

Glass-Transition Temperature of Poly(vinylidene fluoride)-Poly(methyl acrylate) Blends: Influence of Aging and Chain Structure

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ABSTRACT: The glass-transition temperature (T_g) of the poly(vinylidene fluoride) (PVF₂)-poly(methyl acrylate) (PMA) blends increase with aging time. The T_g versus log(time) plots are straight lines whose slope values depend on the head to head (H–H) defect content of PVF₂ samples and on the composition of the blends. The values of polymer–polymer interaction parameters (χ) increase with an increase in the H–H defect of PVF₂ for a fixed composition of the blend. Consequently, the T_g of the blend decreases with an increase in the H–H defect of the PVF₂ sample. However, after aging for longer times this decrease of the T_g with H–H defects is lower than those of the unaged blends. The possible reasons are discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1541–1548, 2001

Key words: glass-transition temperature; poly(vinylidene fluoride); poly(methyl acrylate); polymer blends; aging; head to head defect

INTRODUCTION

Polymer blends have been an important area of research for the past few decades because of industrial and academic interest.^{1–3} The blends may consist of polymers that are both amorphous, one crystalline and one amorphous, or both crystalline. In the first case, the polymer–polymer miscibility is governed solely by the thermodynamics of mixing^{1,2}; however, in the latter two systems the mixing is complicated through the crystallization processes because it has a kinetic effect.^{4,5} In the compatible crystalline polymer and amorphous polymer blends there is a single glass-transition temperature (T_g), but the sys-

tems are two-phase systems (the crystalline phase and the amorphous phase), particularly at a higher concentration of the crystalline polymers. In the other extreme of the concentration spectrum the blend may be a homogeneous single-phase system during its preparation, but an increase in the aging time may transform it into a two-phase system because of the appearance of the crystalline phase.⁴ This is termed as kinetic immiscibility of the crystalline polymer and amorphous polymer blends.^{4,5} In our earlier article⁴ we discussed kinetic immiscibility from the viewpoint of the kinetics of crystallization and its dependence on polymer–polymer interaction parameters, molecular weight, concentration, and so forth. Here we want to discuss the influence of kinetic immiscibility on the T_g of the blends.

Compatible polymer blends usually exhibit a single T_g ,^{1,2} which is situated between the T_g values of the pure components. In crystalline polymer and amorphous polymer blends the same

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Table I Characteristics of PVF₂, VF₂-VF₄ Copolymer, and PMA Samples

Sample	$\bar{M}_w \times 10^{-5}$	PDI	H–H Defect	VF ₄ Content (mol %)	Crystallinity ^a (mol %)	mp (°C)
KF	4.28	1.47	3.5	—	57.3	176.6
KY	7.36	2.04	5.31	—	49.1	164.3
cop-1	1.97	2.07	15.8	9.1	27.7	150.8
PMA	2.57	1.62	—	—	—	—

The two PVF₂ samples are #KF-1000 (KF) and KY-201 (KY). \bar{M}_w , weight-average molecular weight; PDI, polydispersity index.

^a The cop-1 sample was crystallized at 120°C and the PVF₂ samples were crystallized at 144°C for 24 h. The melting point and crystallinity were measured by a DSC 7 at a heating rate of 10°/min.

rule holds, although only the amorphous portion of the crystalline polymer is responsible for this behavior.⁶ This is because the crystalline lamella remains pure even in the blended state. As mentioned above, at the lower crystalline polymer content of the blend the crystallinity is very low and sometimes negligible. But with an increase in aging time the crystallinity grows and it increases at the expense of its amorphous portion, which was in the blended state with the amorphous polymer. Therefore, one would expect some change in the T_g with aging time. We present the manner in which the T_g values of these blends vary with aging time. This is discussed with poly(vinylidene fluoride) (PVF₂) and poly(methyl acrylate) (PMA) blends as an example.

The PVF₂ is not completely isoregic and has a head to head (H–H) defect structure in the chain.⁷ Therefore, it is also interesting to observe how the T_g of the blend varies with different H–H defect content samples.

EXPERIMENTAL

Two unfractionated PVF₂ samples (KF and KY), a vinylidene fluoride-tetrafluoroethylene (VF₂-VF₄) copolymer, and an unfractionated sample of PMA were used in this work. The molecular weight of the sample was measured by GPC, and the H–H defects were determined by ¹⁹F-NMR spectra.⁵ The ¹⁹F spectra were found by dissolving the polymer in *N,N*-dimethyl formamide-*d*₇ (DMF-*d*₇, 10% w/v), and the spectra were recorded by a 282-MHz NMR (Bruker) instrument with CFCl₃ as the internal standard. The H–H defects were calculated by regrouping the intensities of seven carbon sequences into those of five carbon sequences using the method of Wilson and Santee.⁸ The ¹⁹F spectra of the VF₂-VF₄ copolymer also

exhibited heptad features, and the VF₄ content of the copolymer was calculated following the method of Cais and Kometani.⁹ Its H–H defect content was measured using the method of Wilson and Santee⁸ by extending it to deal with the copolymers.¹⁰ The characteristics of the samples are presented in the Table I.

The blends with different compositions were prepared by dissolving the appropriate amount of the two polymers in DMF (total polymer concentration ~ 0.2–0.4%) to homogeneity. They were then dried slowly on a hot plate at 60°C in air and finally at 60°C in a vacuum for 3 days.

About 5 mg of the blends were placed in aluminum capsules and then melted at 227°C in a DSC 7 for 10 min to destroy all the PVF₂ nuclei.¹¹ They were then quenched to room temperature (30°C) and left for different amounts of time. The T_g values of the samples were then measured in the DSC 7 using a heating rate of 10°C/min. The midpoint of the endothermic transition was taken as the T_g and was calculated using a computer attached to the instrument. The T_g values of the melt-quenched samples were determined in the same way. The accuracy of the repeated T_g measurements was ±0.5°C. The melting point (T_m), the enthalpy of fusion, and the enthalpy of crystallization of the PVF₂ in the blends were determined from the endothermic and exothermic peaks of the thermograms. The DSC 7 was calibrated with indium before each set of experiments.

The polymer–polymer interaction parameter (χ) used here to interpret the results was determined from the equilibrium melting point depression. The equilibrium melting points were determined from the Hoffman–Weeks procedure.¹² The melting points were obtained after annealing the samples at a 5–10°C lower temperature than the sample (quenched to 30°C) T_m for 24 h and then

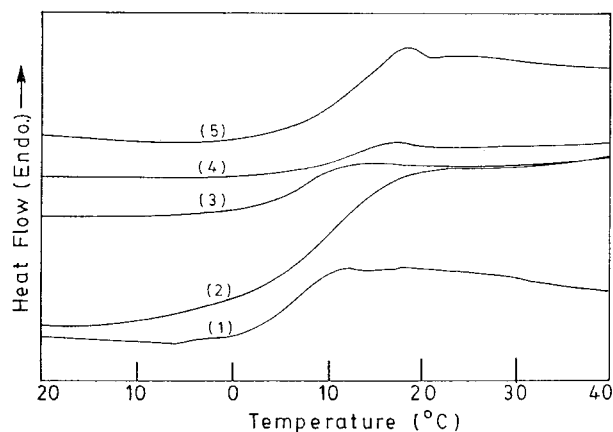


Figure 1 DSC thermograms for cop-1/PMA blends ($W_{\text{cop-1}} = 0.25$) that were (1) melt quenched or aged at 30°C for (2) 60, (3) 180, (4) 365, and (5) 730 days.

scanned at a heating rate of 10°/min in the DSC 7.⁵ These T_m values were plotted with the annealing temperature (T_a). A linear extrapolation of this plot to a $T_m = T_a$ line gave the equilibrium melting point.⁵ The χ values were calculated numerically using the Nishi and Wang expression¹³

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{-RV_c}{\Delta H_u V_a} \left[\frac{\ln \phi_2}{r_2} + \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \times (1 - \phi_2) + \chi(1 - \phi_2)^2 \right] \quad (1)$$

where T_m^0 is the equilibrium melting point of the pure polymer and T_m is that of the blend; V_c and

V_a are the molar volumes of the crystalline polymer and the amorphous polymer, respectively; ϕ_2 is the volume fraction of the crystalline polymer; r_1 and r_2 are the number of segments of the amorphous polymer and the crystalline polymer, respectively; and χ is the polymer–polymer interaction parameter. The χ values were calculated using $\Delta H_u = 1.6$ kcal/mol, $V_a = 70.5$ mL/mol, and $V_c = 33.3$ and 34.1 mL/mol for PVF₂ and cop-1, respectively.⁵

RESULTS

Figure 1 represents the DSC thermograms of one VF₂-VF₄ copolymer/PMA blend ($W_{\text{cop-1}} = 0.25$) aged at 30°C for different times. The figure shows that it is very apparent that the T_g increases with time. The T_g values determined for different PVF₂/PMA blends and aged for different times are presented in Table II. The table also shows that the T_g of the blend increases with an increase in the aging time in all the systems, although they do not reach the T_g of pure PMA (16°C). The increase of the PMA content in the blend also increases the T_g in all three PVF₂ and VF₂-VF₄ copolymer samples.

Figure 2(a)–(c) plots the T_g values of the blends with the PVF₂/copolymer concentration for KF, KY, and cop-1 samples, respectively. The figure makes it clear that the T_g of the blend decreases with the increase in PVF₂ or copolymer concentration. This is because the T_g of PVF₂ is reported

Table II T_g ($\pm 0.5^\circ\text{C}$) of PVF₂/PMA Blends Aged for Different Times

PVF ₂	W_{PVF_2}	Melt Quenched	Aging for				
			7 Days	60 Days	180 Days	365 Days	730 Days
KF	0.25	6.0	6.6	6.0	5.0	6.0	9.0
	0.50	6.5	4.5	5.5	6.9	7.5	7.0
	0.60	-0.5	—	—	—	—	4.0
	0.75	-0.3	—	-2.0	—	—	1.0
KY	0.25	6.5	5.0	8.5	8.2	9.5	14.0
	0.50	-1.5	1.5	4.0	3.0	—	6.0
	0.60	-2.5	—	—	—	—	-1.0
	0.75	-4.0	—	-2.5	—	—	0.0
cop-1	0.25	5.5	4.0	9.0	7.5	10.5	12.0
	0.50	0.0	2.3	3.0	4.9	8.0	7.0
	0.60	-4.0	—	—	—	—	3.0
	0.75	-4.0	—	-2.5	—	—	0.5

The T_g for pure PMA (melt quenched and aged) = 16°C; W_{PVF_2} , the weight fraction of PVF₂.

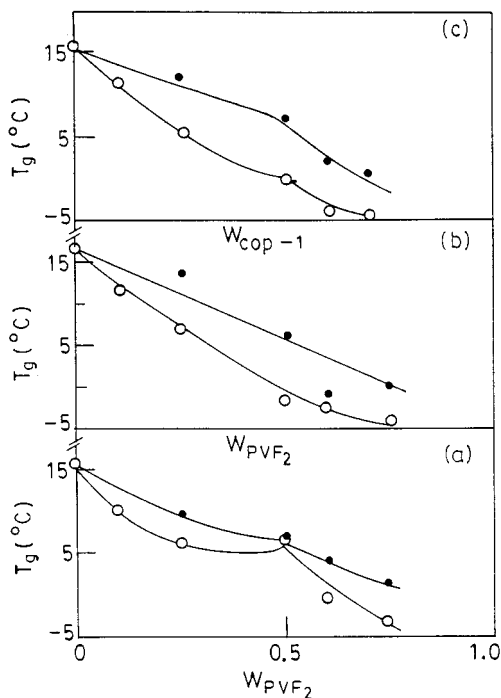


Figure 2 The T_g composition plots of PVF₂/PMA (a) KF PVF₂/PMA, (b) KY PVF₂/PMA, and (c) cop-1/PMA blends that were (○) melt quenched or (●) aged for 730 days.

to be very low (-39°C).¹⁴ It is apparent from the figure that the T_g composition diagrams of the samples aged for 2 years are always at a higher position on the temperature scale than those of the melt-quenched samples. This can be explained from the viewpoint of the kinetic immiscibility of this system as reported earlier.⁴ With the increase in aging time the crystallinity of the samples increases gradually, and this increase in crystallinity is at the cost of the amorphous portion of PVF₂ with which the PMA produced the compatible blends. Therefore, the effective PVF₂ concentration in the blend decreases, causing a higher rise in the T_g composition plot than that in the melt-quenched samples.

A critical analysis of the T_g data with time can be done from the measured crystallinity values with time. The DSC thermograms of the KF PVF₂/PMA blend aged for different times are shown in Figure 3. From the figure it is clear that, apart from the T_g , the longer aged sample shows only one endothermic (melting) peak but the melt quenched and shorter aged samples show two peaks, one being the exotherm and the other the endotherm. The cause of this difference in behavior of the melt-quenched (and shorter aged) sam-

ples and the longer aged materials may be due to the fact that at 30°C (just above the T_g) the growth rate is slow because of the difficulty in the diffusion of the crystalline segments¹⁵; but with an increase in the temperature the diffusion is easier and complete crystallization occurs, showing an exotherm. In the longer aged sample the crystallization is almost complete and so no exotherm is observed. Table III presents the ΔH (J/gm) values of the exothermic and endothermic peaks. The above T_g dependence with time cannot be explained from the enthalpy of fusion values of the endotherms, because it does not represent the true crystallinity with time. An attempt can be made with the difference (Δ) of the endotherm and the exotherm data. A glance at the results in the table indicates that the Δ values increase with time in almost all cases. This explains the increase of the T_g with time. However, a quantitative comparison of the T_g data with Δ is difficult here because of melt recrystallization,^{16,17} which decreases with increasing aging time (Fig. 3).

The T_g composition diagrams are usually explained by the Fox equation,¹⁸

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (2)$$

where W_i represents the weight fraction of the components. In the crystalline polymer/amor-

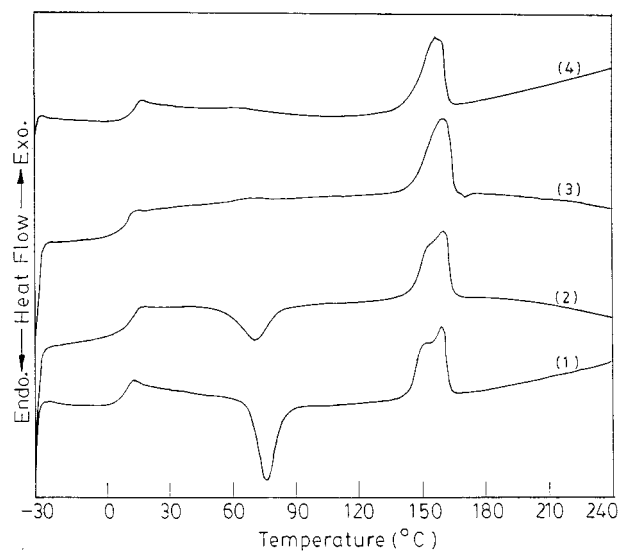


Figure 3 DSC thermograms for KF PVF₂/PMA blends ($W_{\text{PVF}} = 0.25$) that were (1) melt quenched or aged at 30°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ for (2) 7, (3) 180, and (4) 365 days.

Table III Melting Point (°C) and ΔH (J/gm) Values of PVF₂ in PVF₂/PMA Blends Aged for Different Times

PVF ₂	W _{PVF₂}	Melt quenched										7 days			60 days			180 days			365 days		
		T _m	ΔH		T _m	ΔH		T _m	ΔH		T _m	ΔH		T _m	ΔH		T _m	ΔH		T _m	ΔH		
			endo	exo		endo	exo		endo	exo		endo	exo		endo	exo		endo	exo		endo	exo	endo
KF	0.25	159.0	56	52	4	157.4	56	34	22	157.3	59	0	59	157.7	66	0	66	157	54	0	54	0	54
	0.50	167.8	50	0	50	166.2	49	0	49	166.9	50	0	50	167.7	54	0	54	168.6	56	0	56	0	56
KY	0.25	143.8	4	0	4	139.0	40	0	40	138	37	0	37	140.2	44	0	44	140.7	41	0	41	0	41
	0.50	151.4	32	20	12	150	33	0	33	150.6	38	0	38	150.8	36	0	36	151.3	31	0	31	0	31
Cop-1	0.25	0	0	0	0	126.7	33	0	33	127.3	34	0	34	128.1	38	0	38	127.5	34	0	34	0	34
	0.50	137.1	32	26	6	135.0	35	0	35	135.2	35	0	35	136.2	35	0	35	137.1	35	0	35	0	35

* Δ = ΔH_{endo} - ΔH_{exo}

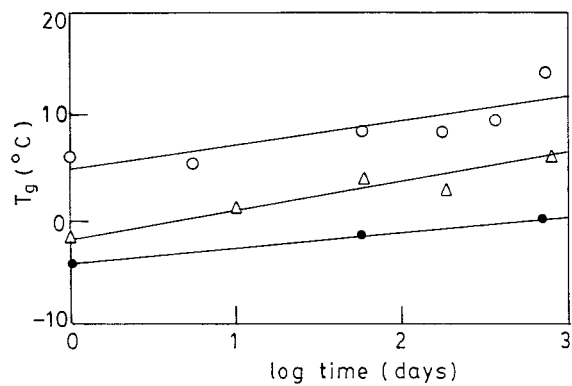


Figure 4 The T_g versus log time plot for the KY PVF₂/PMA blends. W_{PVF_2} = (●) 0.75, (Δ) 0.5, and (○) 0.25.

phous polymer blends the W_1 and W_2 should be calculated by taking only the amorphous fraction of the crystalline polymer into account.^{19,20} With an increase in aging time this amorphous portion decreases,^{4,5} and therefore the T_g of the blend increases. The T_g composition diagrams of the PVF₂/PMA blends are not similar for the three systems. The KF PVF₂ and cop-1 blends show cusp formation in both the melt-quenched and aged samples, but the KY PVF₂ blends do not exhibit this behavior. The cusp formation in the T_g composition diagram is not uncommon to the compatible polymer blends.^{6,21} However, the cause for this difference in behavior for the KY samples is not clear to us. A probable reason may be its higher molecular weight than the others.

To analyze the T_g data with time, we plotted the T_g values with the log of the time, which are shown in Figure 4. From the figure it is clear that the T_g values increase linearly with the log of the time for the time range studied here in all the compositions of the KY PVF₂/PMA system. The increase in the T_g due to aging can therefore be simply expressed as

$$T_g = T_g^0 + K \log t \quad (3)$$

where T_g^0 is the T_g for the melt quenched species and K is a constant that should be dependent on the growth rate of the crystal, the composition of the blend, and the interaction parameter value of the component polymers. The K values are calculated from the least-squares slope and are presented in Table IV. It is apparent from the table that the slope values are dependent on the PVF₂ samples used and the blend composition. The

Table IV Least-Squares Slope (K) of T_g versus $\log t$ Plot

W_{PVF_2}	KF	KY	cop-1
0.25	0.42	2.23	2.42
0.50	0.52	2.42	2.65
0.75	1.32	1.34	1.50

growth of the PVF₂ crystal at a fixed composition of the blend follows the order KF > cop-1 > KY at 30°C.⁴ If only the growth rate is involved the K should also follow the same order KF > cop-1 > KY. But K is found to follow the order cop-1 > KY > KF. Thus, the effect of the growth rate on K is not very significant and it largely depends on the other parameters like χ .²²

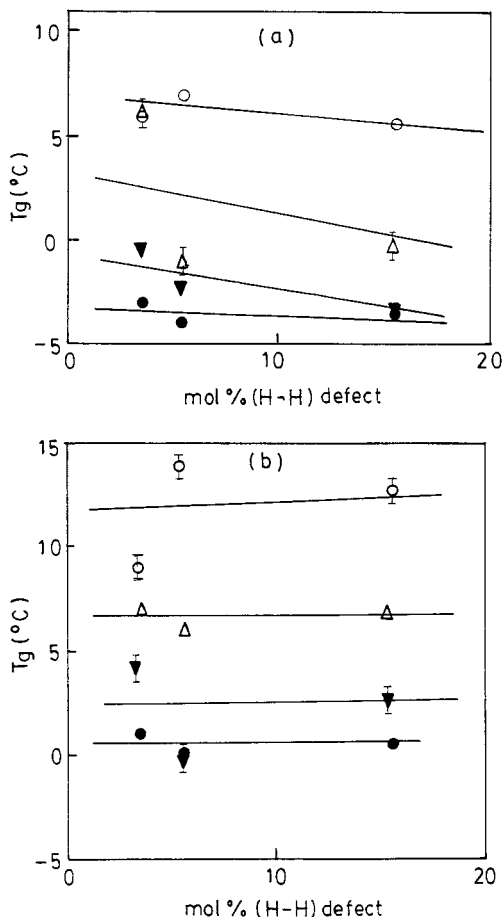


Figure 5 The T_g versus H-H defect plot for the PVF₂/PMA blends for the samples that were (a) melt quenched: W_{PVF_2} = (●) 0.75, (▼) 0.60, (△) 0.5, and (○) 0.25; or (b) aged for 730 days: W_{PVF_2} = (●) 0.75, (▼) 0.60, (△) 0.5, and (○) 0.25.

This effect can be judged from the variation of the T_g with the H-H defect of PVF₂. Figure 5 plots the T_g with the H-H defect for different blend compositions. For the melt-quenched specimen [Fig. 5(a)] the T_g values decrease with the increase in the H-H defect of the PVF₂ samples. However, after aging for 2 years the T_g varies very slowly with the H-H defect [Fig. 5(b)] and it is almost parallel to the H-H defect line. This can be explained by the χ versus the W_{PVF_2} plot shown in Figure 6 where at a fixed blend composition the χ value increases with an increase in the H-H defect of the PVF₂. The χ values are calculated from the T_m^0 data presented in Table V using eq. (1). At the melt-quenched stage, because of the stronger interaction of the lower H-H defect content KF sample, it requires a higher temperature to observe the glass transition because more energy is required to start the segmental mobility than that of the higher H-H defect content sample that has a higher χ value (i.e., lower interaction). But after 2 years of aging the decrease of the T_g with the H-H defect was not observed and it was almost invariant with the H-H defect concentration. This was because the PVF₂ concentration in the amorphous portion of the blend decreased because of its crystallization and specific interaction consequently decreased (χ increased), as is apparent from Figure 6. At a very low PVF₂ concentration the χ values of different defect content samples were almost equal and hence the T_g became almost invariant with the H-H defect concentration.

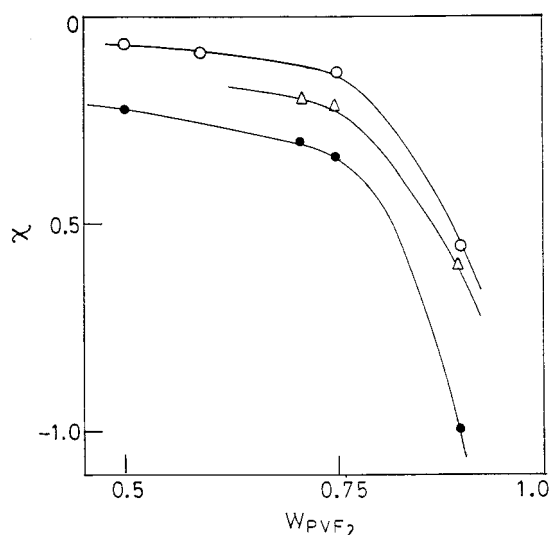


Figure 6 The χ versus W_{PVF_2} plot of PVF₂/PMA blend samples: (●) KF, (△) KY, and (○) cop-1.

Table V T_m^0 Data of PVF₂/PMA Blends

KF		KY		Cop-1	
W_{PVF_2}	$T_m^0 \pm 2$ (°C)	W_{PVF_2}	$T_m^0 \pm 2$ (°C)	W_{PVF_2}	$T_m^0 \pm 2$ (°C)
1.0	205	1.0	192.0	1.0	164.5
0.90	202	0.9	191.5	0.9	163.0
0.75	200	0.75	190.0	0.75	163.0
0.71	199	0.71	189.5	0.6	162.5
0.50	195	—	—	0.5	162.0

If one considers the above effect with respect to the VF₄ content of the VF₂-VF₄ copolymer/PMA blend [as in Fig. 5(a,b)], an almost similar conclusion can be drawn. The cop-1 has a VF₄ content of 9.1 mol % and PVF₂ samples have 0 mol %. In Figure 7(a,b) the T_g values are plotted with the VF₄ content of the copolymer for different blend compositions for the melt-quenched and aged samples, respectively. The average T_g values of KF and KY PVF₂/PMA blends were taken for the sample containing a 0 mol % VF₄ concentration

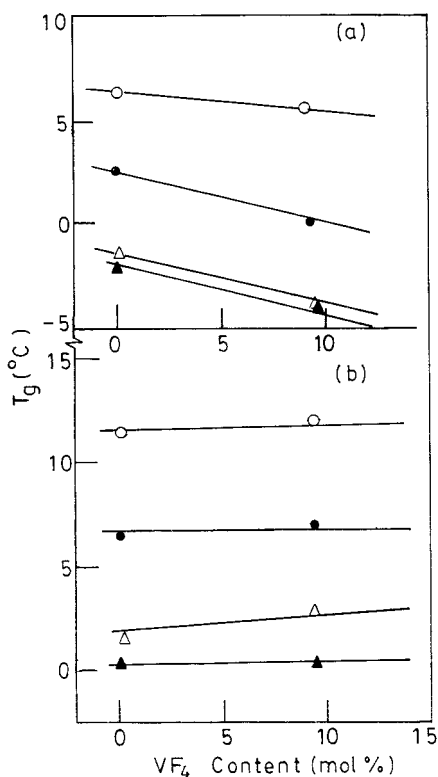


Figure 7 The T_g versus VF₄ content (mol %) plot for the copolymer/PMA blends: (a) melt quenched: W_{cop} = (○) 0.25, (●) 0.5, (△) 0.6, and (▲) 0.75; or (b) aged for 730 days: W_{cop} = (○) 0.25, (●) 0.5, (△) 0.6, and (▲) 0.75.

for each composition. Figure 7(a) shows a sharp decrease of the T_g with the VF₄ content for all the blend compositions for the melt-quenched specimen, and this decrease is lower for $W_{cop-1} = 0.25$ compared to the other compositions. After 2 years of aging there is almost no variation of the T_g with the VF₄ content. The reason for the difference in behavior between the melt-quenched and aged samples is the same as discussed earlier for the H-H defect concentration. The slopes of the variation of the T_g with the H-H defect are slightly lower (~15%) than those of the T_g with the VF₄ content, and this almost similar effect of the copolymer content on the T_g may be due to the fact that the VF₄ unit of the copolymer has a pseudo-(H-H) defect structure. (A —CF₂—CF₂— unit in the copolymer is not followed by a —CH₂—CH₂— linkage as in the H-H defect of the PVF₂.) This slight decrease in slope between the H-H defect and the VF₄ unit may be due to the copolymer effect.

From the Table IV no definite trend for the K values with blend composition is seen for the blends, probably because of the two opposing factors. A decrease in PMA content in the blend increases the growth rate.²³ Consequently, K should have high value, but a decrease in PMA content increases the interaction (χ decreases) and this lowers the K value. Because of these two opposing factors, no definite trend in the value of K with composition is observed.

CONCLUSION

The T_g values of the PVF₂-PMA blends increase with aging time, and the T_g composition diagrams of the aged samples are always at higher temperatures than those of the melt-quenched samples. The T_g of the PVF₂-PMA blends decrease with an increase in the H-H defect content of the PVF₂

samples. This is due to the decrease of polymer-polymer interaction with the increase in the H-H defect of the PVF₂. However, with an increase in aging time the T_g decrease is almost negligible and it may be due to the combined effect of the crystallization of PVF₂ and the composition dependency of the interaction parameter in the blend. In respect to the VF₄ content of the copolymer in the blends, an almost similar conclusion as the T_g variation with H-H defect holds.

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