rectangular glass mold with silicon oil coating for easy demolding and cured at 60 °C for 16 hr and 80 °C for 4 hr to obtain polyurethane elastomers.

2.2.2 Vinyl Polymers

A resin kettle equipped with a nitrogen inlet, stirrer and thermometer was immersed in a water bath. It was charged with desired amount of MMA monomer, 1 per cent by weight of the initiator BPO and 2.5 per cent by weight of DVB. The mixture was stirred to dissolve BPO. The reaction mixture was cast in molds as used for the PU preparation and cured at 60 °C for 18 hr and 80 °C for 4 hr to obtain PMMA. A similar procedure was used to make PS.

2.2.3 Interpenetrating Networks

To obtain IPNs, HTPB was homogeneously mixed with calculated amount of MMA for 4 hr at 50 °C. BPO was then added and stirred until it dissolved. To this mixture, TDI with DBTDL was added slowly. The cross-linking agents, glycerol for PU and DVB for PMMA, were then added to the reaction mixture and mixed for another 5 min. The air entrapped during mixing was removed by applying vacuum. The mixture was then cast in the same manner as described earlier. A schematic illustration of IPN synthesis is shown in Fig. 1.

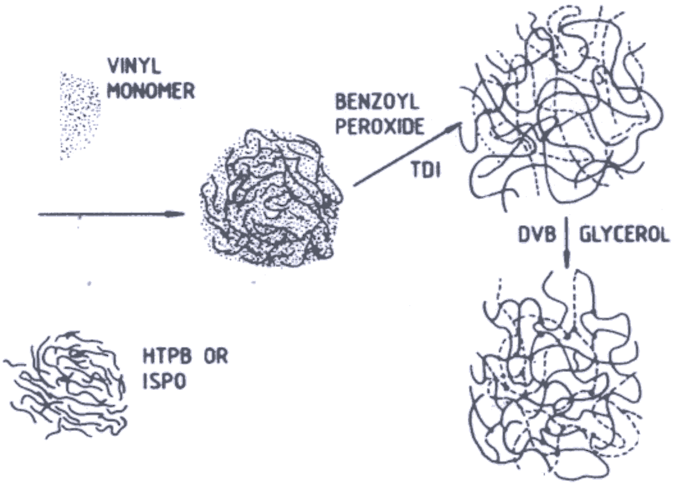


Figure 1. Schematic formation of IPN polyolvinyl monomer.

Four different polymer combinations were made by mixing each of the two polyurethane solutions (based on HTPB and ISPO) with each of the two vinyl monomers (MMA and styrene). Combinations of 20, 40, 60 and 80 per cent PU by weight were made for all the four systems.

2.2.4 Casting of Composite Propellants

To obtain IPN-based propellants, calculated amount of HTPB, MMA and BPO were mixed thoroughly in a beaker in a similar manner used for unfilled IPN synthesis. Ammonium perchlorate (70 per cent by wt) of known particle size was taken in three parts as 1/2, 1/4, and 1/4, and each part was added to the resin with constant stirring. After the addition was over, required amount of TDI, the cross-linking agent (glycerol), the catalyst (DBTDL) for PU formation, and the cross-linking agent (DVB) for MMA were added. The slurry was mixed for further 30 min. and the mass was then poured into an aluminium mold laminated with teflon sheet for easy demolding. Care was taken to remove air bubbles. The propellant was cured at 80 °C for 72 hr to give solid grain. Same procedure was adopted for making other propellant systems.

2.3 Experimental Techniques

The morphological behaviour was studied using JEOL 840 JSM Scanning Electron Microscope. Samples were prepared for SEM by freeze fracturing them in liquid nitrogen and applying a gold coating of 15 nm approximately.

For mechanical strength, test specimen of IPN films were cut into a dumb-bell shape, using a die. The stress-strain properties were determined using an Instron Universal Testing Machine Model 1112, according to ASTM D 638 procedure. The viscosities of the uncured IPN prepolymer mixtures were measured using a Brookfield Synchro-Lectic Viscometer at 25 °C. The densities of the IPNs were determined by the displacement method according to ASTM D 792-86 procedure, at room temperature.

A Shimadzu DTA-40 Simultaneous DTA-TG Thermal Analyser was used to determine the thermal stability. In a typical run, a 10 mg sample was examined employing a heating rate of 10 °C/min in flowing nitrogen atmosphere, maintaining the flow at 50 ml/min. The heat of combustion (calorific value) measurements of the IPNs were made using a constant volume isothermal bomb calorimeter (Toshniwal, India), under a constant pressure of oxygen (20 psi).

A device was fabricated indigenously to determine the burning rate at the atmospheric pressure, in controlled atmosphere. It consists of a propellant strand holder, in a glass enclosure, two electric circuits each for igniting the propellant and providing signals to the electronic timer, and a provision for allowing the flow of inert gas. The propellant strand (60 mm length, 4 mm dia) inhibited by TiO_2 in araldite coating, is mounted in the holder and placed vertically inside the glass chamber, as shown in Fig. 2.

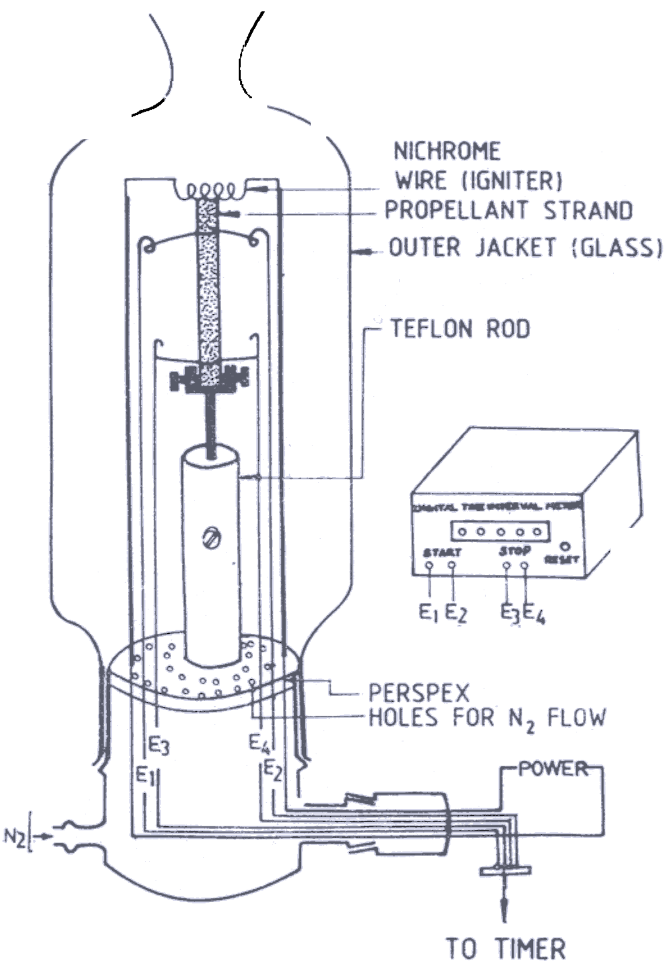
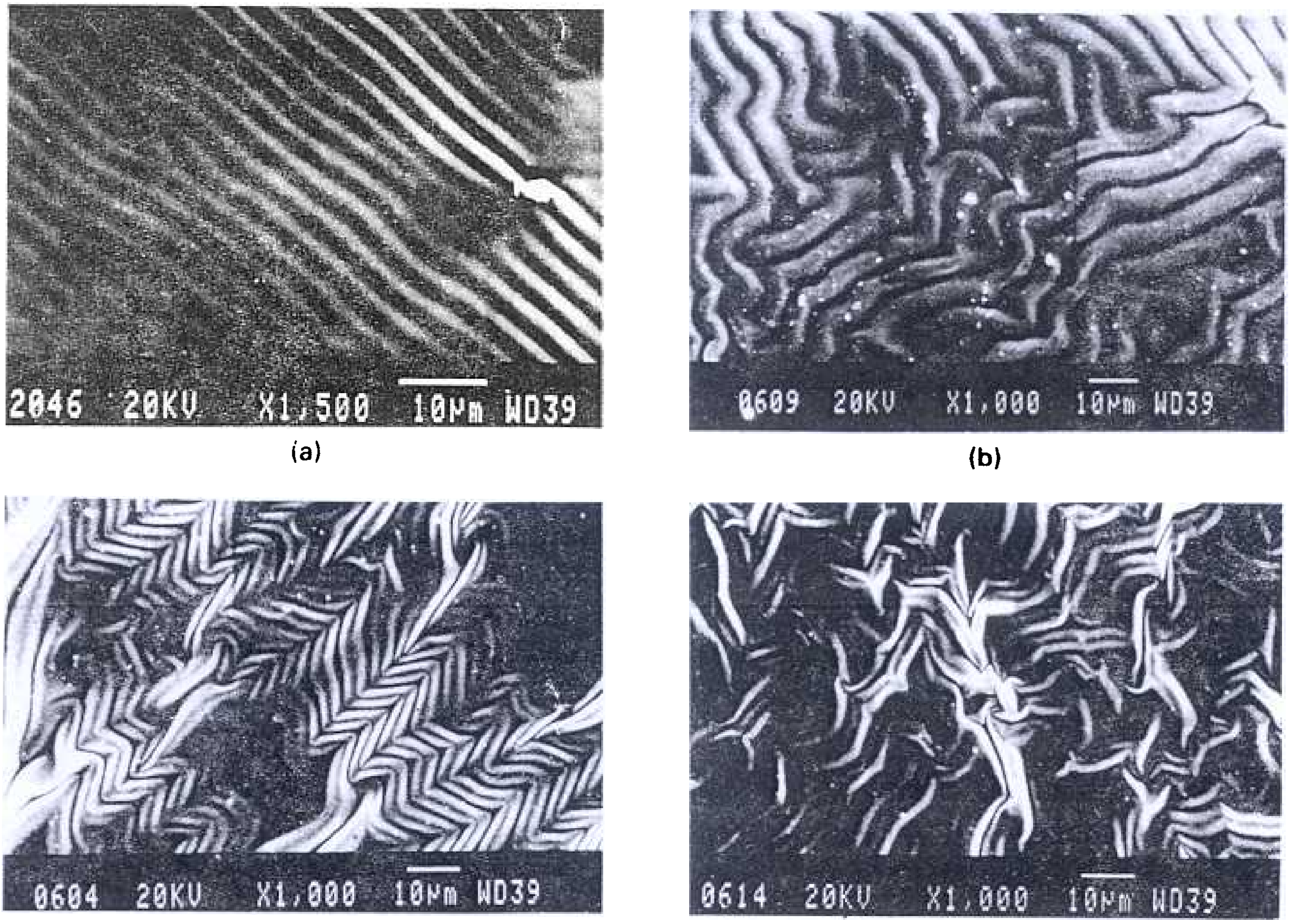


Figure 2. A sketch of the burning rate set-up.

The holder height is so adjusted, that the strand could touch the igniter wire. To measure the burning time, two fuse wires are threaded around the strand at an accurately measured distance and connected to the electronic timer to give start and stop signals. When the propellant is ignited by the heating element, the advancing burning front blows up the fuse at the top end and thereby gives signal to start the timer. When the burning front reaches the fuse wire near the bottom end, it blows, which gives signal to the timer to stop counting. Knowing the distance between the fuse wires and the time, the burning rate can be calculated.

3. RESULTS AND DISCUSSION

The morphology of PU-PMMA and PU-PS IPNs is shown in Fig. 3. The micrographs show the typical



(a) (b) (c) (d)

Figure 3. **SEM micrographs of IPNs with HTPB-based PU, (a) PU-PM (80:20), (b) PU-PM (60:40), (c) PU-PS (80:20), and (d) PU-PS (60:40).**

characteristic of an interpenetrating structure; the vinyl phase appears to be almost uniformly dispersed throughout the PU matrix. The formation of IPN structure is vividly seen by the existence of intricate entanglements, wherein, the polymer chains appear to penetrate inward and outward over one another in the polymer matrix. The PU-PMMA IPNs (Figs 3(a) and 3(b)) show finer phase domains than the PU-PS IPNs (Figs 3(c) and 3(d)). The reason could be that the PMMA is capable of having stronger interactions (hydrogen bonding) compared to PS because of the presence of carbonyl group in PMMA, thereby demonstrating the role played by stronger interactions in compatibilizing the polymers.

The tensile strength and the percentage elongation results are shown in Figs 4 and 5, respectively where the most dramatic characteristic of IPNs were noted. From these figures it is evident that initially as the percentage of PU increases the tensile strength decreases significantly and reaches a minimum at 40 per cent of PU. Then onwards the tensile strength increases reaching a maximum at 80 per cent of PU. The pure PMMA and PS samples were found to be too brittle to cut and hence no reliable measurements could be obtained. However, the values of tensile strength and percentage elongation at break of both PS and PMMA are in the range of 4000 psi and 5 per cent respectively[8]. Further, the tensile strength values of HTPB-based IPNs are higher than that of ISPO-based IPNs while the percentage elongation at break is higher for ISPO-based IPNs. The elongation of the IPNs compositions having up to 60 per cent PU, are about the same as that of PU (the more extensible component) for both HTPB and ISPO-based IPNs. The elongation then drops off as the concentration of MMA or styrene component increases.

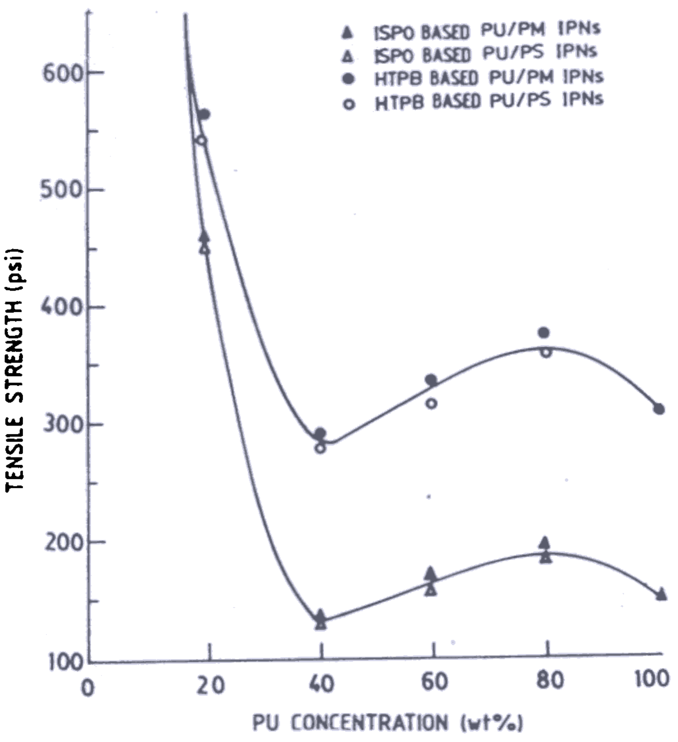


Figure 4. Variation of tensile strength and composition of IPNs.

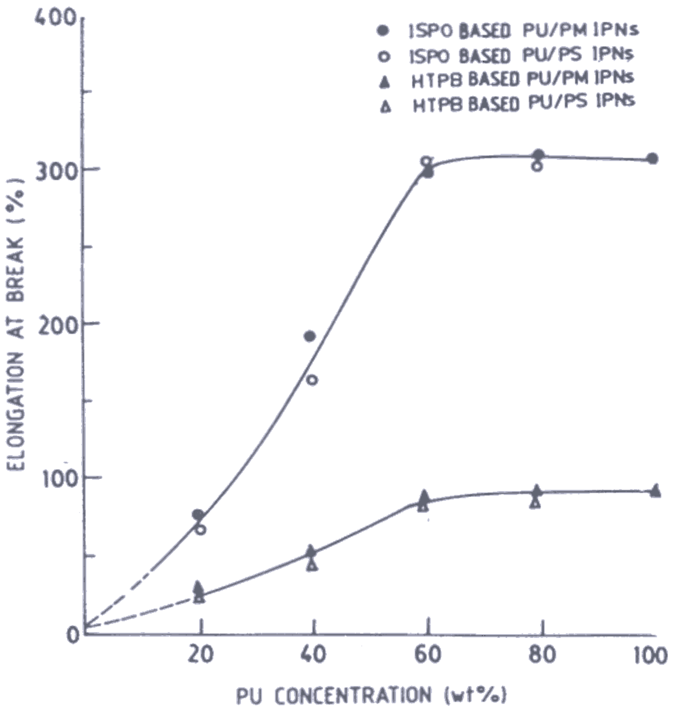


Figure 5. Variation of elongation of break with composition of IPNs.

The decrease in tensile strength at lower concentration (20 per cent) of PU is attributed to the fact that initially PU acts as a plasticiser and reduces the brittleness of the vinyl polymer substantially. The maxima observed in tensile strength at 80 per cent of PU could be a result of the increase in cross-link density due to increased physical crosslinks caused by interpenetration. The nature of intermolecular forces existing in the constituent network is also important in affecting the mechanical properties. The primary interaction occurring in pure urethane is a hydrogen bond between the urethane *C-O* group of one unit with the urethane *N-H* group of another unit. As a result of interpenetration, the tensile strength of IPNs having 60 and 40 per cent PU, is less than that of the IPN having 80 per cent PU. In other words, the strong hydrogen bonding in the constituent (PU) network would be reduced if the network was interpenetrated by other network chains[9], thus reducing the ultimate tensile stress until the increased physical entanglement effect becomes significant. The reason for poor mechanical properties of the ISPO-based IPNs, on the other hand, could be the presence of a pendant hexyl group in the backbone of the polymer. The hexyl group may cause poor packing of the chains in the network making them to move apart. This causes irregularity in the network.

The elongation of the IPNs was found to be about the same as that of PU (the more extensible component) up to 60 per cent content of PU. The constant elongation in the region in which the tensile strength increases steadily, could be a result of the chemical topology of the IPN systems. The constant elongation observed in compositions having 60 to 100 per cent PU is attributed to the presence of topological interpenetration[10]. The presence of topological isomerism is clearly supported by the micrographs of these compositions showing extensive microfolding as a result of higher degree of interpenetration. The elongation drops off as the concentration of MMA or styrene component increases. This could be due to the low extensibility (5 per cent) of the rigid component (PMMA or PS).

As the concentration of the vinyl monomer increases in the IPN composition, the viscosity of the prepolymer mixture decreases significantly as shown in Tables 1 and 2. This factor could be advantageous in propellant technology, as low viscosity of the binder facilitates the mold filling. Further, the problems of using plasticiser to improve the fluidity can be eliminated by the use of dual reactions in an IPN system.

The actual and the calculated densities based on the volume additivity of the components are shown in Tables 1 and 2. It is clear that the actual densities of

Table 1. Viscosity, density and heat of combustion of IPNs with HTPB-based PU

Composition[a]	Viscosity[b] (poise)	Density (g/cc)		Heat of combustion (cal/g)	
		Experimental	Calculated	Experimental	Calculated
IPNs from PU and PM					
PU (100)	64.00	0.945		10227	10451
PU-PM (80:20)	10.50	0.995	0.994	9388	9575
PU-PM (60:40)	5.00	1.051	1.043	8462	8699
PU-PM (20:60)	2.00	1.112	1.093	7931	7823
PU-PM (20:60)	1.00	1.146	1.141	7221	6946
PM (100)	Very low	1.191		6163	6070
IPNs from PU and PS					
PU-PS (80:20)	11.50	0.987	0.966	10196	10332
PU-PS (60:40)	5.00	1.031	0.987	10097	10213
PU-PS (40:60)	2.00	1.038	1.007	10053	10094
PU-PS (20:80)	1.00	1.053	1.028	10017	9975
PS (100)	Very low	1.049		9881	9857

a: percentage shown in parentheses; b: determined in uncured state

Table 2. Viscosity, density and heat of combustion of IPNs with ISPO-based PU

Composition[a]	Viscosity[b] (poise)	Density (g/cc)		Heat of combustion (cal/g)	
		Experimental	Calculated	Experimental	Calculated
IPNs from PU and PM					
PU (100)	21.00	0.997	–	8921	9082
PU-PM (80:20)	5.50	1.039	1.036	8193	8484
PU-PM (60:40)	2.50	1.085	1.075	7652	7877
PU-PM (40:60)	1.25	1.127	1.113	7317	7275
PU-PM (20:80)	0.50	1.151	1.152	6797	6673
PM (100)	Very low	1.191		6163	6070
IPNs from PU and PS					
PU-PS (80:20)	5.75	1.019	1.007	9015	9237
PU-PS (60:40)	2.50	1.042	1.018	9202	9392
PU-PS (40:60)	1.25	1.046	1.028	9483	9547
PU-PS (20:80)	1.00	1.052	1.039	9749	9817
PS (100)	Very low	1.049		9881	9857

a: percentage shown in parenthesis; b: determined in uncured state

IPNs are somewhat higher than the calculated densities. Particularly PU-PS IPNs have significantly increased density. The maximum increase in the PU- PMMA IPN systems is at 40 per cent PU concentration, while that in the PU-PS IPN system is observed at 80 per cent PU concentration. This increased density effect agrees well with the specific volume hypothesis of Kwei[11] At room temperature (25 °C) the specific volumes[12] of PMMA and PS in the rubbery and glassy states are 0.878 and 0.875 cm^3/mole, and 0.865 and 0.942 cm^3/mole, respectively. The difference in specific volumes of the rubbery PMMA chains and glassy PMMA chains is smaller than for polystyrene. Hence the density effect of mixing in PMMA is smaller. This is, however, possible only when extensive mixing of the two different polymer chains has taken place.

The TGA results are shown in Figs 6 to 9. In general, all the IPNs start decomposing around 200 °C. The complete decomposition occurs around 500 °C. The thermograms of the IPNs containing 20 per cent and 40 per cent PU fall in between those of the vinyl polymer (PMMA or PS) and the PU. Thus, these IPNs show seemingly no enhancement in thermal resistance over the individual components. However, IPNs with 60 per cent and 80 per cent PU show improved thermal stability. Their thermograms fall significantly to the right of those of the component networks. It is also seen from the figures that the ISPO-based IPNs are thermally less stable than those based on HTPB systems.

One explanation of the thermal stabilisation of the IPNs could be that several of the volatile products of polybutadiene (PBD) degradation (propene, pentene, 4-vinylcyclohexene), if they diffuse into the PS (or PMMA) phase, could act as radical inhibitors[13] by losing *H* atoms to the PS (or PMMA) radicals with the formation of allylic-type radicals of relatively low reactivity. The 4-vinylcyclohexene, being both of lower volatility and present in greater quantity, appears most likely to be effective in this respect. Also, there are five reactive *H* atoms in the molecule in the α- position to a double bond[14].

Apart from this radical mechanism of degradation of PBD, the presence of PU linkage also could play an important role in the degradation mechanism. As shown by TGA studies, even the ISPO-based IPNs show some enhancement in thermal stability, although they do not possess the PBD group. It is now fairly well established that the radical mechanism plays an important role in the thermal degradation of PU[15]. On the other hand the degradation of PMMA and PS at a temperature of about 150-500 °C has been shown to yield monomers by the stepwise unzipping process[16]. The TGA thermograms in the present study seem to indicate that the enhancement of the weight retention is related to the presence of the unzipped methacrylate or styrene monomer. One possible explanation, therefore, could be that the unzipped monomers act as scavengers for the radicals produced from the PU degradation, thus delaying the further reaction of radicals with volatile amines, alcohols, isocyanates, olefins and carbon dioxide.

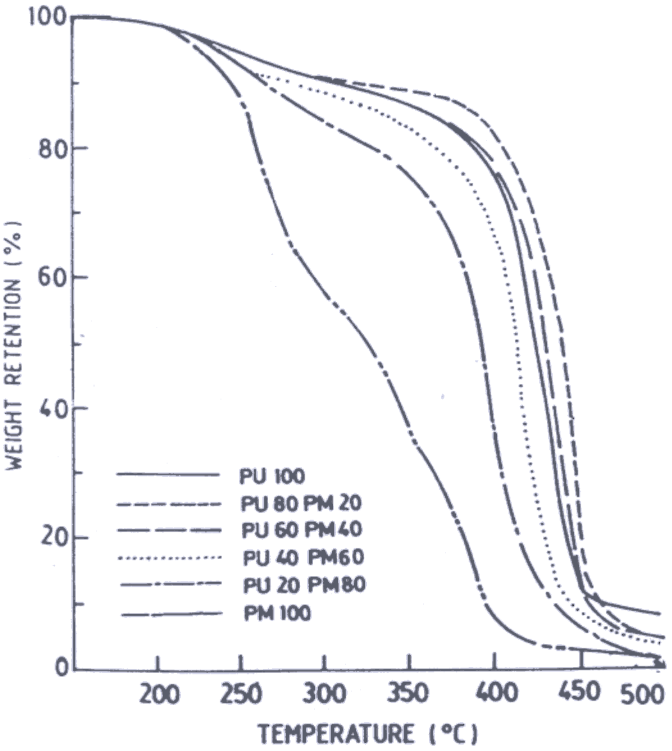


Figure 6. TGA curves of IPNs in the HTPB-based PU and PMMA.

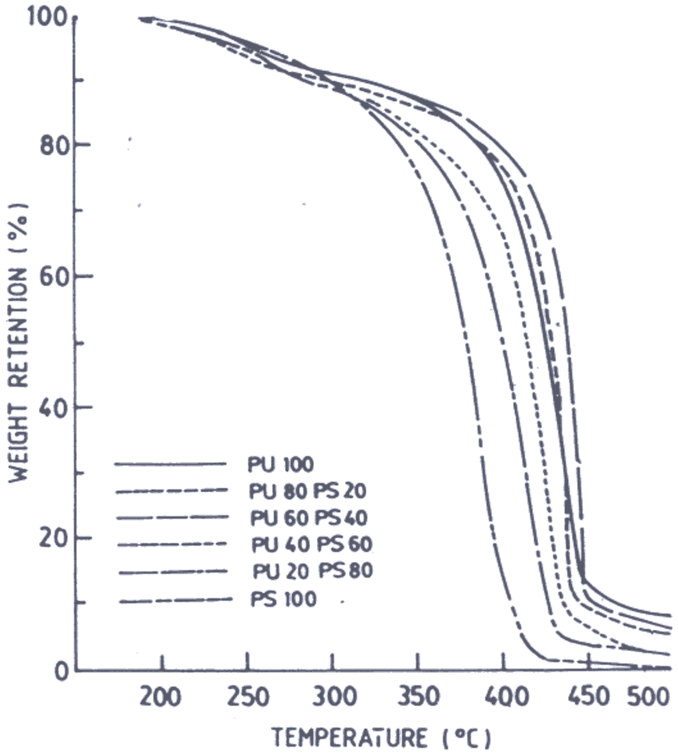


Figure 7. TGA curves of IFNs with HTPB-based PU and PSO.

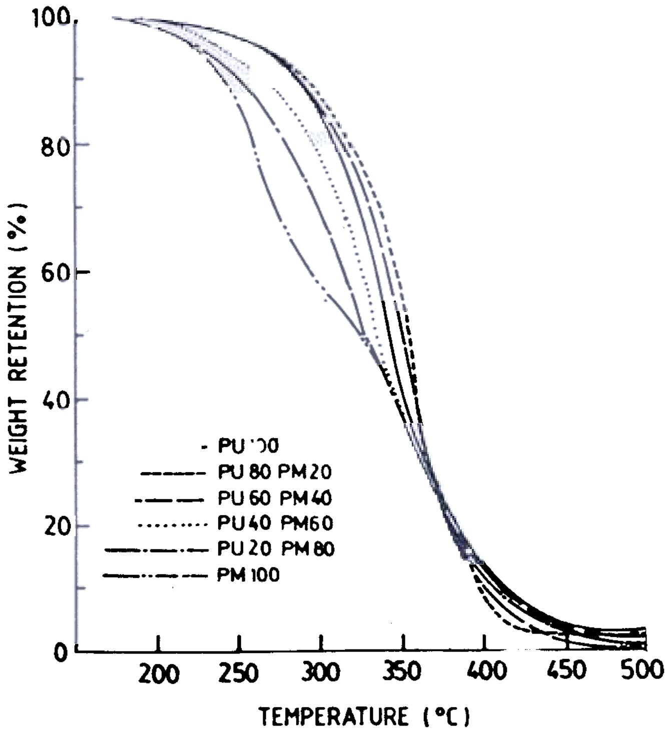


Figure 8. TGA curves of IPNs with ISPO-based PU and PMMA.

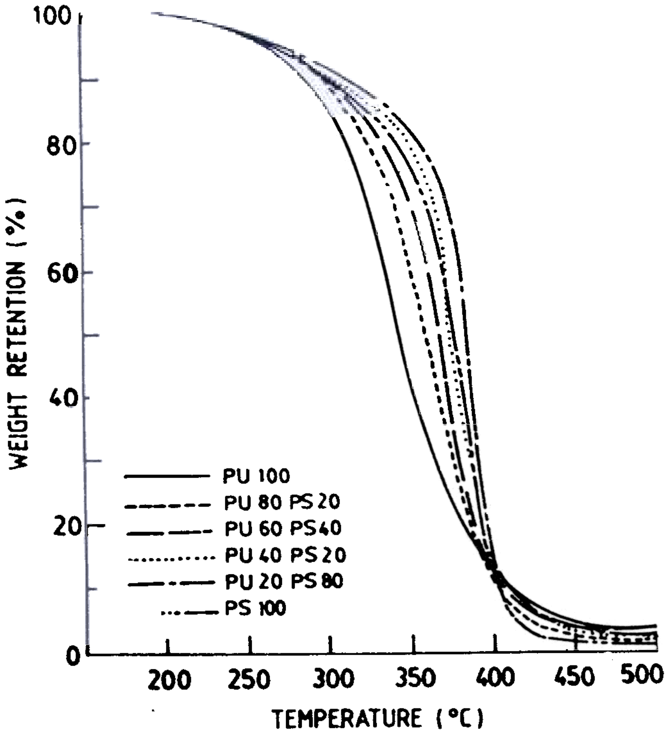


Figure 9. TGA curves of IPNs with ISPO-based PU and PS.

The lower thermal stability of ISPO-based IPNs may also be due to the presence of secondary hydroxyl-urethanes linkage. It has been reported that primary hydroxyl-urethanes are more thermally stable than secondary hydroxyl-based urethane[17]. In addition, ester linkages may contribute to the lower thermal stability of ISPO-based urethanes.

The heat of combustion (ΔH_c) of IPNs and component networks are listed in Tables 1 and 2. It is seen from the Tables that the heats of combustion of the IPNs are of the order of 7-10 kcal/g. The ΔH_c data shows a linear relationship with the PU concentration, i.e., the property is additive, and the ΔH_c values are intermediate between PU and vinyl polymer. It is also seen that IPNs based on HTPB give higher heats of combustion than those based on ISPO. The theoretical heat of combustion values were evaluated by the method given by Jain[18]. Small deviations observed from the calculated values may be due to, apart from some experimental error, the composite nature of the polymer. Moreover, in the calculated ΔH_c values, no allowance has been made for the isocyanate content, which is likely to contribute negatively to the ΔH_c values. This is reflected in the lower observed value of ΔH_c of PU 100 than that calculated in both HTPB and ISPO-based systems. The higher ΔH_c of HTPB-based IPNs are due to the presence of an almost saturated hydrocarbon chain of PU. The addition of PS and PMMA to the HTPB-PU system decreases its heat of combustion. This is because of the low heat of combustion of PS and PMMA as compared to the HTPB-PU. The ΔH_c of ISPO-based PU is less than that of PS, but more than that of PMMA. Increasing the concentration of PS in these IPNs therefore, increases the heat of combustion while the addition of PMMA decreases the ΔH_c value.

The mechanical properties of the propellant processed at a constant level (70 per cent by weight) of solid loading (amount of AP) using the IPNs compositions as binders, are given in Table 3. It is seen that tensile strength of the propellants increases with the increasing concentration of vinyl polymer while the percentage elongation at break decreases.

In the light of these observations, on re-examination of the earlier data on mechanical properties of the unfilled IPNs presented in Figs 4 and 5, it is seen that all the unfilled systems are having higher tensile strength and percentage elongation than the filled system. This can be explained as follows. For any significant contribution to mechanical and other properties by the

Table 3. Mechanical properties and burning rates of IPN-based propellants having 70% (by wt) AP

Composition[a]	Tensile strength (psi)	Elongation at break (%)	Burning rate (mm/s)
Propellants from HTPB-based PU			
PU (100)	123	29	2.64
PU-PM (80:20)	149	26	3.35
PU-PM (70:30)	167	25	3.61
PU-PM (60:40)	198	22	4.28
PU-PS (80:20)	146	26	2.99
PU-PS (70:30)	170	23	3.15
PU-PS (60:40)	185	21	3.42
Propellants from ISPO-based PU			
PU (100)	59	34	Does not sustain burning
PU-PM (80:20)	63	30	1.13
PU-PM (70:30)	76	29	1.69
PU-PM (60:40)	89	29	2.04
PS-PS (80:20)	63	29	Does not sustain burning
PU-PS (70:30)	75	29	0.97
PU-PS (60:40)	90	26	1.32

a: percentage shown in parentheses.

dispersed phase in a two-phase composite, the important requirement is the continuity in the structure. A problem in particulate-filled composite is the poor stress transfer at the filler polymer interface. Because of non-adherence of the filler to the polymer which may give rise to dewetting or cavitation coupled with breakdown of filler agglomerates, discontinuity is created in the structure[19]. The filler particles cannot carry the load, thus making it a weak body. Stress concentrations will be created around the particles, reducing the composite strength further. Decrease in elongation is obviously due to increased rigidity in the presence of the solid AP, which impedes the deformation of IPNs, i.e., the IPN matrix is stiffened by the particulate phase of AP. The particles restrict the mobility and deformability of the IPN matrix by introducing a mechanical restraint, the degree of which depends on the particulate spacing and properties of the particle and matrix.

Furthermore, the HTPB-based PU is a hydrocarbon polymer with amide linkage possessing intermolecular interaction forces. But when filled with AP at higher weight percentage the polymeric networks lie further apart in the filled system than in the unfilled system. Consequently, the hydrogen bonding is disturbed and the interpenetration effect would be minimised. However, the crystalline nature of the vinyl polymer aids in increasing the tensile strength. The percentage elongation at break exhibits only a marginal decrease with increase in vinyl polymer concentration.

The measured strand burning rate data of the propellants in nitrogen atmosphere having the IPN compositions and the polyurethane as binders, are presented in Table 3. Each data point represents the results of atleast three firings. The burning rates of the propellants increase with the vinyl polymer (PMMA/PS) content of the IPNs. Thus, the addition of vinyl monomers, particularly, the methyl methacrylate increases the burning rate significantly. This fact is borne out by the results on both the HTPB and ISPO-based propellants. The higher burning rate of propellants from PMMA-based IPNs is attributed to the good burning characteristics of PMMA[20]. The polystyrene IPN-based propellants produce a lot of smoke due to the presence of aromatic group. The HTPB-IPN-based propellants have higher burning rate than those of ISPO-IPN-based propellants. In fact, the pure ISPO and IPNs with 80 per cent PU and 20 per cent PS-based propellants do not sustain burning. This may be due to the less flammable nature of the ISPO.

4. CONCLUSION

The results of the present work emphasise the advantages of IPNs as binders to suit the different mission requirements of solid rockets. Both the burning rate and the mechanical strength of the propellant grain could be suitably modified as per the specific requirements by simply altering the constituent components or the composition of the IPNs. The IPNs are easy to synthesise and are capable of carrying high solid loading as required in composite propellants.

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