Melting and crystallization behaviour of poly(vinylidene fluoride) samples in its blends with some polyacrylates, poly(vinyl esters) and poly(aryl ether ether ketone)

P. Maiti, J. Chatterjee, D. Rana and A. K. Nandi*
Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India
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The melting and crystallization behaviour of poly(vinylidene fluoride) (PVF_2) blends with each of poly(phenyl acrylate) (PPA), poly(methyl acrylate) (PMA), poly(vinyl benzoate) (PVBz), poly(vinyl acetate) (PVAc) and poly(aryl ether ether ketone) (PEEK) has been studied. Two PVF_2 samples with different amounts of head-to-head defect structure were used. The compatibility of PVF_2 with each of PPA, PVBz and PEEK has been tested by glass transition temperature measurements. The results indicate immiscibility in each case, which is attributed to steric hindrance of the phenyl group. The melting-point depression of PVF_2 in incompatible pairs of the above is less than in compatible pairs. Also, the initial slopes of the melting-point depression curves for lower-defect-content blends (compatible or incompatible) are lower compared with those of higher-defect-content samples. The crystallization kinetics of pure PVF_2, PVF_2 in incompatible blends and PVF_2 in compatible blends at weight fraction $w_{PVF_2}=0.8$ were measured at 147°C. The rate of crystallization of PVF_2 varies as: pure PVF_2 > incompatible blend > compatible blend. Analysis of the Avrami exponent indicates that the nucleation mechanism is the same for all cases, though the growth becomes diffusion-controlled for higher-defect-content PVF_2 samples and for its blends. Comparison of crystallization rate between lower- and higher-defect-content PVF_2 blends again indicates greater miscibility for higher-defect-content samples. The results have been explained qualitatively by homopolymer–copolymer miscibility theory.

(Keywords: poly(vinylidene fluoride); blends; crystallization kinetics)

INTRODUCTION

Poly(vinylidene fluoride) (PVF_2) blends have been extensively studied during the past several years[1]. Many commercial polymers are found to be compatible with this polymer[2–13]. The crystallization and melting behaviour of these compatible pairs are well documented[2–13] and in some cases such studies for incompatible blends[14,15] are also reported. However, no attention has yet been given to these blends with different commercial PVF_2 samples obtained from different chemical companies. Poly(vinylidene fluoride) chains are not completely regiospecific in structure but have both the usual head-to-tail (H-T) $-CF_2-CH_2-$ linkages and the unusual head-to-head (H-H) $-CF_2-CF_2-$ linkages[1,16]. Each H-H linkage is followed by a tail-to-tail (T-T) $-CH_2-CH_2-$ linkage. The amount of these reverse (H-H) linkages differs for different commercial samples and depends on the polymerization conditions[1,17]. From this reverse addition PVF_2 can be considered as a copolymer with $-CF_2-CH_2-$ and $-CF_2-CF_2-CH_2-CH_2-$ units. Recently, much interest has been shown for blends of copolymers and many new theories have been developed for the miscibility of copolymers with homopolymers and copolymers with copolymers[18–22]. It has been clearly established that blending ability depends on copolymer composition. By virtue of a significant amount of H-H defects in its structure, one may expect some dependence of blending of PVF_2 with other polymers on its H-H defect content in the chain. In this paper, we want to delineate this aspect of PVF_2 blends with some polymers whose blending has not been tested with PVF_2 and in some cases we chose some compatible pairs reported in the literature. In the first category we chose poly(phenyl acrylate) (PPA), poly(vinyl benzoate) (PVBz) and poly(aryl ether ether ketone) (PEEK). In the acrylate series, poly(methyl acrylate) and poly(ethyl acrylate) are reported to be miscible with PVF_2 but not the higher homologues[3]; similarly for poly(vinyl esters) only poly(vinyl acetate) (PVAc) is miscible but not the other members[4]. In each case no report has yet been found for the aromatic analogues, e.g. poly(phenyl acrylate) and poly(vinyl benzoate). In this paper the compatibility of the above polymers with PVF_2 will be examined.

Besides the above two polymers, we chose another industrially important, high-performance engineering thermoplastic, poly(aryl ether ether ketone) (PEEK). It is known from the literature that PVF_2 has a specific interaction with the $>C=O$ group[6,23,24]. This favours its miscibility with poly(vinyl methyl ketone)[5] and also

* To whom correspondence should be addressed

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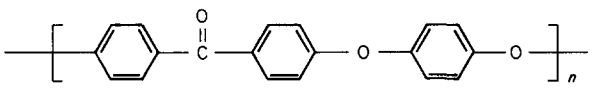
favours its solubility in benzophenone. PEEK has the structure



The keto group is in the main chain with an aryl ether ether linkage. The blending of this polymer with PVF_2 has been tested and results are reported here.

For the investigation of the effect of chain structure on the blending ability of PVF_2 we also used the polymers poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc). Blends with these two polymers help comparison with the properties of PPA and PVBz blends because PMA and PVAc are structural analogues of PPA and PVBz, respectively, and are compatible with PVF_2. In this paper the melting and crystallization behaviour of these polymers has been reported.

EXPERIMENTAL

Materials

Three commercial poly(vinylidene fluoride) samples were used in this work. They were KF-1000 of Kureha Chemical Co., Japan, Solvey-1012 of Solvey Corp. and Kynar KY-201 of Pennwalt Corp., USA. The characteristics of the samples are the same as reported earlier[25]. All the samples were recrystallized from dilute solution (1% w/v) in acetophenone. The PEEK that was used here is PEEK 450G from ICI and it was used as received. The other polymers were prepared in the laboratory. Poly(methyl acrylate) was prepared from benzene solution (20% v/v) of the distilled monomer using azobisisobutyronitrile (AIBN) (0.052% w/v) as initiator and dodecyl mercaptan (0.013% w/v) as chain transfer agent. They were polymerized under nitrogen atmosphere at 60°C. After polymerization for 2 h the polymer was precipitated with petroleum ether and reprecipitated by dissolving in benzene. The precipitated PMA was dried in a vacuum oven at 60°C for three days. Poly(vinyl benzoate) was prepared from benzene solution (27% v/v) using AIBN (0.31% w/v) as initiator at 60°C under nitrogen atmosphere. The resulting polymer was isolated by precipitation using petroleum ether as non-solvent and was purified by the reprecipitation method. The purified sample was dried in vacuum at 80°C for three days. The PPA was prepared using the method described earlier[26]. All the polymers were characterized from g.p.c. (Waters, USA) experiments with an Ultrastyragel column conditioned with toluene. The measurements were carried out taking polystyrene as standard. The molecular weight of PEEK was determined from intrinsic-viscosity measurements[27] in H_2SO_4 solution at 25°C. The characteristics of the polymers are presented in *Table 1*.

The solvents used in this work, *N,N*-dimethylformamide (DMF) (E. Merck) and toluene (E. Merck), were dried and distilled before use. Sulfuric acid (BDH, AR) was used as received.

Blend preparation

Weighed amounts of component polymers for a definite blend composition were dissolved in *N,N*-dimethylformamide at 70°C (oil thermostat). They were then homogenized and solvent was evaporated in an air oven at 50°C and the films were further dried in vacuum at 80°C for three days. For PEEK blends, weighed amounts of PEEK were dissolved in benzophenone at its boiling point. Weighed amounts of PVF_2 samples were added after cooling the PEEK solution to ~150°C where both the polymers make a homogeneous solution. The benzophenone was removed by evaporation in an air oven at 70°C and was further dried at 80°C in a vacuum oven for three days.

Glass transition temperature measurements

All the thermal measurements were done using a Perkin–Elmer DSC-7 (equipped with a 3700 data station), calibrated with indium. About 10 mg of the samples were crimped into aluminium pans and melted at 227°C for 5 min. They were then quenched to 50°C and were scanned at a heating rate of 10°C min^{-1}. For blends with PEEK, the samples were melted at 370°C and quenched to liquid nitrogen temperature. They were scanned at a heating rate of 20°C min^{-1} from 50 to 370°C. The quenching to liquid nitrogen temperature in this system was necessary to observe the glass transition behaviour distinctly.

Crystallinity and melting temperature measurements

The crystallinity and melting points of the blends were measured using a method described earlier[25] to avoid melt recrystallization. After melting at 227°C for 5 min the samples were isothermally crystallized at 144°C for 24 h and the crystallinity and melting points were determined from d.s.c. traces obtained at a heating rate of 10°C min^{-1}. The peak temperatures were taken as the melting points and crystallinities were measured from the endothermic area. For PEEK blends the samples were melted at 370°C and quenched to 50°C and were scanned at a heating rate of 20°C min^{-1} and the peak temperatures were taken as the melting point of PVF_2 and PEEK, respectively.

For the crystallization kinetics study, the samples were melted at 227°C for 5 min to destroy all the nuclei[28,29] and then quenched to 147°C. The kinetics measurements were done by the exothermic method for the Kureha PVF_2 samples and by the endothermic method for the

Table 1 Characteristics of the polymers used in the blends

	PVF_2							
	KF-1000	KY-201	Solvey-1012	PMA	PVAc	PVBz	PPA	PEEK 450G
H-H defect (%)	3.5	5.31	4.06	–	–	–	–	–
M.p. (°C)	176.6	164.3	173.0	–	–	–	–	345
Crystallinity (%)	57.3	49.1	55.0	–	–	–	–	28
$\bar{M}_w$ ($\times 10^{-5}$)	4.4[a]	6.7[a]	6.27[a]	1.93	2.08	0.35	3.53	0.24[a]
PDI	–	–	–	1.65	2.92	2.27	3.97	–

[a] Viscosity-average molecular weight ($\bar{M}_v$)

Kynar PVF_2 samples. In the exothermic method the exotherms at 147°C were recorded and crystallinities obtained at different times were measured from the estimated area at that time. In the endothermic method after crystallization for a predetermined time at 147°C the samples were scanned from 147 to 227°C at a heating rate of 10°C min^{-1} and crystallinities were determined from the peak area. The ΔH_u° for the calculation of the crystallinity of PVF_2 was taken[30] as 104.5 J g^{-1}.

RESULTS AND DISCUSSION

Glass transition temperature (T_g)

Figure 1 shows the glass transition temperature of poly(phenyl acrylate) and poly(vinyl benzoate) in Kureha and Kynar PVF_2 samples. Also in the figure the T_g values of PEEK–Solvey-1012 PVF_2 blends are shown. It is clear from the figure that the T_g values of the PPA, PVBz and PEEK are invariant with blend composition. The T_g of poly(vinylidene fluoride) is −40°C[31,32] and one would always expect a gradual decrease of T_g with PVF_2 content in the above blend systems if they form compatible blends. But the above observation points out that the polymers PPA, PVBz and PEEK are immiscible with PVF_2. To confirm the blending nature of the above blends, the melting point and crystallization kinetics were studied and have been compared with known structural analogue compatible polymer pairs for the former pair of polymers.

Melting points and crystallinity

The melting point of a crystalline polymer is depressed in the presence of a polymeric diluent and is governed by the equation[2]:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{Rv_c}{\Delta H_u v_a}\phi_a^2\chi \qquad (1)$$

where T_m and T_m° are equilibrium melting temperatures of the blend and pure polymer; v_c and v_a are the molar volumes of the repeat units of crystalline and amorphous polymer, respectively; ΔH_u is the enthalpy of fusion of the perfect crystal; ϕ_a is the volume fraction of the amorphous polymer; and χ is the polymer–polymer interaction parameter and is dependent on heat of mixing and is independent of combinatorial entropy of mixing[2,33]. Thus melting-point depression is independent of entropy of mixing of the two polymers and the amount of depression is dependent only on the amount of interaction provided the samples are crystallized and melted in a similar fashion[13,34]. But a correct determination of interaction parameter requires equilibrium melting-point determination very accurately[35]. However, for comparison purposes the non-equilibrium melting-point depression with composition can be used to obtain a qualitative idea of interaction between polymer segments rather than any quantitative measurement. The plots of melting point of PVF_2 with composition in the PPA, PVBz, PMA and PVAc blends are shown in *Figures 2a–d*, respectively. In each figure the melting-point depressions of Kureha and Kynar PVF_2 samples are shown. *Figures 2a* and *2b* represent the melting-point depression for incompatible blends and *Figures 2c* and *2d* represent the same for compatible blends. Here it has been found that the data fit almost a straight line except at some low PVF_2 content compositions. Generally T_m vs. composition plots are curved but for the initial portion of the plot for major cases straight lines can be drawn[2,5]. The slopes for each of the KF and KY PVF_2 in the compatible blends are much higher than those of incompatible blends (*Table 2*). The larger values of slopes in compatible pairs compared to those of incompatible pairs is, therefore, due to more segmental interaction of the components in the former pair than that in the latter pair at the melt. If one compares the slopes of the melting-point depression curves for Kureha and Kynar PVF_2 blends in each figure, it is apparent that whether compatible or incompatible the slopes for KY blends are much greater than those of KF blends. The absolute values of the slopes of KY blends are about 2–3 times larger than those of KF blends (*Table 2*). This, therefore, points out that KY PVF_2 experiences more interaction with the component polymers (compatible or incompatible) than that of KF PVF_2 blends. Apart from the larger molecular weight of the KY-201, it also has higher H-H defect concentration (*Table 1*) than the KF-1000 PVF_2 sample. But the molecular weight has an effect only on the entropy of mixing, which has no influence on melting-point depression. This greater concentration of defect or co-units, therefore, favours more mixing of the PVF_2 with other polymers. In the case of PEEK–PVF_2 blends the melting point–composition diagrams are shown in *Figure 2e*. In this system the melting points of Solvey-1012 PVF_2 blends show a unique pattern, which indicates phase separation in the melt in analogy with a polymer–small molecular diluent system[36]. (KF-1000 was not used here because of inconsistent results owing to degradation of this commercial polymer in the melting process. For the other cases the degradation rate is much slower.) However, KY-201–PEEK blends show a melting-point depression of PVF_2 in a similar fashion as for PPA and PVBz blends. In this diagram the melting point of PEEK with composition has been shown. There is a small decrease of melting point of PEEK with increasing PVF_2 content.

The crystallinities of the blends crystallized at 144°C have been plotted with composition and are shown in *Figure 3*. In *Figure 3a* the crystallinities of PVF_2 in PPA and PMA blends are shown, whereas in *Figure 3b* the crystallinities of PVF_2 in its PVBz and PVAc blends are showing. In *Figure 3a* the crystallinities of KF-1000 with compatible and incompatible polymers

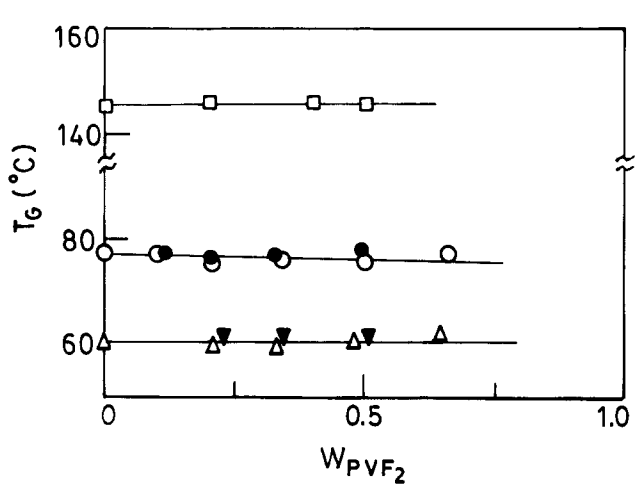


Figure 1 The T_g vs. composition (weight fraction) plot for PVF_2–PPA blends (△, ▼), for PVF_2–PVBz blends (○, ●) and for PVF_2(Solvey)–PEEK blends (□). Open symbols for Kureha (KF) PVF_2 and filled symbols for Kynar (KY) PVF_2

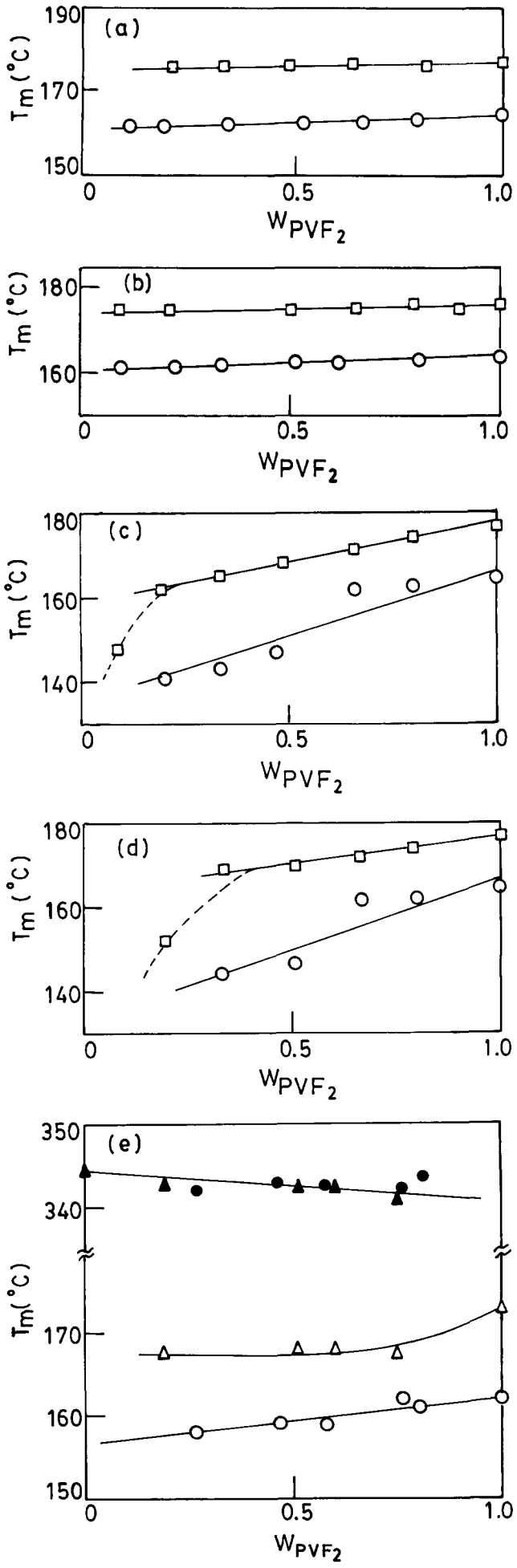


Figure 2 The T_m vs. composition plots of PVF_2 blends for Kureha (KF) PVF_2 (□) and for Kynar (KY) PVF_2 (○). (a) PVF_2 + PPA blends. (b) PVF_2 + PVBz blends. (c) PVF_2 + PMA blends. (d) PVF_2 + PVAc blends. (e) PVF_2 + PEEK blends: (△) Solvey PVF_2 + PEEK blends; (○) Kynar PVF_2 + PEEK blends; the filled symbols in the upper part of the figure indicate the melting points of PEEK for the respective blends

Table 2 Slopes of T_m vs. composition curve (initial portion) of PVF_2 in its blends

Blends of PVF_2 with	Slopes for		Ratio of slopes of KY and KF blends
	KF-1000	KY-201	
PPA	1.41	2.71	1.92
PVBz	1.08	2.78	2.58
PMA	18.53	34.54	1.86
PVAc	11.92	33.90	2.84
PEEK[a]	–	2.37	–

[a] The slope of PEEK–Solvey system was not calculated because of indication of phase separation at melt (see text)

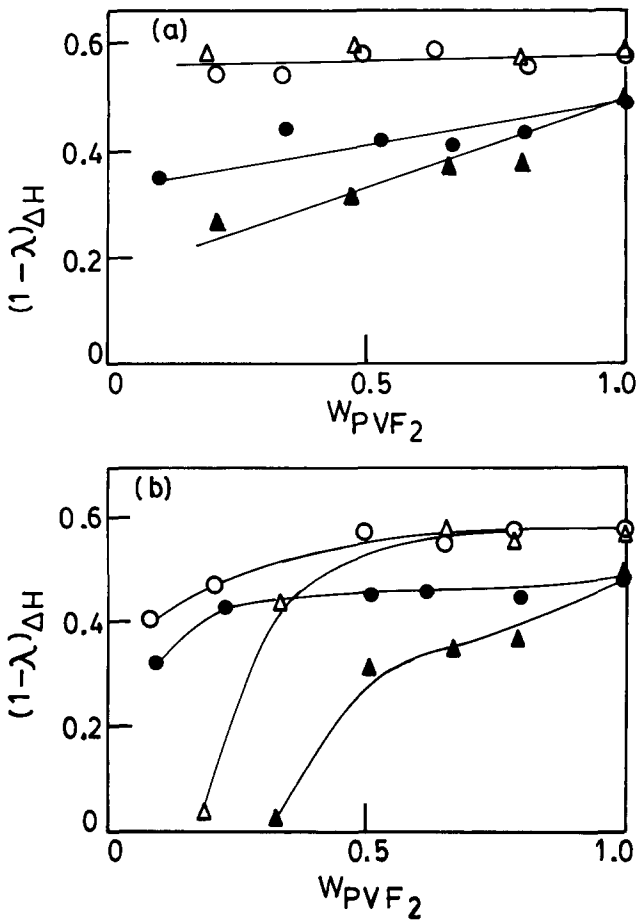


Figure 3 Crystallinity $(1-\lambda)_{\Delta H}$ of PVF_2 (open symbols, Kureha PVF_2; and filled symbols, Kynar PVF_2) in its blends (a) with PPA (○) and PMA (△), and (b) with PVBz (○) and with PVAc (△)

(PMA and PPA, respectively) do not differ at all after 24 h of crystallization. However, in the KY-201 sample the crystallinities of blends decrease with blend composition and for a compatible pair the absolute value of the slope of the straight line is greater than that of an incompatible system. In *Figure 3b* the situation is somewhat different from that of *Figure 3a*. Here for the KF system in the PVF_2-rich zone ($w_{PVF_2} > 0.5$) there is practically no

depression of crystallinity, but at $w_{PVF_2} < 0.5$ there is some depression in crystallinity, the depression being larger for compatible blends. In this figure, the KY-201 system exhibits a larger depression of crystallinities with blend composition for the compatible blend compared with the incompatible blend. The difference in crystallinities for compatible and incompatible polymer pairs is due to the stronger interaction of the components in the melt for compatible pairs.

Crystallization kinetics

The growth rate of polymer crystals in polymer blends should differ from that of the neat system because of dilution of the crystallizing unit. The growth rate (G) in the diluted system can be expressed as a modified form of Hoffman–Lauritzen equation[37]:

$$G = G_0 \phi_1 \beta_g \exp[-K_g/T_c(\Delta T)f] \quad (2)$$

where G_0 is the pre-exponential factor, ϕ_1 is the volume fraction of the crystalline polymer, β_g is the transport factor, K_g is related to the end and lateral surface energies, ΔT is the undercooling, T_c is the crystallization temperature and f is a correction factor. Thus, one would always expect a lower crystal growth rate of the crystalline polymer in its blends (compatible or incompatible) than in neat polymer because $\phi_1 < 1$ except in cases where nucleation[15] occurs. In compatible blends there is more interaction between the segments of the two polymers in the melt compared to that of incompatible polymer pairs. The interaction of the polymer segments is manifested in the nucleation term of equation (2) and particularly in the undercooling (ΔT) term. The more the interaction, the greater is the equilibrium melting-point depression and hence the smaller is the undercooling experienced by the crystalline polymer. Thus increased interaction causes slower crystallization rate. From the comparison of crystallization isotherms of incompatible and compatible blends at a fixed composition of the crystalline polymer, one would be able to get an idea about the dilution effect on crystallization and about the interaction, hence the miscibility of the compatible pair in the melt.

In the experiment we choose the temperature 147°C where all the samples used here crystallize isothermally from the melt at a moderate rate. The results are shown in *Figures 4–7* where crystallinities are plotted against log(time). In each figure, curve a corresponds to the crystallization isotherm of pure PVF_2 (KF or KY), curve b those of the blends with incompatible and curve c those of the blends with compatible analogue. From

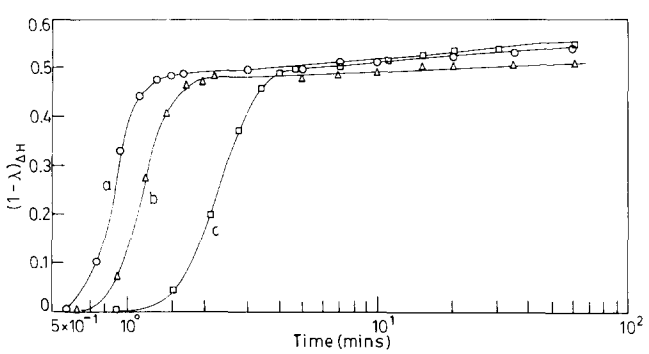


Figure 4 Crystallization isotherms of PVF_2 at 147°C: (a) Kureha PVF_2, (b) Kureha PVF_2 + PPA ($w_{PVF_2} = 0.8$) and (c) Kureha PVF_2 + PMA ($w_{PVF_2} = 0.8$)

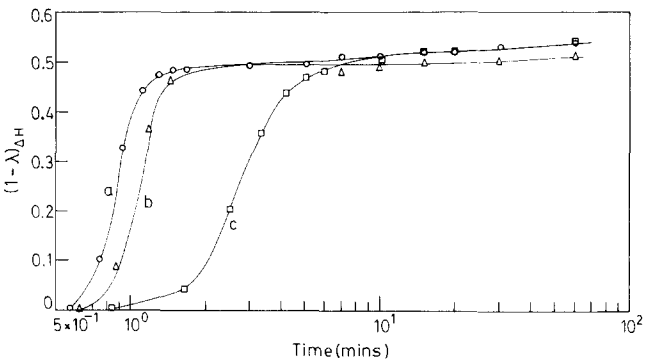


Figure 5 Crystallization isotherms of PVF_2 at 147°C: (a) Kureha PVF_2, (b) Kureha PVF_2 + PVBz ($w_{PVF_2} = 0.8$) and (c) Kureha PVF_2 + PVA ($w_{PVF_2} = 0.8$)

Figures 4–7 it is very much apparent that the rate of crystallization changes as c < b < a. The slower rate of crystallization for curve b is due to the dilution of crystallizing unit and the distance of the curve b from curve a should be the same for the two incompatible polymers (PPA and PVBz) in log(time) scale if only the dilution effect is operating. However, every polymer pair (compatible or incompatible) has some amount of segmental interaction, the magnitude of which dictates the compatibility. Thus it is very difficult to separate out the dilution effect alone. However, an approximation can be made that the growth rate in an incompatible polymer pair may be treated as the dilution effect, considering the interaction between the two polymers is very close to zero.

The crystallization isotherms of *Figures 4–7* will now be analysed based on the above discussion. In *Figures 4* and *5* the crystallization isotherms of KF-1000 in PMA and PVAc blends clearly point out that there is a significant amount of interaction between PVF_2–PMA and PVF_2–PVAc pairs compared to that of PVF_2–PPA and PVF_2–PVBz pairs, respectively. Similarly if one considers the crystallization isotherms of KY-201 in *Figures 6* and *7* the slower crystallization rate compared to incompatible pairs clearly indicates more interaction in compatible pairs. To get a quantitative idea about the interaction, we measured the time required to obtain 10% crystallinity ($\tau_{0.1}$) for each case. The results are shown in *Table 3*. The $\tau_{0.1}$ difference (b − a) for KF–PPA is 0.21 min and is almost the same (0.16 min) as that of KF-PVBz within experimental accuracy. Disregarding the small interaction (if any) within the above pairs, this decrease in crystallization rate may be attributed to the dilution effect due to the other component of the PVF_2 blend. The $\tau_{0.1}$ (c − b), therefore, corresponds to an index of interaction of PVF_2 segments with the segments of other components in the compatible blend. The $\tau_{0.1}$ (c − b) for PMA is 0.8 min while that for PVAc is 1.1 min. If we analyse the KY-201 system in a similar fashion, $\tau_{0.1}$ (b − a) = 14.1 min for KY–PPA blends and $\tau_{0.1}$ (b − a) = 15.6 min for KY–PVBz system. The $\tau_{0.1}$ (c − b) = 60.5 min and 82 min for KY–PMA and KY–PVAc systems, respectively.

The comparison of $\tau_{0.1}$ values of KF-1000 and KY-201 blends can also be done in another way. From *Table 3* it is clear that $\tau_{0.1}$ of KY-201 is exactly 10 times larger than that of KF-1000 in the neat system. This difference in behaviour between the two samples lies in the head-to-head structural irregularity present in the system: the higher the defect content, the greater is the hindrance to crystallization at a particular T_c (ref. 29). In analogy

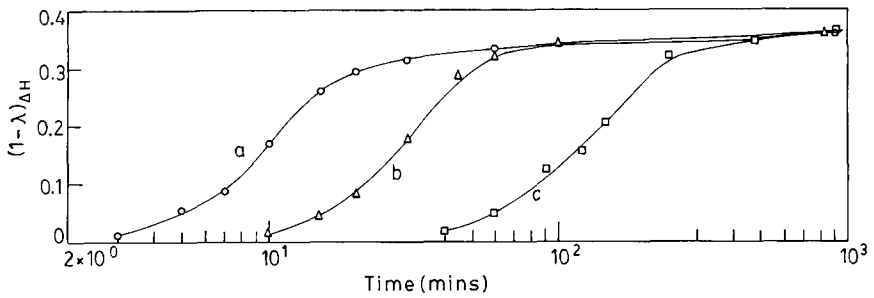


Figure 6 Crystallization isotherms of PVF_2 at 147°C: (a) Kynar PVF_2, (b) Kynar PVF_2 + PPA ($w_{PVF_2}=0.8$) and (c) Kynar PVF_2 + PMA ($w_{PVF_2}=0.8$)

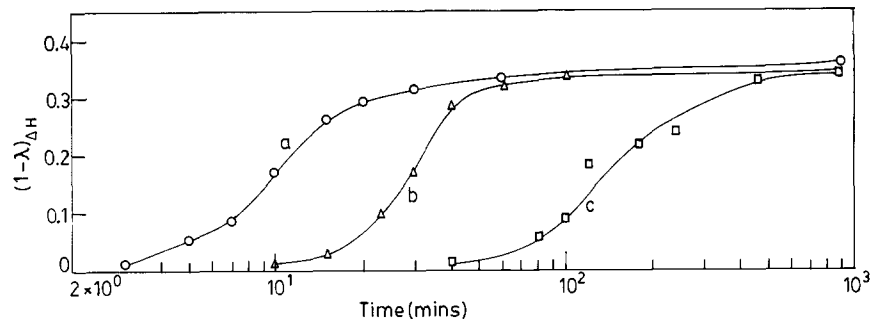


Figure 7 Crystallization isotherms of PVF_2 at 147°C: (a) Kynar PVF_2, (b) Kynar PVF_2 + PVBz ($w_{PVF_2}=0.8$) and (c) Kynar PVF_2 + PVAc ($w_{PVF_2}=0.8$)

Table 3 Time required to obtain 10% crystallinity, $\tau_{0.1}$ (min), of PVF_2 for its blends at 147°C

	Blends of KF-1000 with		Blends of KY-201 with	
Curves	PMA & PPA	PVAc & PVBz	PMA & PPA	PVAc & PVBz
a	0.74	0.74	7.4	7.4
b	0.95	0.90	21.5	23.0
c	1.75	2.05	82.0	105.0

to curve a, one would always expect for curves b and c exactly 10 times greater $\tau_{0.1}$ values for KY-201 blends compared to those of KF-1000 blends. However, for both curves it is more than the expected value: In the Kynar system the expected value of $\tau_{0.1}$ for curve b is ~10 min, but actually it is two times greater than the expected value. Similarly for the compatible system (curve c) the expected $\tau_{0.1}$ value for KY-201 blends is ~20 min, but actually it is 4–5 times larger than this expected value. The probable reason for this behaviour lies in the greater amount of interaction in the KY blends compared to that of KF blends. Also in this kinetic analysis it is clear that PVF_2–PVAc miscibility is more than that of PVF_2–PMA miscibility. But from the melting-point study this difference was not observed. A probable reason is that, though PMA and PVAc have almost the same weight-average molecular weight ($\bar{M}_w$) (*Table 1*), they differ in polydispersity. The PVAc has higher polydispersity value than (almost double that of) PMA. So there is a larger number of low-molecular-weight polymers for PVAc than for PMA. This low-molecular-weight component contributes more entropy of mixing to the miscibility of the polymers. This entropy effect is not seen in the melting-point depression analysis, as discussed earlier.

The nucleation and growth mechanism of PVF_2 crystals in its blends will now be illuminated. For this purpose the Avrami exponent n is calculated. The Avrami equation for the amount of transformation at time t is[36]:

$$1-\lambda_t = 1-\exp(-kt^n) \quad (3)$$

where k is the overall rate constant and n denotes the nature of the nucleation and growth process. For a small amount of transformation, equation (3) reduces to the Goler–Sachs form:

$$1-\lambda_t = kt^n$$

where n and k have the same significance[36]. Applying the Goler–Sachs equation for crystallization in polymer blends, we want to analyse our crystallization kinetics data. The n values are presented in *Table 4*. From the table it is clear that in the neat system KF-1000 has n value close to 3 and KY-201 has n value close to 2 within error limits. Thus at this temperature two polymer samples, having different amounts of H-H defect structure, differ in nucleation and growth mechanism[29]. For the former case it is two-dimensional nucleation with linear growth, while in the latter case it is two-dimensional nucleation with diffusion-controlled growth[36]. In the case of an incompatible pair, no change in n value is observed

Table 4 Avrami exponent n (± 0.2) at 147°C for crystallization of PVF_2 and its blends

Curves	Blends of KF-1000 with		Blends of KY-201 with	
	PMA & PPA	PVAc & PVBz	PMA & PPA	PVAc & PVBz
a	3.3	3.3	2.1	2.1
b	3.3	3.5	1.9	2.0
c	2.8	2.6	1.8	1.9

practically, but in the case of compatible pairs, there is some decrease in the value of n particularly for the KF system. Here, the nucleation mechanism appears to remain the same though there is some increasing tendency for diffusion-controlled growth.

CONCLUSION

To sum up our discussion we want to explore the cause of immiscibility of PVF_2 with the newly studied polymers. Here the melting-point depression is much lower than that of the compatible polymer pairs of PVF_2. But it is well known that PVF_2 has a specific interaction with

$$>C=O \qquad \text{or} \qquad -C(=O)-O-$$

groups[23,24,38,39]. The incompatibility in these cases may be due to steric hindrance of the bulkier phenyl group, which hinders the favourable contacts of the interacting groups required for mixing.

Also to conclude our discussion on the difference in behaviour of KF-1000 and KY-201 blends, it appears that for the higher-defect-content sample the interaction with the component (compatible or incompatible) is more comparable to that of lower-defect-content sample. From the copolymer–homopolymer miscibility theory of Paul and Barlow[20] the effective interaction parameter can be expressed as:

$$B = B_{HT}\phi_1 + B_{HH}\phi_2 - B_{HT/HH}\phi_1\phi_2 \qquad (4)$$

where B_{HT} is the polymer–polymer interaction parameter with pure H-T PVF_2 chain, B_{HH} is the interaction parameter for pure H-H addition, $B_{HT/HH}$ is the interaction parameter of H-T units with H-H adducts, ϕ_1 is the volume fraction of H-T units and ϕ_2 is the volume fraction of H-H adducts. To make the effective interaction parameter negative (favouring miscibility) $B_{HT/HH}$ should be positive, i.e. H-T linkages should disfavour H-H and T-T linkages. Actually there is ample evidence from resonance and steric viewpoints that H-T addition is normal[40] and so there is always a repulsion between H-T and H-H adducts in the chain. However, for a quantitative investigation of the above equation, determination of values of B is necessary and has been undertaken with sharp PVF_2 fractions having smaller structural polydispersity. Of course, equation (4) correctly predicts a dependence of chain microstructure on the blending ability of PVF_2.

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