PII: S0032-3861(96)00757-4

Polymer Vol. 38 No. 9, pp. 2171–2174, 1997

0032-3861/97/$17.00 + 0.00

Kinetic immiscibility of crystalline polymer/ amorphous polymer blends

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(Received 7 May 1996)

In crystalline polymer/amorphous polymer blends the crystalline component crystallizes out, however low its concentration in the blend, if the blends are left at room temperature for months/years after its preparation, provided the diffusion is permissible at room temperature. This phenomenon has been termed 'kinetic immiscibility' in crystalline polymer/amorphous polymer blend. Blends of poly(vinylidene fluoride) (PVF_2) samples with poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc) have been studied with varying concentration, molecular weight and H–H defect of PVF_2. The crystallization rate of PVF_2 in the blends was measured by d.s.c. in the endothermic way and has been explained by the modified Lauritzen–Hoffman (L–H) growth rate theory applicable to the blends. The results suggest that the nucleation term, transport term and the concentration of crystallizing unit are the governing factors for the kinetic immiscibility. The molecular weight of the crystalline polymer has a significant effect on its crystallization in the blend because it directly effects the diffusion processes retarding the depletion of amorphous polymer from the crystalline growth front. This study places a warning on the use of transparent homogeneous crystalline polymer/amorphous polymer blends. © 1997 Elsevier Science Ltd.

(Keywords: kinetic immiscibility; poly(vinylidene fluoride); poly(methyl acrylate))

INTRODUCTION

The thermodynamic condition for the miscibility of polymers in the liquid state are (i) the Gibbs free energy of mixing (ΔG_m) must be negative and (ii) the compositional variation of ΔG_m should be concave upward[1,2]. But there is a class of polymer blends where in spite of the fulfilment of the above conditions they may be phase separated, not at the time of blending, but may be after several days or after several months or even after several years of its preparation. This class of blends are the miscible blends of crystalline polymer with amorphous polymers and the phenomenon has been termed 'kinetic immiscibility' of the crystalline polymer from the miscible blend[3]. Here, though the thermodynamic conditions of not forming liquid–liquid phase separation is fulfilled, there is another force, viz. the crystallization force which is always operating in the system. Actually, it is a competition between the thermodynamic force of mixing and the crystallization force of demixing which persists in such blends and it will be shown in this paper how crystallization force wins the race!

EXPERIMENTAL

The unfractionated poly(vinylidene fluoride) (PVF_2) samples (KF and KY) and a vinylidene fluoride–tetrafluoroethylene (VF_2–VF_4) copolymer have been blended with poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc). The characterization of the samples used in this study, has been made using the methods reported earlier[3] and the characteristics of the samples are presented in *Table 1*. The blends of varying compositions were made using *N,N*-dimethyl formamide as common solvent with the same procedure as reported earlier[3].

The crystallization of the samples were performed by quenching the samples from the melt at 227°C to room temperature (30°C). After leaving for certain times (minutes, days or months) they were heated in DSC-7 from 50°C to 227°C at the heating rate of $10° \mathrm{min}^{-1}$. The crystallinity was calculated from the endotherm using the 3700 data station equipped with the DSC-7. It was calibrated with indium before use. The ΔH_u^0 value for this polymer was taken equal to 1600 cal mol^{-1}[4].

RESULTS

Figure 1 represents the crystallization isotherms of KF + PMA, KY + PMA and Cop-1 + PMA blends crystallized by keeping the melt at room temperature (~30°C) for several days for the blend composition $w_{PVF_2} = 0.10$ (w = weight fraction). From the figure it is apparent that the KF/PMA crystallizes very fast ($\tau_{0.1} = 1.5$ min where $\tau_{0.1}$ is the time required to get 10% crystallinity of PVF_2), KY/PMA crystallizes more slowly ($\tau_{0.1} = 10$ days), whereas the Cop-1/PMA blend crystallizes at a rate intermediate of the two ($\tau_{0.1} = 4$ days). *Figure 2* also represents similar results for KF/PVAc and KY/PVAc blends for different blend compositions. From the figure it is clear that at the blend composition of $w_{PVF_2} = 0.20$ the KF/PVAc system has $\tau_{0.1} = 12$ days whereas for the KY/PVAc system $\tau_{0.10} = 210$ days. The KF/PVAc ($w_{KF} = 0.10$) attains

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Table 1 Characteristics of the PVF_2, VF_2–VF_4 copolymer, PMA and PVAc samples

Sample	$\bar{M}_w$ 10^{-5}	PDI	H–H defect (mol%)	T_m [a]	$(1-\lambda)_{\Delta H}$ [a]
KF-1000 (KF)	4.28	1.47	3.5	176.6	57.3
KY-201 (KY)	7.36	2.04	5.31	164.3	49.1
VF_2–VF_4 copolymer (Cop-1)	1.97	2.07	15.8	150.8	27.7
PMA	2.57	1.62		-	–
PVAc	2.08	2.92	–		–

[a] The T_m and $(1-\lambda)_{\Delta H}$ of PVF_2 were measured in d.s.c. by crystallizing the sample at 144°C for 24 h and Cop-1 was crystallized at 120°C for 24 h

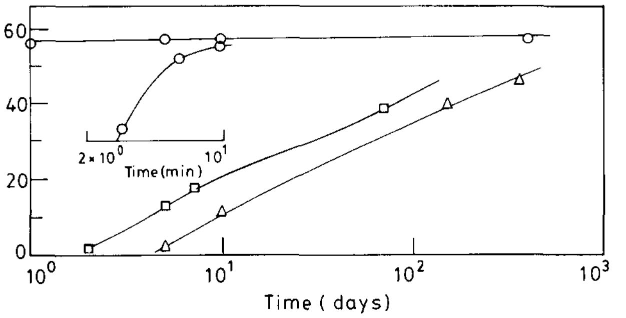

Figure 1 Plot of crystallinity $(1-\lambda)_{\Delta H}$ vs log time (days) for PVF_2/PMA and Cop-1/PMA blends $w_{PVF_2/Cop\text{-}1} = 0.10$ crystallized at 30°C. ○, KF PVF_2/PMA; △, KY PVF_2/PMA; and □, Cop-1/PMA. (Inset drawing indicates the same plot with time in minutes)

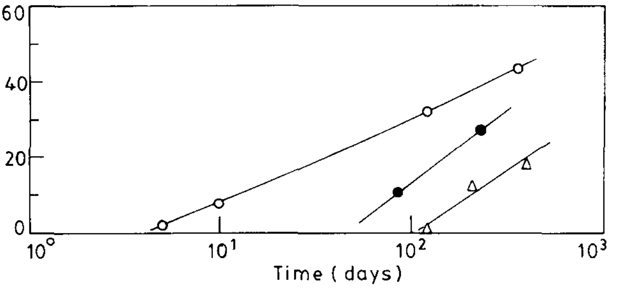

Figure 2 Plot of crystallinity $(1-\lambda)_{\Delta H}$ vs log time (days) for PVF_2/PVAc blends crystallized at 30°C; for $w_{PVF_2} = 0.20$; ○, KF PVF_2/PVAc; △, KY PVF_2/PVAc blends; and ●, for $w_{PVF_2} = 0.10$ of KF PVF_2/PVAc blend

10% crystallinity of PVF_2 in 80 days. Thus a transparent film of PVF_2/Cop-1 blends becomes gradually opaque by crystallization if it is left for several days/months after its preparation.

So it is clear from the figures that though they are miscible in the melt as well as in the solid state (at the initial stage) they gradually become immiscible in the solid state producing the PVF_2/Cop-1 crystals. The thermodynamic force of mixing of the two polymers is sufficient enough[3] but after keeping for longer periods the crystallization of PVF_2 takes place, indicating that the crystallization force is greater than the blending interaction. The crystallization rate of polymer blends is governed by the modified Lauritzen–Hoffman (L–H) equation[5]

$$G = G_o\,\phi_2\,\exp\left(\frac{-U^*}{R(T-T_\alpha)}\right) \times \exp\left(\frac{-K_g(i)}{T(T_m^o - T)} + \frac{0.2T_m^o \ln\phi_2}{T_m^o - T}\right) \qquad (1)$$

where G is the crystal growth rate, ϕ_2 is the volume fraction of the crystalline polymer, U^* is the activation energy of transport, $T_\alpha = (T_g - 30°)$K, T is the temperature of crystallization, T_m^o is the equilibrium melting point of the crystal in the blend, $K_g(i)$ is the nucleation constant of the ith regime: $K_g(\mathrm{I}) = 2K_g(\mathrm{II}) = K_g(\mathrm{III})$ with $K_g(\mathrm{I}) = 4b\sigma\sigma_e T_m^o / k\Delta h_f$, where σ and σ_e are the lateral and end surface free energies, respectively, b is the stem width, k the Boltzmann constant and Δh_f is the enthalpy of fusion per unit volume. The first and second exponent terms are usually called transport term and nucleation term, respectively[6].

As mentioned in the Introduction the miscibility is governed by the thermodynamics, so from the χ values, as presented in *Table 2*, it can be easily concluded that the miscibility in the PVF_2/PMA blend follow the order KF > KY > Cop-1. The enthalpy of mixing calculated from the χ values using the extended form of Van laar–Hildebrand Scatchard equation was found to be $-5\,\mathrm{cal\,mol^{-1}}$ for this composition[10]. So it is much weaker than the crystallization enthalpy ($1600\,\mathrm{cal\,mol^{-1}}$)

Table 2 Kinetic and thermodynamic parameters of PVF_2/PMA and PVF_2/PVAc blends ($w_{PVF_2} = 0.10$)

	PVF_2/PMA system			PVF_2/PVAc system		
Sample	T_g(°C) [a]	ΔT [b]	χ [c]	T_g(°C) [a]	ΔT	χ
KF	4	157	−0.15	23 (14)	-	–
KY	4	151	−0.11	23 (14)		
Cop-1	5	130	−0.03			

( ) indicates T_g value for $w_{PVF_2} = 0.20$

[a] T_g values were calculated using Fox equation[7] and T_g of $PVF_2 = -39°C$[8], PMA = 10°C[9] and PVAc = 32°C[9]

[b] The undercooling (ΔT) at 30°C has been calculated from the plot of T_m^o vs composition of the blends of ref. 3

[c] From plots of χ (obtained numerically)[3,10] vs composition

for PVF_2[4]. Consequently, the crystallization is inevitable and this will make the system immiscible. Since crystallization is a kinetically controlled process so this immiscibility has been termed as kinetic immiscibility[3].

According to equation (1) the kinetic immiscibility of the crystalline polymer in the blend is governed by three factors: (1) the nucleation term, i.e. the undercooling ($T_m^o - T$), (2) the transport term, i.e. the T_g of the blend and (3) the composition of the blend. In the case of PVF_2/PMA blends (*Figure 1*) the undercoolings at 30°C for KF, KY and Cop-1 is 157°, 151° and 130°, respectively (*Table 2*). Therefore, according to the equation (1) the crystallization rate would be in the order of KF > KY > Cop-1, provided they all crystallize in the same regime. Since the undercooling is very large so crystallization in regime III is expected for all the cases[11]. [From the isothermal crystallization rate study of the PVF_2 fractions the onset of regime III crystallization temperature at the composition $w_{PVF_2} = 0.10$ is expected to be at 139 and 127°C for KF PVF_2 and KY PVF_2 systems, respectively[12] (it is obtained from the extrapolation of regime III transition temperature vs composition plot). For the Cop-1 system, assuming linearity of regime III transition temperature with H–H defect, it is ~80°C. So we can safely conclude that the crystallization at 30°C for all the systems produce regime III crystals.] But from *Figure 1* it is clear that the crystallization rate is in the order KF > Cop-1 > KY in their blends. To explain the anomaly, the influence of the second factor of the kinetic immiscibility has been explored. The T_g of the PVF_2/PMA blend at $w_{PVF_2} = 0.10$ is 4°C and is, therefore, closer to the crystallization temperature (30°C). So the transport term has a large influence on the crystallization rate of these blends and this appears to be true because the undercooling of the blends is really very large and in the neat PVF_2 such a large undercooling produces quenched crystals[13]. Instead, here we observed a much slower rate and this happens due to the slower rate of ejection of the PMA from the growth front. The ejection of PMA from the crystal–liquid interface of the melt is dependent on the mutual diffusion which varies inversely with the degree of polymerization[14–16] of the components in the blend. Among the PVF_2/Cop-1 samples KY PVF_2 has the highest molecular weight so the rate of depletion of PMA from the growth front in this system is slower than the others and consequently, the crystallization rate of KY/PMA blend is slower. In the crystallization of polymers from the pure melt the molecular weight has no significant influence in the transport term, provided T_g is invariant in that molecular weight region[6], but it has significant influence in the crystallization rate of the blend as presented in the PVF_2/poly(methyl methacrylate) (PMMA) system, where the diffusion has been studied by varying the molecular weight of PMMA[16]. In this work they showed that the crystallization rate in regime I and regime III crystallization is dependent on the mutual diffusion and during the crystallization in the regime II it is dependent on both the self and mutual diffusion. The diffusion coefficient is inversely related to the degree of polymerization of the crystalline component[14–16] and so the crystallization rate will be slower with increasing the molecular weight of the crystalline polymer in the blend. This is the probable cause for the higher crystallization rate of Cop-1 than that of KY PVF_2 in their blends with PMA, though the undercooling of Cop-1/PMA is lower than that of KY/PMA blend.

The crystallization isotherms of the PVF_2/PVAc system (*Figure 2)* can similarly be explained. Though the exact value of undercooling of KF PVF_2/PVAc and KY PVF_2/PVAc is not known, a similar dependence of T_m^o with H–H defect in this system to that of PVF_2/PMA blends is expected because the interaction is of the same nature[3]. So the KF PVF_2 has higher undercooling than that of KY PVF_2 at 30°C and also the molecular weight of KF PVF_2 is lower than that of KY PVF_2. Consequently, the KF PVF_2 has higher crystallization rate than that of KY PVF_2 in the blend. The T_g of the blend is 23°C and is much closer to the crystallization temperature (30°C). So, the crystallization rate of each PVF_2/PVAc blends is much slower than that of PVF_2/PMA blends at identical blend composition ($w_{PVF2} = 0.10$). Here also the influence of concentration of crystalline polymer on the kinetic immiscibility can be discussed. In *Figure 2* we observed a greater crystallization rate of PVF_2 for the composition $w_{PVF_2} = 0.20$ compared to that at $w_{PVF_2} = 0.1$ in the PVF_2/PVAc blend. This is in accordance with equation (1). Therefore, the larger PVF_2 content blends crystallize at faster rates producing opaque films during its preparation either by solvent cast or by melt quenched method.

DISCUSSION

It is pertinent here to discuss the kinetic data of the PVF_2/PMA system reported in the literature[17]. From the kinetic results of isothermal crystallization of 147°C for the PVF_2/PMA and PVF_2/PVAc blends ($w_{PVF_2} = 0.80$) it is apparent that KY PVF_2 crystallizes at much slower rate than expected. In the neat polymer KY PVF_2 crystallizes at about a ten times slower rate than that of KF PVF_2 due to the larger amount of H–H defect present in KY PVF_2[12,17]. A similar slowness in crystallization rate of KY PVF_2 in the blend is expected if the interaction of the two polymers is the same with PMA. However, we found that the interaction of KF PVF_2 is stronger than that of KY PVF_2 with PMA[3]. Consequently KY PVF_2 should crystallize at somewhat higher rate than the slowness present in the neat PVF_2 from the blend. Instead we observe a 4–5 times slower rate of KY PVF_2 than the expected value, for crystallization in the blend[17]. Here the reason is not due to larger interaction of KY PVF_2 with PMA, as predicted there[17], but lies in the slower depletion of PMA from the crystal growth front in the KY PVF_2 blend than that in KF PVF_2 blends as discussed above. So the kinetic immiscibility in the crystalline polymer/amorphous polymer blend is dependent on the molecular weights of the components, undercooling, blend composition and the glass transition temperature of the blend. In some recent treatment, the expression of growth rate in the polymer blends has been modified by introducing a correction factor ($T_m^o \Delta G_m / \Delta H_u^o$) in the undercooling term of Lauritzen–Hoffman growth rate equation[18]. Since in this case the crystallization enthalpy (ΔH_u^o) is ~300 times larger than the enthalpy of mixing and also the entropy of mixing in the polymer blends is much smaller[1], so the contribution of the correction factor in the growth rate of this system is almost negligible. Therefore, the growth rate is governed mainly by the crystallization kinetic parameters as discussed above.

CONCLUSION

Thus to conclude these results it is apparent that in a blend of crystalline polymer with amorphous polymer the crystalline component will crystallize out however small its concentration in the miscible blend, provided the diffusion is permissible at that temperature. This is because the crystalline state is thermodynamically of lower energy state than the glassy state which is a metastable state[19]. This kinetic immiscibility of crystalline polymer in the crystalline polymer/amorphous polymer blend, therefore, places a warning on its use where a transparent blend is required and the higher molecular weight components would be a better choice to make such a blend. However, in this case it may also be technologically important to produce time-regulated piezosensors by the choice of appropriate PVF_2/copolymer samples and blend composition.

ACKNOWLEDGEMENTS

We acknowledge Prof. N. Gvodzic, Michigan Molecular Institute, USA for his valuable discussion at the International Symposium of Macromolecules, VSSC, Trivandrum, India and we also acknowledge CSIR (grant No. 4(112)/91 EMR11), New Delhi for financial support of the work.

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