Effect of structure on stress relaxation of polymer blends in glassy state

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Short-term stress-relaxation measurements were performed on blends of poly(methyl methacrylate) with poly(styrene-*co*-acrylonitrile), of polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide) and poly(methyl methacrylate) with poly(vinylidene fluoride), at different temperatures below the glass transition region and a constant strain of 0.5%. Stress-relaxation moduli were analysed using the Williams–Watts equation. For amorphous blends, a universal value for the distribution parameter β of 0.41 was found, and the relaxation time τ showed a power-law correlation with ageing temperature and ageing time. The time and temperature dependences of τ changed with blend composition in systems containing polymers with dissimilar chemical structures, while little variation was observed in systems consisting of molecules of similar structures. Stress relaxation proceeded much faster in semicrystalline systems than in amorphous systems.

(Keywords: physical ageing; stress relaxation; polymer blends; morphology; Williams–Watts equation)

INTRODUCTION

It has been known for some time now that, immediately upon cooling to below their glass transition temperatures, polymeric glasses are characterized by a departure from the equilibrium configurations. The ensuing drive towards equilibrium in the glassy state, which occurs with time, is referred to as structural relaxation, and the concurring change in structure-sensitive properties (such as volume and enthalpy) is often termed physical ageing. At temperatures below the glass transition, the application of a small external mechanical load can also cause time-dependent changes (relaxation) in properties of materials. Correlations between externally applied mechanical loads and the ensuing changes in properties constitute one of the topics of viscoelasticity[1].

Viscoelastic response of various glasses was investigated by Struik[2], who used 'short-term' creep tests in which the ageing time is at least 10 times the measuring time. Struik's method of short-term creep measurement was adapted in this study for the analysis of stress relaxation. This technique is essentially an isostructural measurement[3], which allows one to evaluate the effect of the ongoing structural relaxation on the viscoelastic behaviour of a glass.

We have also investigated how structures of the components and morphology of the blend affect the short-term stress-relaxation behaviour of the blend. Three polymer blends, each a distinct combination of two miscible constituents, were studied. The first system, blends of poly(methyl methacrylate) (PMMA) with poly(styrene-*co*-acrylonitrile) (SAN), consists of two vinyl polymers of close T_g values. The second system, blends of polystyrene (PS) with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), consists of one vinyl polymer (PS) and one polymer with aromatic rings and ether links in the backbone (PPO). The third system, blends of poly(methyl methacrylate) (PMMA) with poly(vinylidene fluoride) (PVDF), consists of two vinyl polymers, one of which (PVDF) is crystallizable.

Two sets of blends were 'pretreated' and the reasons for that are described below. In earlier studies, it has been reported that annealing causes a slowdown in the rate of stress relaxation[4] and creep[5] in PMMA, probably due to a better packing of molecules after annealing. It would be interesting then to see whether annealing has a similar effect on blends of PMMA with SAN. (Methyl methacrylate, styrene and acrylonitrile are all vinyl monomers, but in terms of molecular volume, acrylonitrile is smaller than the others.) Samples of PMMA/SAN blends were pretreated by annealing, and their thermal and stress-relaxation behaviour evaluated and compared with those of non-annealed blends.

We also set out to investigate what effect (if any) the presence of a crystalline phase in a blend may have on stress relaxation. For that purpose, we decided to prepare two blends, one amorphous and one semicrystalline, but with identical composition in the amorphous phase. In other words, the ratio of blend components would be the same in the amorphous sample and in the amorphous phase of the semicrystalline sample. This is possible with blends of PMMA and PVDF, whose morphology, in a certain composition range[6–8], is characterized by crystalline domains dispersed in an amorphous matrix. Semicrystalline PMMA/PVDF 50/50 blend was processed and pretreated (see 'Experimental') to induce maximum crystallinity and, assuming distinct amorphous/crystalline region morphology, the composition of the amorphous phase was determined from calorimetric measurements to be PMMA/PVDF 70/30. A comparison between this blend and a fully amorphous PMMA/PVDF 70/30 blend would then allow us to deduce directly the effect of crystalline phase on stress relaxation.

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The main objectives of this study are: (1) to establish an accurate procedure for the quantitative analysis of stress relaxation in the glassy state; (2) to probe the effects of molecular structures of the constituents on the stress relaxation of polymer blends; and (3) to investigate how morphology and ageing temperature affect stress relaxation of polymer blends containing crystalline phase.

EXPERIMENTAL

Materials

The following polymers were used in this investigation: poly(methyl methacrylate) (PMMA), Plexiglas VS-100 from Rohm and Haas; poly(styrene-*co*-acrylonitrile) (SAN), Tyril-1000 Natural from Dow Chemical; poly-(2,6-dimethyl-1,4-phenylene oxide) (PPO), Noryl-696 from General Electric; polystyrene (PS), an experimental product prepared courtesy of Dow Chemical; and poly(vinylidene fluoride) (PVDF), Kynar 721 from Pennwalt.

Processing

The blends were first dry tumbled and then processed by extrusion in a twin-screw extruder (courtesy of Werner-Pfleiderer Co.). To avoid inclusion of moisture, all materials were dried before and after extrusion at a temperature about 20°C below T_g for 24 h.

The pellets were then compression moulded into 1/16 inch (~1.6 mm) thick sheets in a laboratory hot press. Standard type-II dumb-bell-shaped specimens were machined from the moulded sheets prepared according to the specifications outlined in ASTM D-638.

Pretreatments

Pretreatments were required in preparing 'thermally treated' PMMA/SAN samples and semicrystalline PMMA/PVDF samples.. A set of PMMA/SAN samples was thermally treated at 150°C for 240 h. Semicrystalline PMMA/PVDF 50/50 blend was prepared as follows. The 'as-machined' specimen was first heated to 200°C for 30 min, at which temperature all crystalline regions melted (the melting point of crystalline PVDF is about 170°C). The amorphous melt was then placed into an oven and allowed to recrystallize at 120°C for 30 min. During this period, the melting and the recrystallization were monitored in a differential scanning calorimeter. In earlier tests, it was found that the equilibrium (maximum) degree of crystallinity was attained after annealing at 120°C for 30 min. As shown in *Figure 1*, the degree of crystallinity (measured by the heat of melting) increased with time during the first 30 min and then levelled off.

Measurements

Differential scanning calorimetry (d.s.c.). The glass transition temperature of each blend was determined by d.s.c. The inflection-point temperature in the glass transition region was taken as the T_g.

For samples of PMMA/PVDF 50/50 blend, in addition to T_g, the following thermal properties were also measured: the melting point (T_m) and the heat of melting (ΔH_m) of the 'as-machined' sample; and the T_m of the recrystallized sample. The latter were followed as a function of time at the recrystallization temperature (T_c).

Stress relaxation. Stress-relaxation measurements were carried out in an Instron tester equipped with a temperature chamber. Before testing, each specimen was heated to about 20°C above its T_g and maintained there for 30 min to erase the effects of previous thermal treatments. The specimen was then quenched by dipping it into a tube surrounded by dry ice. After quenching, the specimen was quickly secured between a pair of grips inside the Instron temperature chamber, which was preheated to the desired ageing temperature. Three ageing temperatures were used in this study: 20, 35 and 50°C below the T_g of each blend. The temperature in the chamber was calibrated with a mercury thermometer with an accuracy of ± 0.1°C.

The moment the temperature chamber closed, the ageing process started. The measurements were taken according to the schedule suggested by Struik[2], which consisted of alternating ageing and measuring periods. The duration of each measuring period was one-tenth of the total span between the onset of ageing and the beginning of measuring period. A strain rate of 0.01 min^{-1} was applied for 30 s at the beginning of each measurement to impose a strain of 0.5%, which was kept constant for the duration of the measurement. The exerted tensile force was recorded from the beginning.

Theoretically, true stress-relaxation modulus is obtained when the strain is applied instantaneously. However, in an experiment a finite strain rate must be employed. Methods to overcome this drawback have been proposed and recently reviewed[9]. In this study, the uncertainty of the experimentally measured data was about 1%, as determined by the smallest division on the recording chart. According to Smith[10], the deviation between experimental and true stress-relaxation moduli reduces to less than 1% after an interval of time equal to 10 times the constant-strain-rate period. Based on this argument, data collected after 5 min—i.e. 10 times the 30 s required to achieve the 0.5% strain in this study—from the onset of the measurement were assumed to represent accurately the true stress-relaxation moduli and were used in our analysis.

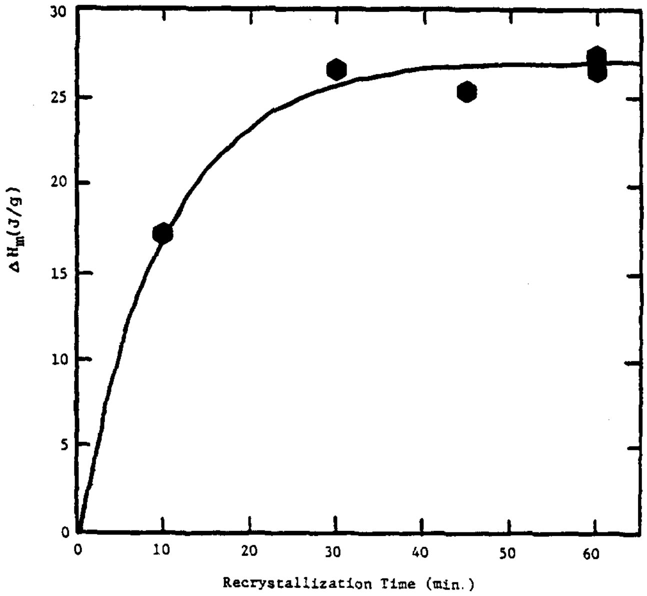

Figure 1 Heat of melting of a PVDF/PMMA 50/50 blend as a function of recrystallization time. $T_c = 120$°C

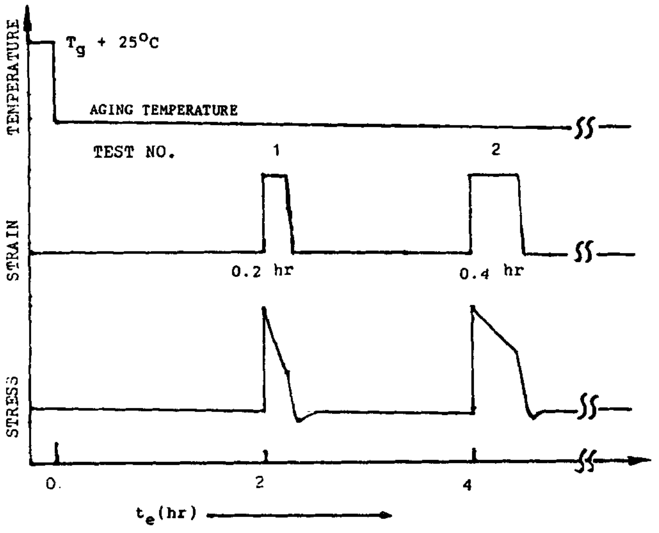

Figure 2 Schematic representation of the measuring schedule for short-term stress-relaxation test, showing temperature, stress and strain as functions of time

A schematic representation of the relationships between stress, strain, temperature and time during measurement is shown in *Figure 2*. The schedule shown has been designed to meet the two requirements of a short-term measurement: (1) the measuring time is much shorter than the ageing time, and (2) the imposed strain is small and within the linear viscoelastic range. These two factors assure that the superimposed measuring periods do not affect the progress of physical ageing. At the end of the measurement, the strain was released by manually turning the control knob to reset the lower grip to the pre-test position. As a result of this procedure, the stress first dips to negative values then gradually returns to zero.

RESULTS

The Williams–Watts equation[11], which had been used successfully to describe various relaxation phenomena in the glassy state, was used to fit the stress-relaxation data in this investigation:

$$E(t)/E_0 = \exp[-(t/\tau)^{\beta}] \tag{1}$$

where $0 \leqslant \beta \leqslant 1$. Chow and Prest have shown that the relaxation phenomena described by the Williams–Watts equation are controlled by continuous relaxation spectra[12]. Parameter β has physical meaning in that it describes the intensity distribution of the spectrum. The higher the value of β, the narrower the intensity peak, and in the extreme case of $\beta = 1$, there is only one possible value for the relaxation time. Parameter τ is a characteristic relaxation time. Although τ is always in the neighbourhood of the intensity peak of the spectrum, it is not necessarily at the peak. The relaxation-time spectrum and its corresponding intensity distribution, tabulated with β as a parameter, have been published[13]. The third parameter E_0 is the stress-relaxation modulus at time zero, which would be obtainable when the strain was applied instantaneously.

The three parameters of the Williams–Watts equation, E_0, β and τ, are not independent, and an optimization process in which all three parameters are variable will result in more than one set of parameters that can fit the data within the experimental uncertainty. This problem can be bypassed if one of the parameters is kept constant during the optimization. Since a first approximation for E_0 can be obtained from extrapolation of the experimental data, we started our analysis by estimating one such value for E_0. This initial value of E_0, determined for each data set, was used to calculate β and τ. Taking logarithms of both sides of the Williams–Watts equation (1) yields:

$$-\ln \phi(t) = -\ln[E(t)/E_0] = (t/\tau)^{\beta} \tag{2}$$

Again, taking logarithms of both sides of equation (2) gives:

$$\ln[-\ln \phi(t)] = \beta(\ln t - \ln \tau) \tag{3}$$

A plot of $\ln[-\ln \phi(t)]$ *versus* $\ln t$ will yield a straight line of slope β and Y intercept of $-\beta \ln \tau$. The pre-exponential factor E_0 in the Williams–Watts equation is simply a scaling factor, and thus in our analysis the effect of structural relaxation on the stress-relaxation behaviour of polymer blends is expressed in terms of changes in β and τ.

Blends of poly(methyl methacrylate) and poly(styrene-co-*acrylonitrile) (PMMA/SAN)*

The resulting values of β from all data sets for PMMA/SAN blends were found to lie within a narrow range around 0.41. We then accepted this constant as the true value for β and proceeded to calculate refined values for E_0 and τ. With $\beta = 0.41$ equation (1) becomes

$$E(t) = E_0 \exp[-(t/\tau)^{0.41}] \tag{4}$$

By taking logarithms of both sides of equation (4) we have:

$$\ln E(t) = \ln E_0 - (1/\tau)^{0.41} t^{0.41} \tag{5}$$

A linear regression of $\ln E(t)$ *versus* $t^{0.41}$ will give Y intercept of $\ln E_0$ and slope of $-(1/\tau)^{0.41}$. Relaxation time τ is a function of blend composition, ageing temperature and ageing time. We recall here that ageing temperatures for all blends were determined with reference to their respective T_g values. A plot of T_g (measured by d.s.c.) as a function of blend composition is shown in *Figure 3*. The optimum τ for each experimental condition is listed in *Table 1*. A comparison of data listed in *Table 1* with those reported in ref. 14 will reveal some minor discrepancies between them, which are caused by an additional step in the optimization procedure employed in this study, designed to refine values for τ and E_0 when β is known.

An analysis of data shown in *Table 1* revealed good linear correlations between $\ln \tau$ and both $\ln(T_g - T)$ and $\ln t_e$ which suggested that τ can be expressed in the following form:

$$\ln \tau = a(S) + C_T \ln(T_g - T) + C_t \ln t_e \tag{6}$$

where S is the weight fraction of SAN in the blend, T is the ageing temperature and t_e is the ageing time. The function $a(S)$ was best fitted by a second-order polynomial equation:

$$a(S) = -7.728 + 0.3195S + 0.7277S^2$$

Also, by best fitting, it was found that the temperature coefficient C_T was 3.33, and the time coefficient C_t was 1.01. In *Figure 4* experimental stress-relaxation data are

Table 1 Williams–Watts parameter τ (min) for a series of PMMA/SAN blends, $\beta = 0.41$

Ageing temperature, T (°C)	Ageing time, t_e (h)	Composition (wt% SAN)					
		0	20	40	60	80	100
$T_g - 20$	2	31	40	22	28	36	55
	4	39	41	52	66	78	116
	8	71	81	115	132	136	232
$T_g - 35$	2	123	206	168	173	244	310
	4	253	279	339	404	533	631
	8	523	529	582	772	1146	1134
$T_g - 50$	2	418	553	602	590	782	1150
	4	800	900	1507	1323	1666	2203
	8	1501	1589	2048	2870	5354	4691
	a	−7.72	−7.65	−7.49	−7.25	−7.02	−6.68
	C_T				3.325		
	C_t				1.013		

Table 2 Effect of thermal treatment on τ (min) and other characteristic properties of PMMA/SAN blends, $\beta = 0.41$

Ageing temperature, T (°C)	Ageing time, t_e (h)	Composition (wt% SAN)					
		0		40		60	
		Treated	Not treated	Treated	Not treated	Treated	Not treated
$T_g - 20$	2	–[b]	31	47	22	53	28
	4	64	39	93	52	106	66
	8	92	71	228	115	128	132
T_g (°C)		96.7	94.1	102.7	99.8	104.9	102.5
Width of the transition region (°C)[a]		25	30	36	41	38	42

[a] Determined by d.s.c.

[b] Not available

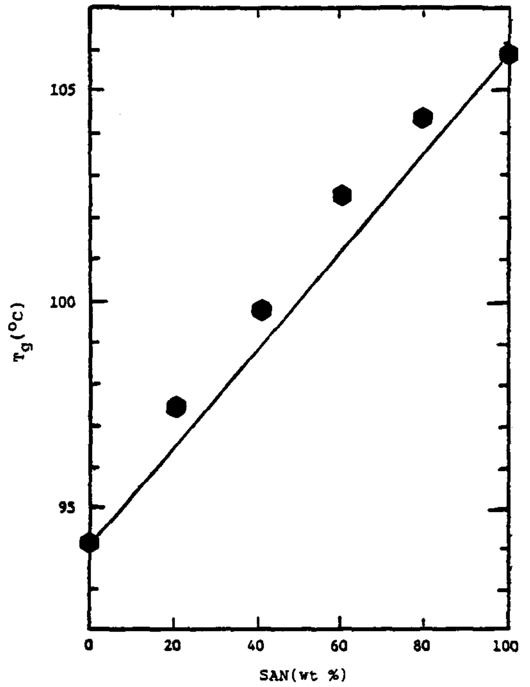

Figure 3 Glass transition temperatures as a function of composition for a series of PMMA/SAN blends

plotted as a function of measuring time. The accompanying best-fit curves were calculated from the Williams–Watts equation (1) with parameters $\beta = 0.41$ and τ calculated from the power-law formula of equation (6).

Interestingly, a small but noticeable change in the properties of PMMA/SAN blends was observed upon thermal treatment at 150°C for 240 h. The stress-relaxation curves of thermally treated blends were best described with $\beta = 0.41$, and τ about twice the value of the corresponding non-treated blend. The T_g of the thermally treated blend as determined by d.s.c. was about 2°C higher than that of its non-treated counterpart, while the transition region of the treated sample was about 5°C narrower. A comparison of properties of treated and non-treated samples is shown in *Table 2*.

Blends of polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide) (PS/PPO)

Stress relaxation of PS/PPO blends was also described with the Williams–Watts equation. In comparison with PMMA/SAN blends, differences were noticed with respect to the effects of ageing temperature and ageing time. Ageing temperatures for all compositions were also determined with reference to their respective T_g values. In *Figure 5*, a plot of T_g as a function of blend composition

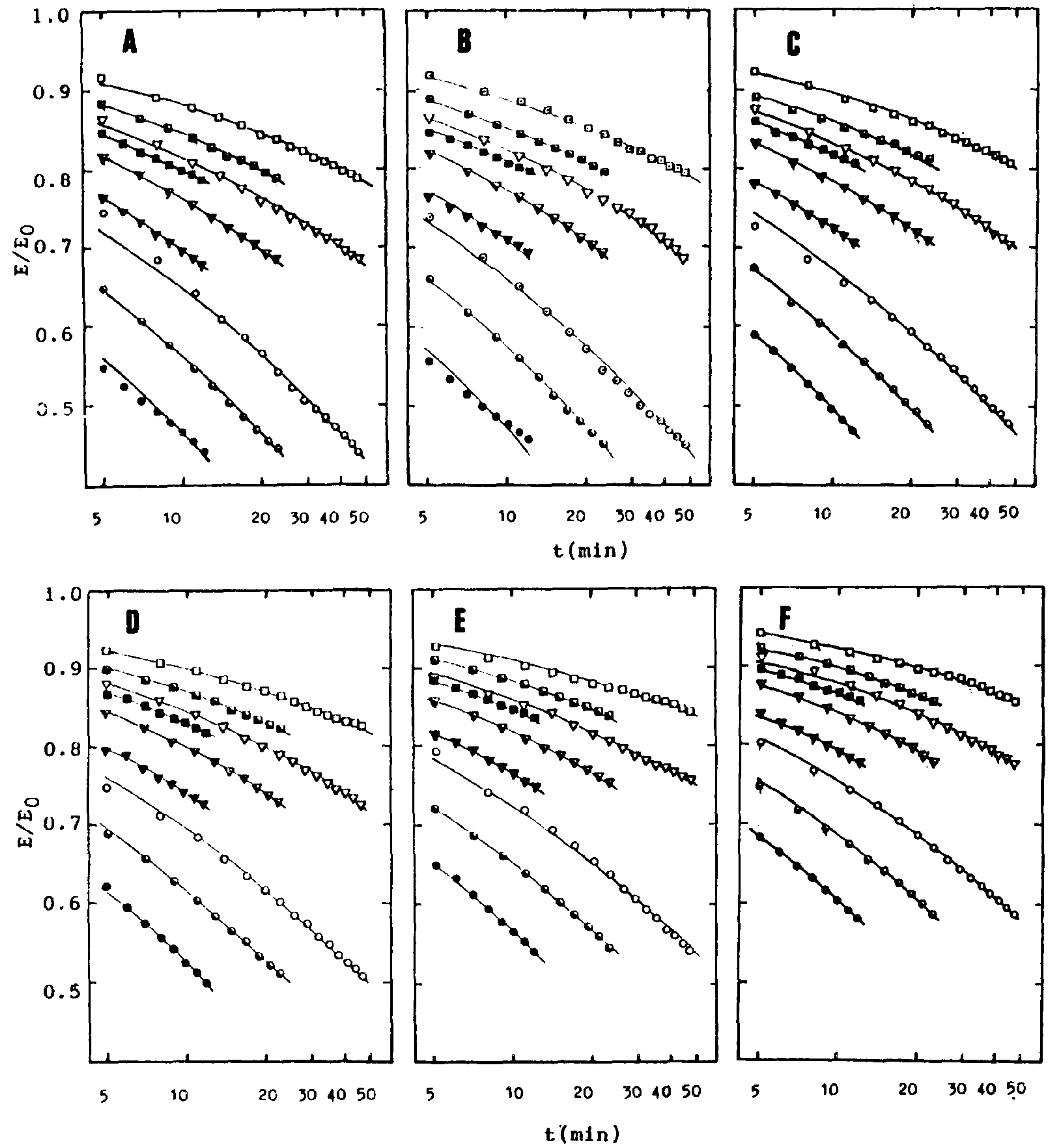

Figure 4 Short-term stress relaxation in a series of PMMA/SAN blends: (A) 100% PMMA by weight; (B) 80%; (C) 60%; (D) 40%; (E) 20%; and (F) 0%. Samples physically aged at: $T_g - 50°C$ for 2 h (■), 4 h (◧) and 8 h (□); $T_g - 35°C$ for 2 h (▼), 4 h (▼) and 8 h (▽); $T_g - 20°C$ for 2 h (●), 4 h (◐) and 8 h (○)

is shown. Our optimization procedure yielded the value of 0.41 for β, while the optimum τ values are listed in *Table 3*. Again, equation (6) was found to describe τ well, and the corresponding power-law parameters were obtained by regressional analysis. The temperature coefficient C_T varied with composition from about 3.6 for either component to about 5.2 for the middle compositions of the series. The time coefficient C_t showed a stronger composition dependence. It was 0.36 for PPO, 0.69 for PPO/PS 80/20 blend, and levelled off at about 0.9 for the rest of the series. Experimental stress-relaxation data for PS/PPO blends and the best-fit curves calculated from equations (1) and (6) are shown in *Figure 6*. By comparing stress-relaxation curves for PMMA/SAN (*Figure 4*) and PS/PPO (*Figure 6*) blends, one can notice that for PS/PPO blends relaxation curves obtained at different temperatures are located further apart from each other than their PMMA/SAN blend counterparts. This indicates a more profound influence of temperature on PS/PPO blends. The stronger temperature effect is also reflected by the larger C_T.

Blends of poly(methyl methacrylate) and poly(vinylidene fluoride) (PMMA/PVDF)

A semicrystalline morphology was induced in a sample of PMMA/PVDF 50/50 blend by recrystallization at 120°C for 30 min. The morphology of a semicrystalline PMMA/PVDF blend is thought to consist of dispersed crystalline domains in an amorphous matrix[6–8]. The heat of melting for crystalline PVDF was reported[15] as 1425 cal mol^{-1}. With that information and our calorimetric data, it was calculated that the degree of crystallinity of the recrystallized sample was 57% based on the weight of PVDF in the blend. In the miscible amorphous phase of the sample, which contains PMMA and amorphous PVDF, the content of the latter was calculated to be 30% by weight. A single T_g was observed in the recrystallized blend at 84°C. It was also found that

Table 3 Williams–Watts parameter τ (min) for a series of PS/PPO blends, $\beta = 0.41$

Ageing temperature, T (°C)	Ageing time, t_e (h)	(Composition (wt% PS)) 0	20	40	60	80	100
$T_g - 20$	2	14	18	6	6	19	24
	4	34	32	8	10	36	57
	8	37	43	12	16	64	107
$T_g - 35$	2	166	159	68	128	278	241
	4	178	273	144	237	578	444
	8	188	425	312	416	1019	785
$T_g - 50$	2	631	973	420	418	1139	976
	4	645	1235	1079	1181	1528	1851
	8	926	2607	1818	2365	3009	3812
	a	−8.08	−10.34	−14.55	−14.35	−10.42	−8.07
	C_T	3.61	4.24	5.15	5.15	4.31	3.68
	C_t	0.357	0.683	0.885	0.936	0.838	0.849

Table 4 Williams–Watts parameters β and τ (min) for a series of PMMA/PVDF blends

		Composition (wt% PVDF)					
		0		30		50	
Ageing temperature, T (°C)	Ageing time, t_e (h)	β	τ (min)	β	τ (min)	β	τ (min)
$T_g - 20$	2	0.41	31	0.41	13	<0.1	<1
	4	0.41	39	0.41	33	<0.1	<1
	8	0.41	71	0.41	75	<0.1	<1
$T_g - 35$	2	0.41	123	0.41	125	0.2	12
	4	0.41	253	0.41	222	0.2	27
	8	0.41	523	0.41	486	0.2	12

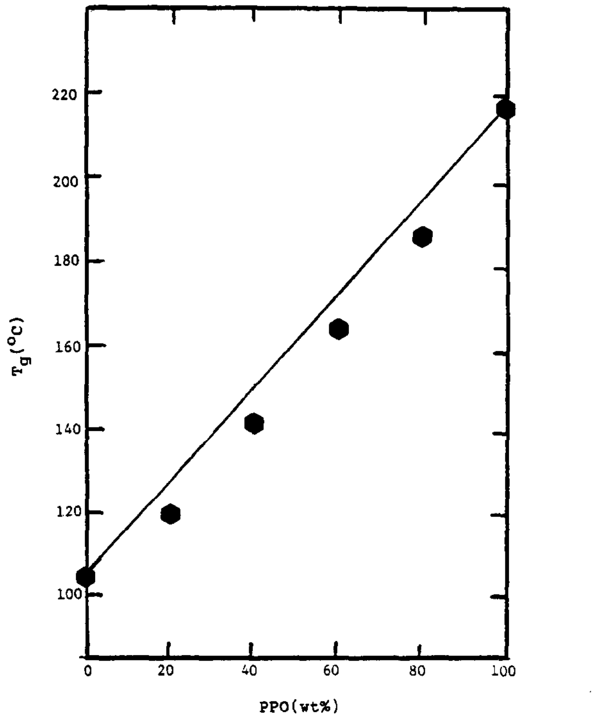

Figure 5 Glass transition temperatures as a function of composition for a series of PS/PPO blends

heat treatment at temperatures more than 15°C below the T_c (120°C) have no effect on either the heat of melting or the melting point of the recrystallized blend. This finding assured that a constant degree of crystallinity persisted throughout the course of physical ageing because all the temperatures encountered were well below the T_c.

We immediately noticed that the stress-relaxation behaviour of this semicrystalline blend is quite different from the typical behaviour of amorphous blends, which are usually described with $\beta = 0.41$ and τ of the order of 100 min at comparable temperatures. Here, at $T_g - 20$°C, stress relaxation was best described with β of less than 0.1 and τ below 1 min, while at $T_g - 35$°C, the best results were obtained with β of about 0.2 and τ of about 10 min. We then proceeded to look at the amorphous PMMA/PVDF 70/30 blend, which, as described in the 'Introduction', has the same composition as the amorphous phase in the semicrystalline blend. Interestingly, the stress-relaxation curves of the fully amorphous sample were fitted with $\beta = 0.41$ and τ described by the power-law formula (equation (6)) with temperature coefficient $C_T = 3.6$ and time coefficient $C_t = 1.1$. These values are very similar to those for PMMA/SAN blends. A comparison of the Williams–Watts parameters for PMMA/PVDF blends of different morphologies is shown in *Table 4*.

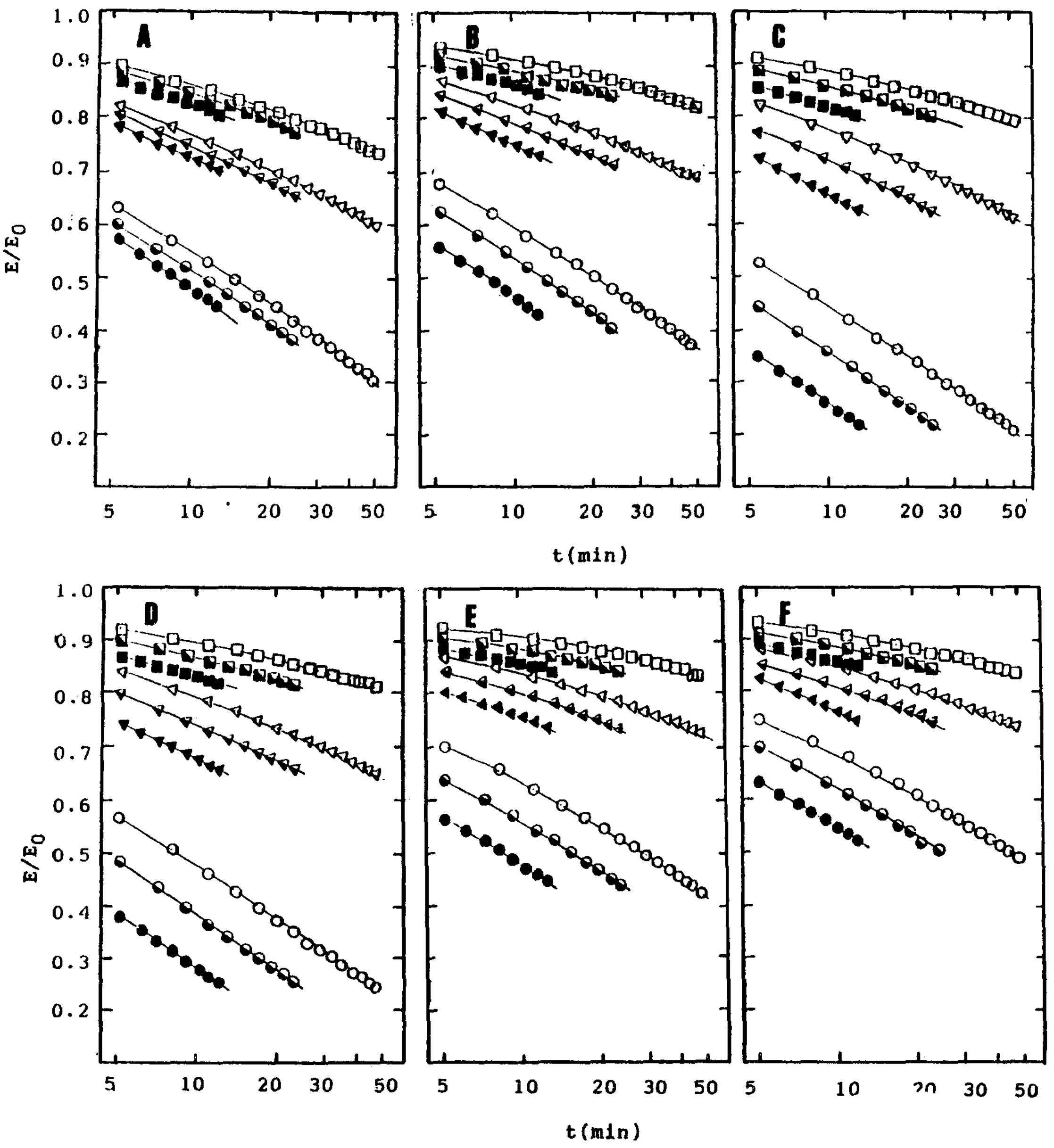

Figure 6 Short-term stress relaxation in a series of PS/PPO blends: (A) 100% PS by weight; (B) 80%; (C) 60%; (D) 40%; (E) 20%; and (F) 0%. Samples physically aged at: $T_g - 50°C$ for 2 h (■), 4 h (◩) and 8 h (□); $T_g - 35°C$ for 2 h (▼), 4 h (⧨) and 8 h (▽); $T_g - 20°C$ for 2 h (●), 4 h (◐) and 8 h (○)

DISCUSSION

Effect of molecular structure on stress relaxation

The most conspicuous result of this investigation is the universal constant β ($=0.41$) for stress relaxation in various glasses, including blends of PMMA and SAN, PS and PPO, and PMMA and amorphous PVDF, which is between those reported in the literature. Rekhson and Mazurin have reported $\beta = 0.5$ for stress-relaxation modulus in inorganic glasses[16], and Struik has found a common $\beta = 0.33$ for creep compliance in glasses of different chemical nature[2].

The formula for τ obtained in our analysis (equation (6)) indicates a simple power-law relationship between relaxation time and both ageing temperature and ageing time. The ageing time coefficient C_t was one of the subjects Struik investigated in depth and discussed in his monograph[2], but the ageing temperature coefficient C_T has not previously been reported in the literature. We found, however, that Struik has investigated the effect of temperature on relaxation time. By plotting his data for PMMA and SAN in the form of $\ln \tau$ *versus* $\ln(T_g - T)$, instead of the original τ *versus* T, we found a constant C_T for each polymer in the temperature range from $T_g - 20°C$ to $T_g - 50°C$. A comparison of our values for these two coefficients with Struik's is shown in *Table 5*. As can be seen in this table, C_T values for both PMMA and SAN as well as C_T values for SAN are in excellent agreement; only C_T values for PMMA differ somewhat. This discrepancy is at least partly due to an arbitrary choice of T_g for the literature value; the T_g of PMMA was not given, and our calculation was based on $T_g = 110°C$. Depending on factors such as the molecular weight, the molecular-weight distribution and the presence of additives, T_g of PMMA can vary within a range of about 40°C.

By comparing stress relaxation in PMMA/SAN, PS/PPO and amorphous PMMA/PVDF blends, one

Table 5 Experimental and literature values for coefficients in the power-law formula for the relaxation time

C_T	Material	Type of measurement	Source
3.33	PMMA	Short-term stress relaxation	This work
2.29	PMMA	Short-term creep	Struik[2]
3.33	SAN	Short-term stress relaxation	This work
3.32	SAN	Short-term creep	Struik[2]
C_t	Material	Type of measurement	Source
1.01	PMMA	Short-term stress relaxation	This work
0.89–0.99	PMMA	Short-term creep	Struik[2]
1.01	SAN	Short-term stress relaxation	This work
0.88–0.94	SAN	Short-term creep	Struik[2]

can gain insights into how the model parameters, such as β, C_T and C_t, correlate with the molecular parameters, such as similarity and compatibility between the components of the blend. For example, the value of $\beta = 0.41$ is common to these three systems and as such it can be taken to indicate an amorphous and compatible structure. The C_T for PS/PPO blends changes from 3.6 for individual components to 5.2 for the middle compositions in the series. The observed increase in C_T might be due to the mixing of two dissimilar components; PS is a flexible vinyl polymer, while PPO has a bulky backbone containing aromatic rings. Thus the value of C_T reflects the relative proportion of each component in the blend. In contrast, in PMMA/SAN blends, where both components are vinyl polymers, C_T is insensitive to the variation in blend composition. The time coefficient C_t for PS/PPO blends changes drastically with blend composition, from 0.36 for PPO, to 0.69 for PPO/PS, 80/20 blend, to 0.9 for other compositions. Considering that vinyl polymers tested in this study, including SAN, PMMA, PS and PVDF, and their blends, i.e. PMMA/SAN and PMMA/PVDF, all have C_t at about unity, we think the observed wide variation in C_t of PS/PPO blends might be a result of the differences in chain mobility between the two components, reflecting disparity in their chemical structures.

Effect of spatial arrangement on stress relaxation

An extended period of exposure of PMMA/SAN blends to elevated temperature was found to result in a slightly higher T_g, a narrower transition region and a higher τ for stress relaxation. However, parameters β, C_T and C_t did not change with this treatment. A slightly higher T_g and a narrower transition region imply a more compact spatial arrangement of the molecules, which is in agreement with the higher τ observed. On the other hand, the insensitivity of β, C_T and C_t to this structural change suggests that these three parameters represent characteristics of the blends that were not altered by the thermal treatment, such as the amorphous structure, the nature of the repeat units and the relative amount of each component. The last finding is related to and in agreement with observations discussed in the previous section.

Let us now revert our attention again to PMMA/PVDF blends. The d.s.c. thermogram of the PMMA/PVDF (50/50) blend showed a glass transition temperature at 84°C and a melting peak at 170°C, representing the two major phases in the system, amorphous and crystalline, respectively. The crystalline PVDF phase contained 57% of the total PVDF present (calculated based upon the heat of melting), while the amorphous phase with $T_g = 84$°C corresponded to a PMMA/PVDF 87/13 and not 70/30 blend as originally postulated. An explanation for the stress-relaxation behaviour of this system can be offered in terms of morphology in which the major phases are separated by an interphase region with a T_g gradient resulting from the varying PMMA/PVDF ratio. At 64°C ($T_g - 20$°C), a large part of the interphase may be in or near the rubbery state (T_g of PVDF is at ca. -40°C), and the system shows rubberlike stress relaxation with a short relaxation time. With decreasing temperature, more of the interphase begins to exhibit glassy state characteristics, and at 49°C ($T_g - 35$°C) the stress relaxation of this system is characterized by behaviour between those of glasses and rubbers ($\beta = 0.2$ and $\tau = 10$ min). Although a similar concept of the three-phase morphology in PMMA/PVDF blends has also been suggested by Hahn *et al.*[17], further research is required to resolve this issue.

From the above discussion, it is clear that differences in stress-relaxation behaviour correlate with differences in the molecular structure, although a rigorous correspondence between them has not been established with the present data. Nevertheless, the validity of the concept that the stress relaxation is sensitive to the molecular nature is confirmed. The applicability of a power-law formula for τ in the temperature range investigated is also firmly established, although it remained to be evaluated outside the temperature range employed in this study. At temperatures above T_g, the proper expressions for τ should be of the WLF type or its equivalent. At temperatures more than 50°C below T_g, the behaviour of τ has yet to be studied.

CONCLUSIONS

The effect of structural relaxation on the stress-relaxation behaviour of polymer blends was studied. Short-term stress-relaxation measurements were performed on three different systems at $T_g - 20$°C, $T_g - 35$°C and $T_g - 50$°C. The stress-relaxation data were fitted with the Williams–Watts equation:

$$E(t)/E_0 = \exp[-(t/\tau)^\beta]$$

and the effect of physical ageing was analysed in terms of changes in β and τ. It was found that:

Values for β obtained through optimization fell within a narrow range centred at 0.41 for all amorphous systems investigated.

A power-law formula for τ, in the form of:

$$\ln\tau = a + C_T \ln(T_g - T) + C_t \ln t_e$$

with constant C_T and C_t was found for blends of PMMA with SAN.

Exposure of blends of PMMA and SAN to 150°C for 240 h raised τ and T_g, and resulted in a narrower transition region, but did not affect β, C_T and C_t.

For blends of PS with PPO, a universal value for β and power-law formula for τ held, but the parameters C_T and C_t varied with the blend composition.

The stress-relaxation behaviour of a semicrystalline blend of PMMA with PVDF (50/50) was consistent with that predicted from a three-phase morphology.

The stress-relaxation of an amorphous blend of PMMA with PVDF (of 30 wt% PVDF) was fitted with parameters comparable to those for PMMA/SAN blends.

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