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Thermal and Morphology Studies of PVC-PS Blends

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Thermal properties and morphology of blends of polyvinyl chloride (PVC) and polystyrene (PS) prepared by three mixing techniques namely solution casting, precipitation of solution by non-solvent and melt extrusion have been studied over a wide range of compositions. It was observed that the glass transition temperature (Tg), melting point (Tm) and enthalpy change at melting (ΔH) and Cp were influenced by the composition of the blends and also Tg, Tm and ΔH were altered from their theoretical values.

INTRODUCTION

It is well known that synergistic improvements in properties can be achieved by formation of alloys, blends, copolymers etc. Therefore the properties and characteristics of polymer blends have been studied extensively, in recent years from both experimental and theoretical point of view. Polyvinyl chloride has an excellent combination of low cost, versatility and properties. Mixtures of PVC involving styrene/styrene derivatives have considerable technological importance. PVC-PS melt extruded foams are used as fire resistant materials. In this paper we report a detailed investigation on the thermal properties and morphology of PVC-PS blends prepared by three mixing techniques namely precipitation of solution by non-solvent, solution casting and melt extrusion over a wide range of composition.

EXPERIMENTAL

Blends of PVC with PS are prepared by a variety of methods such as precipitation from solution by non-solvent, solution casting and melt extrusion.

Precipitation by non-solvent: 2% Solution of both PVC and PS were prepared in the common solvent tetrahydrofuran seperately. The solutions were optically clear. Blends of PVC/PS in all compositions, namely 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 and 0/100 were prepared by mixing the required amounts of the above 2% solution of PVC and PS. In each case, the blend was shaken well and thoroughly mixed for ten minutes. Then it was poured slowly into excess of ethanol while thoroughly shaking. The blend was precipitated and filtered out. It was then dried in vacuum at 40°C for 48 h to ensure complete solvent removal. The dried blend on grinding gave a fine white powder.

Solutions casting: Solution containing 3% total polymer in varying ratios of PS/PVC as 1.00, 0.90, 0.80, 0.70, 0.60, 0.50, 0.40, 0.30, 0.20, 0.10 and 0.00 were prepared in tetrahydrofuran. The solutions were clear for all the blend compositions. Blend solutions were poured on glass plates at room temperature. Blend films of all the above compositions prepared were dried under vacuum and preserved in desiccator. Cast films were slightly opaque by visual observation in all compositions.

Melt extrusion: PVC-PS blends of all compositions were prepared in powder form, mixed in a mixer and then used for melt extrusion. To limit thermal dehydrochlorination of PVC 3% by weight of lead based stabilizer was used. Blend of any composition can be extruded through a die of specified length and diameter under prescribed conditions of temperature and pressure. A pre-heat time of 5 min is set in the apparatus so that the blends in all compositions are pre-heated for 5 min at a constant temperature of 165°C. It is then extruded through the die under a load of 10 kg. The extruded blends are opaque in nature except for 100% composition of PS in which case it is transparent. Thus blends of all compositions are prepared in the melt extruded form at the same temperature of 165°C and under the same load of 10 kg. Extrusion is carried out under a temperature much below the degradation temperature of the blends. Extrusion above 195°C results in considerable degradation. Extrusion of blends is also carried out by changing the load as well as the temperature.

Glass transition and melting temperature are determined using Mettler differential calorimeter DSC TA 4000. Screening method is employed for study. Measurements are carried out in an air atmosphere over a temperature range from 40 to 400°C and at a heating rate of 10°C/min. Integration of the melting point endotherm to give ΔH values is done automatically. Specific heat (C_p) of a sample is determined as a function of temperature by the C_p method. The heat flow of the sample, measured at constant heat rate, is directly proportional to the specific heat of the substance.

RESULTS AND DISCUSSION

Influence of composition on the T_g and T_m of melt extruded PVC-PS blends is given in Table 1. Blends exhibited a single T_g different from the glass transition temperatures of the pure components implying extensive mixing of the two polymers. This single T_g behaviour is seen over the entire composition range. This agrees with the results of Eboatue and Olojo who have reported single T_g behaviour for PVC-PS blends in the powder form.[1] It is also observed that transition region for blends is broader than those of the pure components. Broadening slightly increased with increase in PVC constant. The extra breadth of transition may arise from strength of interaction between the components.[2] Similar type of broadening is seen in other miscible polymer blends also.[3–6]

TABLE-1

GLASS TRANSITION TEMPERATURE (T_g), MELTING TEMPERATURE (T_m), ENTHALPY OF FUSION (ΔH), SPECIFIC HEAT (C_p) AND DENSITY VALUES OF MELT EXTRUDED PVC-PS BLENDS

Blend composition PVC/PS	Glass transition temperatures			Melting temperatures		Enthalphy		Specific heat at 100°C J/g/Kg	Density	
	Experimental °C	From Nielson's equation °C	From Fox equation °C	Experimental °C	Theoretical °C	Experimental kJ/g	Theoretical kJ/g		Experimental g/c.c.	Theoretical g/c.c.
PS (0/100)	120	—	—	186.1	—	5.08	—	-236.37	1.061	—
B-1 (10/90)	119	118	117.7	266.1	189.1	2.30	5.31	—	1.100	1.092
B-2 (20/80)	122	116	114.9	294.3	192.1	13.71	5.55	—	1.129	1.122
B-3 (30/70)	123	114	113.6	288.1	195.1	17.02	5.79	-59.46	1.160	1.153
B-4 (40/60)	118	112	111.1	276.3	198.1	19.13	6.03	—	1.211	1.184
B-5 (50/50)	125	110	108.7	291.1	202.2	18.60	6.27	-0.36	1.264	1.215
B-6 (60/40)	118	108	107.5	204.0	204.2	42.12	6.51	-52.89	1.286	1.245
B-7 (70/30)	110	106	105.3	249.6	207.2	14.98	6.75	—	1.316	1.276
B-8 (80/20)	123	104	103.4	273.6	210.2	12.23	6.98	-30.75	1.347	1.307
B-9 (90/10)	110	102	101.7	270.7	213.2	10.90	7.22	—	1.363	1.337
PVC (100/10)	100	—	—	216.2	—	7.46	—	-0.14	1.368	—

A moderate level of broadening is generally recognized as an indication of microheterogenity.[7] This inhomogenity may be due to particulate structures or molecular aggregates bound by crystallites of PVC.[8–11] Soni *et al.*[12] have observed microheterogenity in plasticised PVC due to the presence of unplasticised microdomains of PVC. Hence a certain amount of heterogenity may be expected in this miscible system also. The glass transition temperature for all the blends have been predicted using Fox equation[13]and Neilson equation.[14] T_g of the miscible blends can be predicted using Fox equation

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

where W_1 and W_2 are the weight fractions of the components, T_{g1} and T_{g2} the corresponding glass transition temperature. Theoretical values of T_g are also found out using Neilson equation.

$$T_g \text{ (theoretical)} = W_1T_{g1} + W_2T_{g2}$$

where T_{g1}, T_{g2}, W_1 and W_2 refer to the T_g's and weight fractions of the constituents respectively. The observed T_g's are found to be higher than the predicted T_g using above equation. The blends show a positive deviation from predicted value implying strong intermolecular interaction between the polymers. Min *et al.*[15] have explained the positive deviation from additive T_g values by the occurrence of either steric hindrance or close packing, both restricting the motion of the molecules at the transition point. Maximum T_g is observed around 1 : 1 molar ratio. This indicates phase mixing has reached a maximum around 1 : 1 composition. These observations show that there are either chemical or physical interactions between the two polymers. Interaction may be the interlocking of the chains of blends. As a result, the thermo-mechanical properties such as T_g and T_m are affected. The relatively highly T_g at 1 : 1 mole ratio envisages maximum interaction at this point. Such a behaviour has also been observed in other polystyrene blends.[16]

Obsreved T_m and ΔH vary non-linearly with composition and a maximum is observed around equimolar composition. The values of T_m and ΔH are higher than theoretical values for all composition of blends. The observed high values of T_m and ΔH may be attributed to the dercease in the free volume due to extensive mixing of the components. The decrease in the free volume is reflected in the density values of the blends. Specific heat values (C_p) at 100°C are calculated for few blends and these values are found to be decreasing with increase in the PVC content. The reduction in C_p at T_g of each component is attributed to the dissolution of that component in the conjugate phase.[17,18] Unlike other blends, blend of 50/50 composition has a very low C_p value. This is explained on the basis of maximum phase mixing.

T_g, T_m, ΔH and C_p values of powder and solvent cast blends are also determined (Table 2). It is seen that these values differ depending on the preparation techniques.

TABLE-2
GLASS TRANSITION TEMPERATURE (T_g) MELTING TEMPERATURE (T_m), ENTHALPY (ΔH) AND SPECIFIC HEAT (C_p) VALUES OF B-3 AND B-8 COMPOSITIONS OF PVC-PS BLENDS

Parameter	Powder		Film		Melt extruded	
	B-3	B-8	B-3	B-8	B-3	B-8
T_g (°C)	112.00	115.00	111.00	114.00	123.00	123.00
T_m (°C)	268.60	257.70	291.10	340.00	288.00	273.00
H (kJ/g)	3.34	3.81	12.97	38.90	17.02	12.23
C_p (J/g/K)	−119.60	−105.20	−202.60	—	−59.46	−30.75

Density Measurements

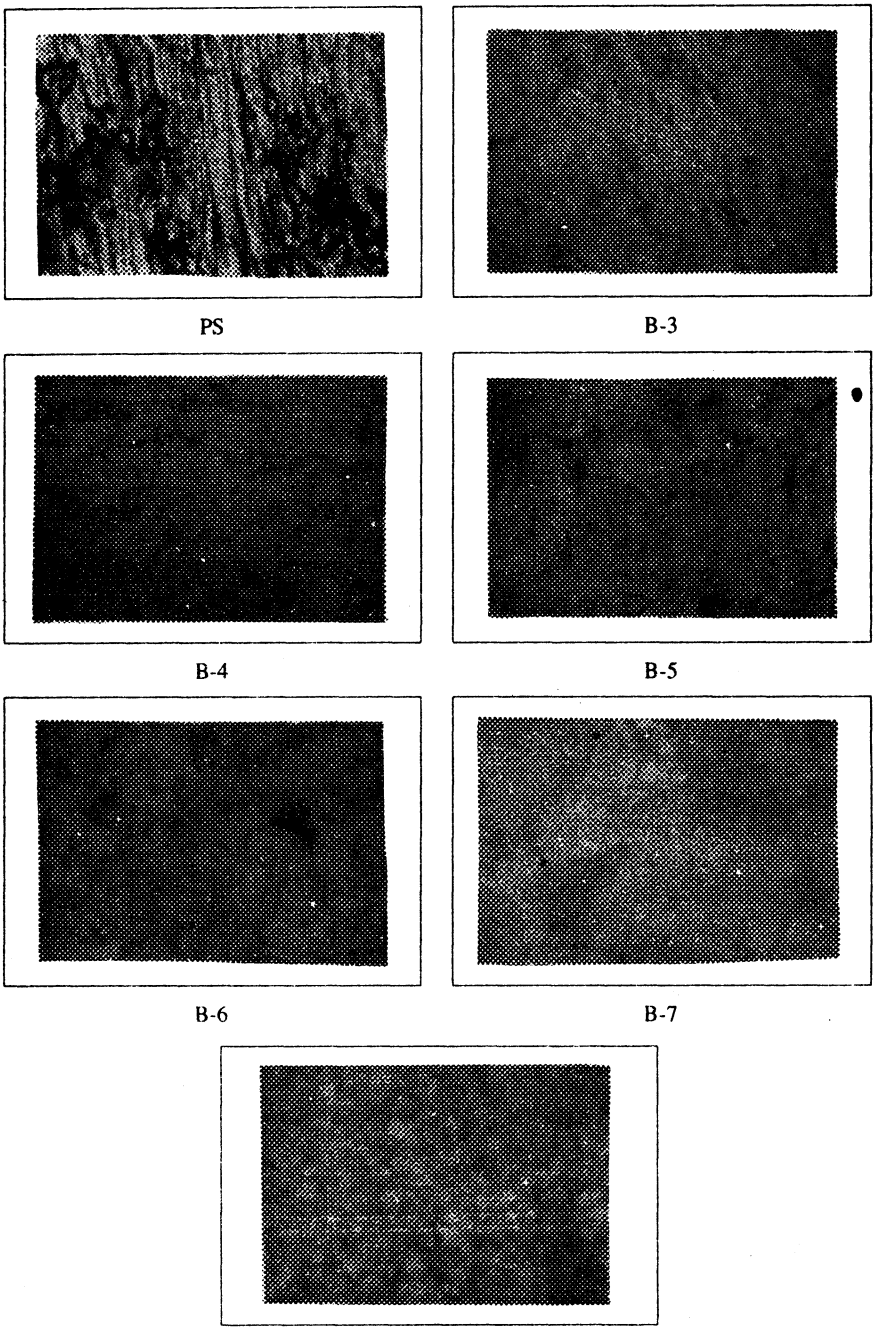
Density measurements of the melt extruded samples have been foundout using hydrostatic method of weighing. Experimental and theoretical values of density are given in Table 1. It is found that experimental values are higher than the calculated values. This can be understood in terms of packing densification in the blends. Packing densification affects the T_m and ΔH of the blends and this is found to be so. Similar nature of density dependence of blend composition in miscible blends of PVC have been noticed earlier.[19]

Morphology Studies

For studying the morphology of the blends, the samples prepared by all the three methods namely precipitation from nonsolvent, solution casting and melt extrusion have been used. Optical micrographs are obtained by Leitz optical microscope (OPTI PHOT) equipped with phase contrast and with magnification of 100x. Melt extruded blends with thickness in micron range are prepared and used for the morphology study. In the case of powder, samples, optical micrographs are taken using finely powered samples with particle size in micron range.

The main physical factors that determine the final morphology of the blends are component ratio, their intrinsic melt viscosity, rate of shear during melt mixing and presence of other ingredients.[20] If the processing history is same, then composition ratios and melt viscosity differences of the components determine the morphology. The phase structures of the blends have been characterised by optical microscopy and the optical micrographs are shown in Micrographs Group 1, Group 2 and Group 3. It is evident from the figure that there is considerable morphology change with change in the composition of the melt extruded blends. Further it is seen that a very different morphology is obtained for cast films and powder samples and morphology is highly dependent on the preparation techniques. The morphology of melt extruded pure PS (Micrographs Group 1) shows that molecules have been oriented to some extent during extrusion. During the formation of the blend, an entirely different morphology is obtained. It can be seen from the micrographs that the morphology change is prominent with the increase in the PVC content. Both homopolymers are distributed homogeneously

Group-1



PS

B-3

B-4

B-5

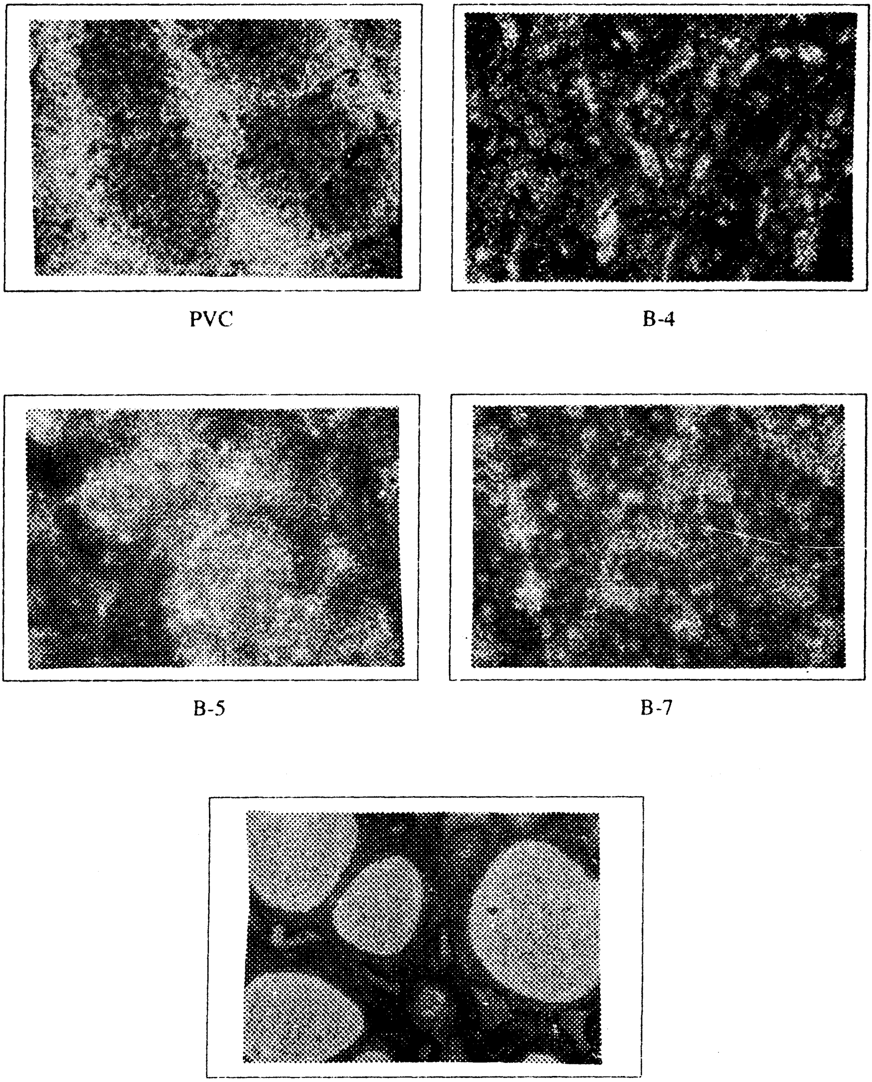
B-6

B-7

PVC

Optical micrographs of melt-PVC extruded PVC/PS blends

Group-2



PVC

B-4

B-5

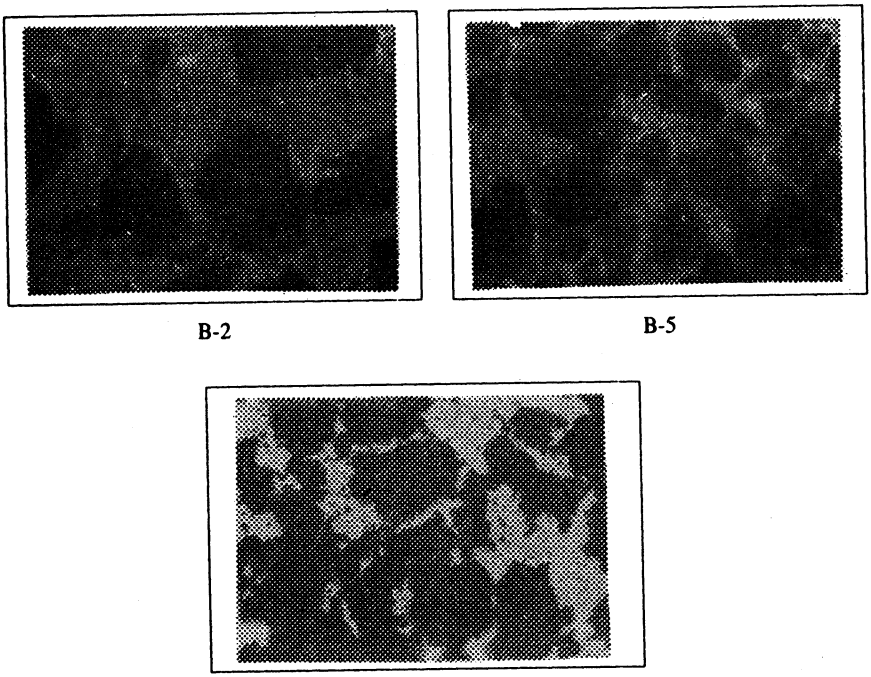
B-7

PS

Optical micrographs of PVC/PS blend films

and the blends seem to be compatible. A few white spots in the case of films are probably the solvent flow marks on the surface of the sample caused during sample preparation.

Group-3



B-2

B-5

B-7

Optical microgrpahs of PVC/PS blends (powder form)

Conclusion

Melt extruded blends of PVC and PS are miscible in each other. These blends have a single T_g and moderate level broadening of T_g transition occurs with increasing PVC content. The microheterogenity in the blend is due to the particle structure of PVC perturbing the mutual solubility of PVC and PS at molecular level. The higher values of T_g, T_m and ΔH observed for all the compositions from the theoretical value reveal that PVC and PS form compatible mixtures at all compositions as a result of strong intermolecular interaction. Maximum deviation of these thermomechanical properties from the theoretical values occurs around equimolar compositions. The results obtained from DSC are further confirmed from density measurements and optical microscopy. The experimental densities of all the blends are higher than their theoretical values showing packing densification in all the blends. Morphology studies also reveal good phase mixing.

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