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Thermal, flame and mechanical behaviour of ternary blends of poly(vinyl chloride), poly(ethylene-co-vinyl acetate) and poly(styrene-co-acrylonitrile)

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Abstract

An attempt is made to prepare a novel set of polymer blends based on poly(vinyl chloride) (PVC), poly(ethylene-co-vinyl acetate) (EVA) and poly(styrene-co-acrylonitrile) (SAN). The thermal, flame and mechanical behaviour of these blends was investigated. Ternary blends of PVC/EVA/SAN were found to have excellent thermal stability and mechanical properties as compared to pure PVC and binary blends. Measurement of smoke and volatile gas evolution also revealed that the ternary blends are very efficient in flame retardant applications.

INTRODUCTION

The rapid increase in the use of polymers in many consumer-oriented applications has generated considerable interest in the flammability and thermal characteristics of polymeric materials. The smoke contribution and the level of toxic gases generated during the burning of polymeric materials are receiving increased attention. PVC has been used extensively to formulate fire-resistant compounds due to both its inherent flame-resistance properties and its good mechanical properties [1]. However, the thermal stability of PVC is very poor: thermal degradation starts at 100–150°C in the absence of oxygen, with corrosive dehydrochlorination, resulting in longer polyenes. Also, the cyclization of aromatic triene units into aromatic products, such as benzene, a second elimination of residual hydrogen chloride, and the breakdown of longer polyene units into higher

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hydrocarbons occur at higher temperatures [2]. Therefore, in practical applications of PVC-based formulations, their thermal and flame behaviour are very important.

Sanghi et al. [3] and Varughese et al. [4] have shown that the blending of PVC with other polymers has a strong influence on the thermal stability and flammability. Sen et al. [1] have developed low-halogen cable-sheathing compounds by blending PVC and functionalized polyolefins. The thermal stability of these blends strongly depends on the compatibility of the homopolymers. Recently, Varughese [5] has shown that the thermal stability of blends based on epoxidized natural rubber (ENR) and PVC is greatly influenced by their interaction.

PVC is reported to have excellent flame resistance and good tensile properties. EVA has superior low smoke characteristics. SAN is noted for its excellent chemical resistance and mechanical properties. Therefore, by preparing ternary blends of PVC/EVA/SAN, we can combine the excellent low smoke characteristics of EVA, the good flame retardant properties of PVC and the superior mechanical properties of SAN. Because EVA acts as an excellent impact modifier for brittle thermoplastics, the resulting ternary blend is expected to have good impact resistance.

In the present paper, we report on the flammability characteristics, thermal behaviour and mechanical properties of ternary blends of SAN, PVC and EVA (PVC/EVA/SAN). Attempts have been made to correlate the properties with the compatibility of the system.

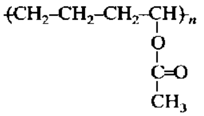
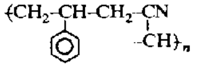
EXPERIMENTAL

Details of the materials used are given in Table 1. Blends were prepared by solution-casting from a 1:1 mixture of THF and cyclohexanone, which is a common solvent. The films were dried under vacuum at 50°C for three weeks.

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were carried out in a Shimadzu DT-40 thermal analyser in a nitrogen atmosphere at a heating rate of 10°C min^{-1}. The limiting oxygen index (LOI) values of the samples were determined according to ASTM-D 2863–81. Smoke characteristics of the blends were determined gravimetrically. The static thermal stability of the blends was determined by a previously reported method [1]. About 100 mg of each sample were placed in a long test tube and heated to a constant temperature of 200°C in an oil bath. Congored paper was hung from the mouth of the closed tube with cotton. The stability time was taken as the time at which the congored paper turned brown. The amount of volatile gas evolved was also determined.

TABLE 1

Details of the materials used

Abbreviation	Polymer	Structure	T_g/°C	Intrinsic viscosity/ dl g^{-1}	Other characteristics	Source
PVC	Poly(vinyl chloride)	$\text{-(}CH_2\text{-}CHCl\text{)-}_n$	81	1.12	K value; 65	Plastics & Chemicals Ltd., Madras
EVA	Poly(ethylene-co-vinyl acetate)	 $\text{-(}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH(OC(=O)CH_3)\text{)-}_n$	−40	1.06	VA content, 54%	Exxon Chemical Co., USA
SAN	Poly(styrene-co-acrylonitrile		106	1.425	Acrylonitrile content, 28%	Aldrich Chemical Co., USA

Mechanical properties were studied in a Zwick Universal Testing Machine (1497 model) according to ASTM-D 412-80.

RESULTS AND DISCUSSION

Thermogravimetric traces of PVC, EVA and SAN are shown in Figs. 1, 2 and 3, respectively. The thermal degradation of PVC starts at about 110°C and about 68% weight loss occurs at 380°C (Fig. 1). For EVA (Fig. 2), the initial thermal decomposition starts at 320°C and the weight loss after first step (up to 380°C) is only 40%.

The DTG trace of PVC shows three peaks. The first minor peak at 110°C corresponds to the dehydrochlorination, together with the liberation of a little benzene and ethylene. The second major peak between 250 and 320°C and the peak between 400 and 500°C correspond to the thermal degradation of PVC, resulting in volatile products including aromatic and aliphatic compounds. The intramolecular cyclization of polyene sequences accounts for the formation of benzene and aromatic products [5].

The DTG trace of EVA (Fig. 2) exhibits two major peaks. The first corresponds to the thermal degradation of EVA without rupture of the backbone. The second peak between 400 and 500°C corresponds to the scission of the conjugated polyene left after deacetylation [2].

The thermogravimetric trace of pure SAN is given in Fig. 3. The first

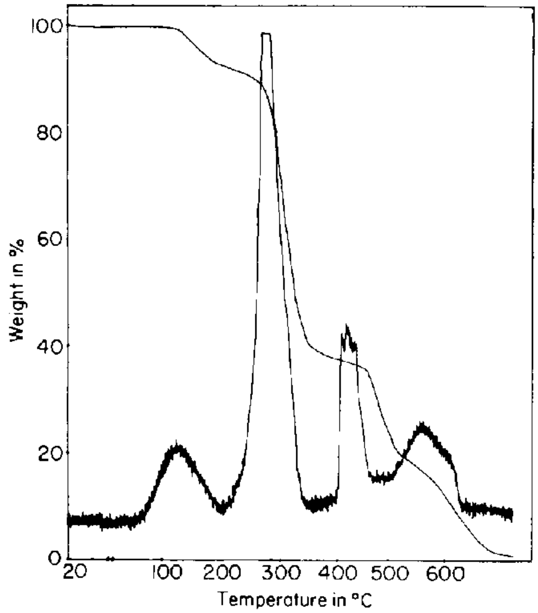


Fig. 1. TGA and DTG curves of PVC.

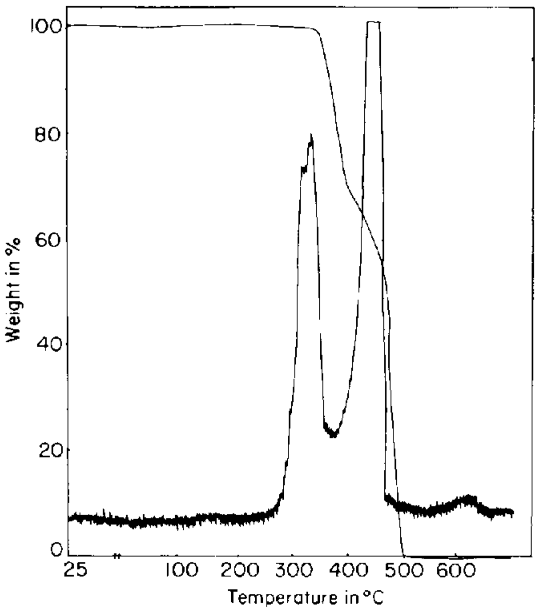


Fig. 2. TGA and DTG curves of EVA.

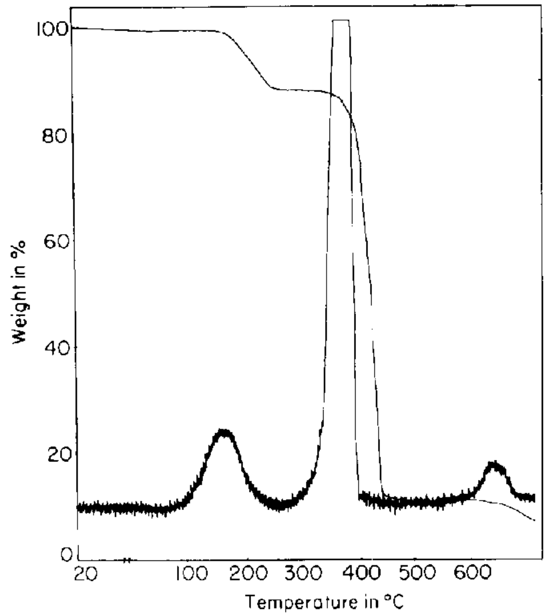


Fig. 3. TGA and DTG curves of SAN.

step at 160°C involves a small-scale degradation, with a weight loss of 10%, due to the elimination of minor low molecular weight fractions such as ammonia and hydrogen cyanide. The second step involves the breakdown of the polymer backbone with the loss of volatiles [2]. There was about 10% residue at the end of the thermal decomposition (600°C). The DTG trace of SAN shown in Fig. 3 exhibits two peaks corresponding to the two steps of degradation. The first is a minor peak associated with the initial thermal decomposition. The major peak at about 380°C corresponds to the chain scission.

In our earlier studies [6], the thermal behaviours of PVC/EVA, PVC/SAN and SAN/EVA blends were investigated. For the completely miscible PVC/EVA system, blending considerably improved the thermal stability of PVC. However, in the case of the partially miscible PVC/SAN and the immiscible EVA/SAN blends, the blending had only a negligible effect on the thermal stability of the system. The important properties of these binary blends are summarized in Table 2. It is interesting to note that the observed tensile strength values are higher than the weighted average additivity values for the miscible PVC/EVA blends. The synergism in tensile strength and the enhancement of the thermal stability of PVC/EVA blends are associated with the molecular-level miscibility of the component polymers in the blend, as reported earlier [7]. Several authors, including our research group [8], have reported that strong hydrogen bonding interactions are responsible for the miscibility of PVC/EVA blends. The static

TABLE 2

Comparison of the properties of PVC, EVA, SAN, and PVC/EVA/, PVC/SAN, and EVA/SAN blends

Blend system	Tensile strength/ N mm^{-2}	Elongation at break/%	LOI	T_0/°C	T_{50}/°C	Percentage of volatile gas at 200°C	Smoke density/%	Static thermal stability/min
PVC	22.9	203	38	110	345	32	86	90
EVA	4.5	1350	17	320	452	0	6	No colour change even after 720 min
SAN	29.3	2	17	160	420	20	78	No colour change even after 540 min
PVC/EVA 50/50	14.7 (13.6) [a]	330 (776) [a]	21	270 (215) [a]	430 (398) [a]	5	22	355
PVC/SAN 50/50	24.3 (26.0) [a]	6 (102) [a]	18	150 (135) [a]	380 (382) [a]	12	82	120
EVA/SAN 50/50	8.7 (16.9) [a]	40 (676) [a]	17	150 (240) [a]	435 (436) [a]	10	59	No colour change

[a] Additive value.

thermal stability, limiting oxygen index (LOI), volatile gas evolution and smoke density of the polymers and blends show that by blending PVC with EVA, the static thermal stability of PVC increases. The percentages of volatile gas evolution and smoke density decrease with addition of EVA. As expected, the LOI values of the blend decrease with increasing concentration of EVA. In the case of PVC/SAN blends, SAN slightly increases the static thermal stability at 200°C. Mechanical property measurements show that the observed tensile strength and elongation-at-break values are lower than the additive values. This is associated with the microheterogeneity of the system, as reported earlier [8, 9]. For EVA/SAN blend also, the observed mechanical properties are lower than the additive values. This is associated with the lack of interaction between the two phases. Our earlier studies [8] on the miscibility of EVA/SAN blends indicated that there is no interaction between the polymers in these blends. Thermal studies also indicated that there is no interaction between the component polymers in EVA/SAN blends.

The ternary blends of PVC/EVA/SAN mostly form a miscible system. Spectroscopic studies show that there is a very strong interaction between the components [10] in the blend. In these ternary blends, PVC acts as an interfacial agent between the immiscible EVA/SAN pairs. This is because PVC is completely miscible with EVA and partially miscible with SAN.

Thermogravimetric traces of PVC/EVA/SAN ternary blends of four different compositions are given in Figs. 4–7. In all the three miscible

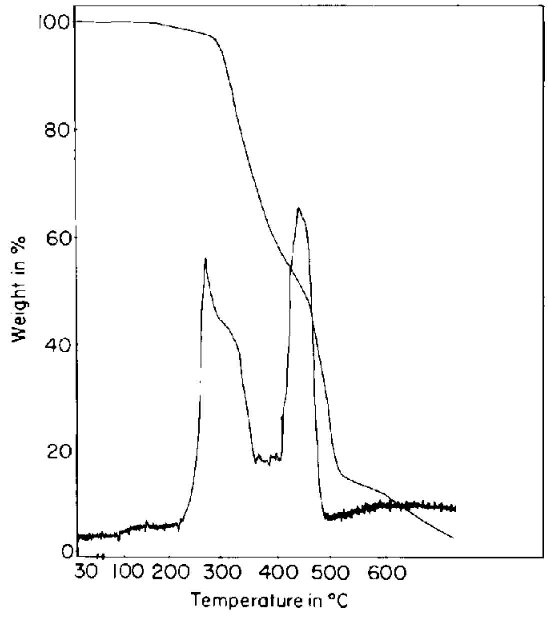


Fig. 4. TGA and DTG curves of miscible PVC/EVA/SAN 35/35/30 blend.

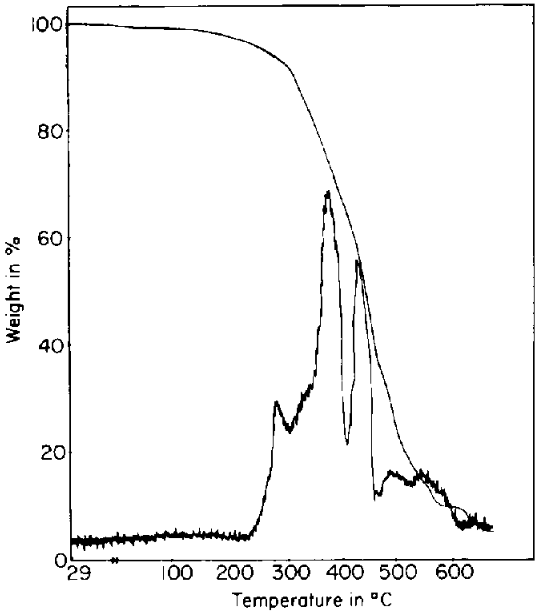


Fig. 5. TGA and DTG curves of miscible PVC/EVA/SAN 15/35/50 blend.

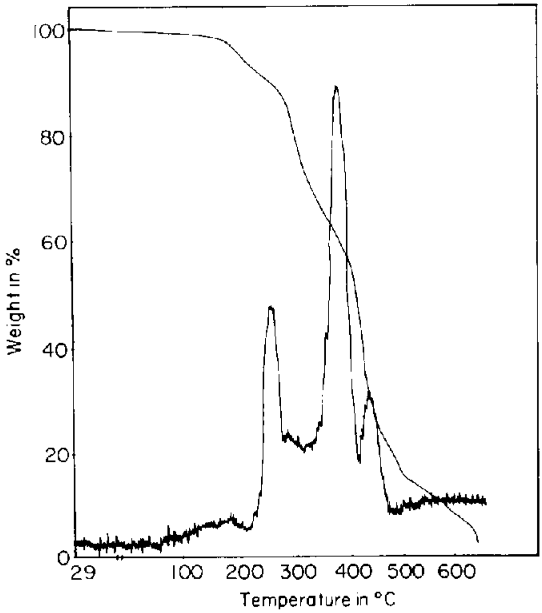


Fig. 6. TGA and DTG curves of miscible PVC/EVA/SAN 35/15/50 blend.

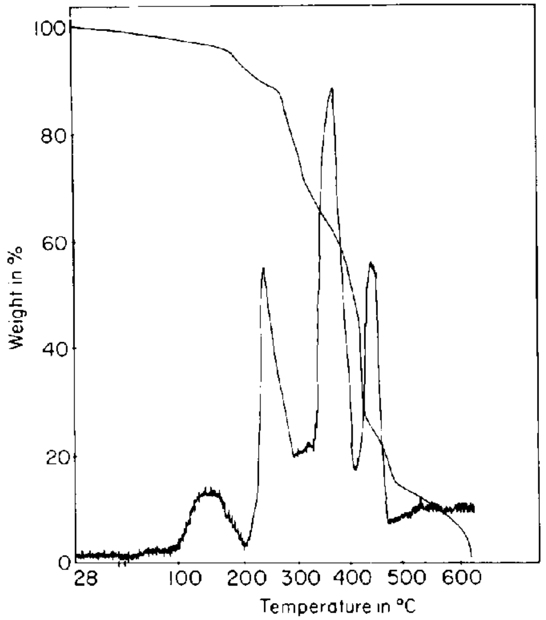


Fig. 7. TGA and DTG curves of immiscible PVC/EVA/SAN 15/15/70 blend.

compositions (Figs. 4–6), the dehydrochlorination step of PVC at 110°C disappears. The weight loss corresponding to the first degradation at about 280°C is only about 5% for the PVC/EVA/SAN (35/35/30) blend (Fig. 4). However, for pure PVC (Fig. 1) and SAN (Fig. 3), as seen earlier, the degradation starts at 110 and 160°C, respectively. At about 280°C, the weight loss from PVC and SAN are both higher than 10%. Therefore we can conclude that in this miscible ternary blend, EVA decreases the rate of elimination of volatile products from SAN and PVC. The second degradation in the ternary blend (Fig. 4) at about 420°C corresponds to a weight loss of about 80%. The DTG trace shows a major peak at this temperature indicating chain scission of the polymers, leaving about 15% residue at 500°C.

For the PVC/EVA/SAN 15/35/50 ternary blend system (Fig. 5), the initial degradation step at 290°C corresponds to a weight loss of about 7%. The second and third steps occur at 390 and 445°C, respectively, leaving a residue of about 21% at 500°C. The DTG trace shown in Fig. 5 exhibits three peaks. The initial peak corresponds to the elimination of volatile products. It is interesting to note that EVA improves the initial thermal decomposition behaviour of both PVC and SAN in the ternary blends. The peaks at higher temperatures are associated with chain scission and cyclization reactions. The third ternary blend within the miscible region shows a similar decomposition behaviour (Fig. 6).

In order to understand the influence of miscibility on thermal properties, the thermogravimetric traces of one of the immiscible compositions (PVC/EVA/SAN 15/15/70) is given in Fig. 7. Four degradation processes are recognisable. The first step starts at 110°C. The corresponding DTG peak between 100 and 200°C shows that the degradation behaviours of SAN and PVC are unaffected by blending in this composition. The remaining three peaks at 240, 380 and 420°C also indicate that the decomposition behaviours of the individual polymers are retained in the blend. The T_0 and T_{50} values of a few ternary blends are given in Table 3. It is found that the miscible ternary blends have improved T_0 and T_{50} values. However, for the immiscible composition, the observed T_0 value is lower than that of the additive. This suggests that the improvements in thermal properties are strongly dependant on the miscibility of the polymers in the blends.

The static thermal stability results given in Table 3 show that the rate of dehydrochlorination is substantially lower in the miscible ternary blends as compared to those of the immiscible blends of PVC and of the pure polymers (PVC and SAN). The amount of voaltile gas evolved at 200°C is decreased and the smoke characteristics of the blends are improved in the miscible compositions. Comparing the properties of miscible and immiscible compositions, we find that the properties depend on the miscibility of the system. All the properties of miscible blends are superior to those of immiscible blends.

The mechanical properties of the blends as shown in Table 3 indicate that the ternary blends exhibit superior tensile properties. It can be seen that the tensile strength varies as a function of composition. The observed tensile strength values of the miscible blends are found to be higher than the weighted average values of the individual polymers. The synergism in tensile strength is associated with the strong specific interactions that lead to better molecular packing [11]. However, the observed elongation-at-break values are lower than the additive values. In the case of the immiscible ternary blends, both the observed tensile strength and the elongation-at-break values are lower than the additive values.

The limiting oxygen index values (Table 3) of the blends suggest that the ternary blends have superior flame resistance. As expected, the LOI values decrease with decreasing amount of PVC in the blends. The flammability characteristics of the ternary blends are found to be comparable to those of PVC/EVA blend which is reported to be an excellent flame retardant system (Table 2).

The properties of the binary and ternary blends, tensile strength, T_{50} and T_0, have been plotted as a function of composition in a ternary phase diagram (Fig. 8), where the miscible and immiscible regions are indicated [7]. The phase diagram was generated by LCST (lower critical solution temperature) and IR spectroscopy measurements. It is interesting to note that most of the blends in the miscible region exhibit excellent mechanical

TABLE 3

Comparison of properties between PVC, EVA, SAN and PVC/EVA/SAN ternary blends

Blend system	Tensile strength/ N mm^{-2}	Elongation at break/%	LOI	T_0/°C	T_{50}/°C	Percentage of volatile gas at 200°C	Smoke density/%	Static thermal stability/min
PVC	22.9	203	38	110	345	32	86	90
EVA	4.5	1350	17	320	452	0	6	No colour change even after 720 min
SAN	29.3	2	17	160	420	20	78	No colour change even after 540 min
PVC/EVA/SAN 66.5/28.5/5	18.8 (17.9) [a]	196 (519) [a]	22.5	272 (172) [a]	412 (379) [a]	5	33	275
PVC/EVA/SAN 49/21/30	43 (30.8)	10 (383) [a]	20	270 (169) [a]	420 (390) [a]	7	17	272
PVC/EVA/SAN 35/35/30	20.2 (18.3) [a]	31 (544) [a]	21	280 (198)	445 (404) [a]	10	19	355
PVC/EVA/SAN 15/15/70 [b]	16.3 (20.3) [a]	18 (234)	19	160 (176) [a]	420 (413) [a]	22	29	128

[a] Additive value. [b] Immiscible composition.

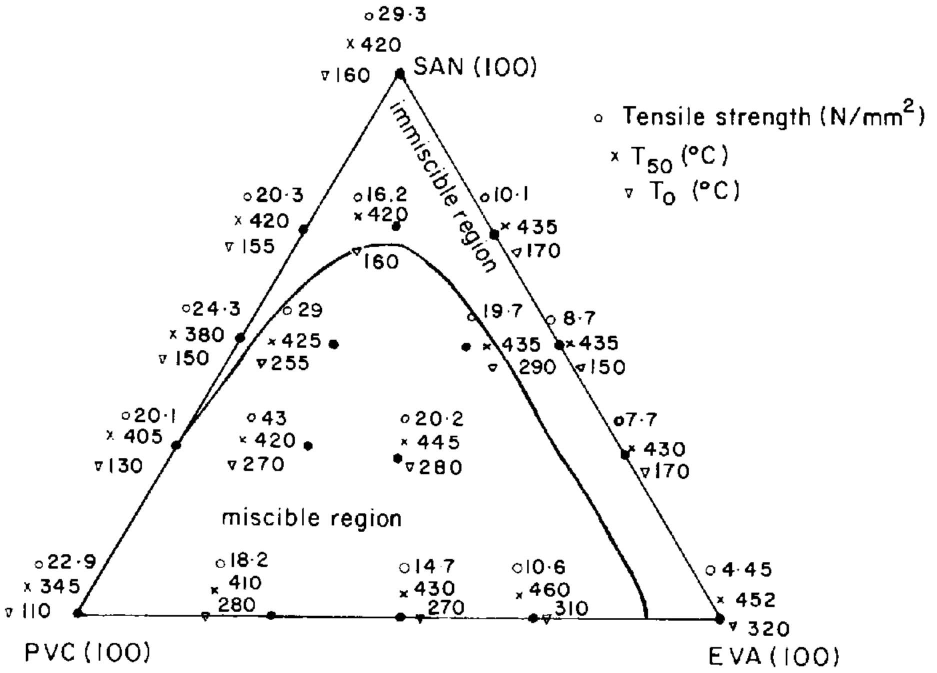


Fig. 8. Ternary phase diagram showing the effect of blend composition on T_0, T_{50} and tensile strength of PVC/EVA, PVC/SAN, EVA/SAN and PVC/EVA/SAN blends.

and flame retardant properties, and that the properties of the ternary blends in the immiscible region are inferior to those in the miscible region.

CONCLUSION

Thermal, flame and mechanical behaviours of ternary blends based on PVC, EVA and SAN (PVC/EVA/SAN) have been studied. The thermal stability of the blends is found to depend on the miscibility of the homopolymers. Thermal studies of miscible PVC/EVA/SAN ternary blends show that the overall thermal stability of these blends is superior to those of PVC, SAN, and PVC/SAN and SAN/EVA blends. In the PVC/EVA/SAN ternary system, there is a thermodynamically miscible region in which PVC acts as an interfacial agent for the immiscible SAN/EVA system. The tensile strength, and T_0 and T_{50} values of the ternary blends in the miscible region exhibit synergism. Interestingly, most of the properties of the ternary blend in the immiscible region lie below the additivity line. Their properties are, in general, inferior to those of the miscible blends.

Finally, it is important to mention that the miscible PVC/EVA/SAN ternary blend can be used successfully as a matrix polymer for flame retardant formulations.

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