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The Influence of Filler Particles on the Mobility of Polymer Molecules

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ABSTRACT

A statistical experiment has been conducted to investigate the influence of silica fillers on the mobility of poly(vinyl chloride-co-vinyl acetate) molecules as reflected in glass transition temperatures. Measurement of glass transitions was made graphically from DSC curves. The data showed that the glass transition was affected by the presence of filler. The effect was dependent on the type and level of filler in the polymer. The filler was of either large or small particle size, or had had surface treatment to form trimethylsilyl groups. Significant interaction effects were found between filler types, filler level, and the level of polar vinyl acetate groups in the copolymer.

INTRODUCTION

The glass transition is a kinetic phenomenon observed when a polymer is cooled below a temperature (T_g) where segmental motion is

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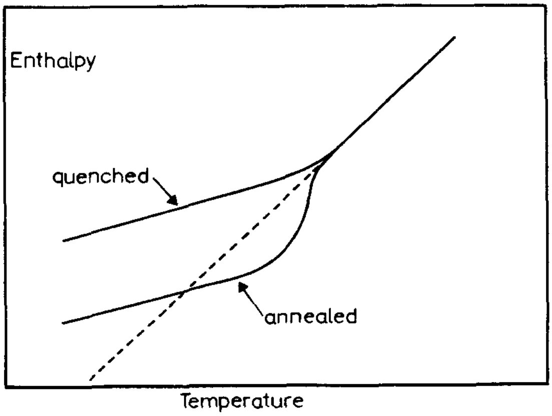

FIG. 1. Diagrammatic enthalpy-temperature curves.

no longer possible. The free volume that was available for segmental motion becomes frozen in at T_g. Upon annealing at a temperature below T_g, the glass approaches an equilibrium state as the excess voids gradually diffuse from the polymer. As a result of annealing, the enthalpy of the polymer decreases, the strength increases, and the toughness decreases.

When the heating rate is faster than the prior cooling rate (or the polymer has been annealed), a superheating phenomenon occurs. The enthalpy overshoots the equilibrium curve and then a sudden expansion occurs. The heating curve then moves back to the equilibrium curve as shown in Fig. 1 [1].

This overshoot in the enthalpy curve is observed as a peak in the heat capacity curve (DSC curve) as shown in Fig. 2.

The T_g measured from such a DSC curve increases depending on either the amount by which the heating rate is greater than the cooling rate or the time of annealing. A change in the measured T_g can also be brought about by changing the heating rate of the DSC scan. The measured T_g of a polymer will thus depend on sample history and instrument heating rate [2]. The enthalpy of relaxation will also depend on these parameters.

It is well known that the T_g of a polymer can be modified by introduction of a plasticizer or by copolymerization with a second monomer. T_g can also be changed by restricting molecular motion by cross-linking or by increasing crystallinity. A similar effect should be possible by adding a filler which will restrict motion by adsorption of polymer onto its surface, thus increasing T_g. It has been pointed

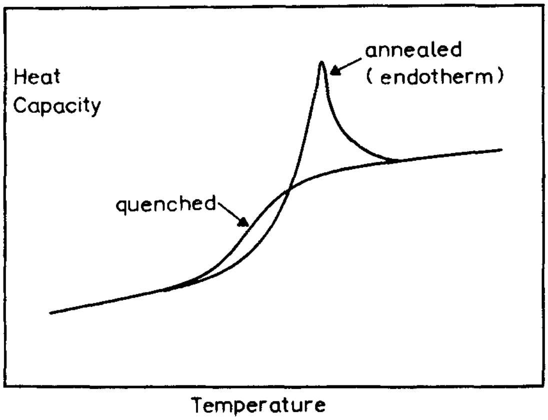

FIG. 2. DSC curves for annealed and quenched polymers.

out that the presence of filler could alter the thermal stress induced by cooling below T_g [3, 4]. This may effect the enthalpy of relaxation as well as the T_g. Torsion pendulum experiments have been used to relate increases in T_g to heats of adsorption of model compounds of the polymers on filler surfaces [5]. Cured epoxy resins filled with quartz or glass powder have been used to show that an increase in filler concentration is accompanied by an increase in the modulus of elasticity, T_g, the free volume fraction at T_g, and the volume coefficient of thermal expansion [6]. Dynamic mechanical measurements showed that an increase in T_g could be explained first in terms of the surface area onto which polymer is adsorbed and second the extent of polymer-filler interactions [7].

In this work the effect of filler on glass transition was investigated for silica-filled poly(vinyl chloride-co-vinyl acetate) samples. A statistical experiment was designed to test the effects of filler level and type in the presence of different concentrations of vinyl acetate in the copolymer. Some measurements of the enthalpy of relaxation are also presented.

EXPERIMENTAL

Samples were prepared from 5-10% (m/v) solutions of the polymers in butanone. Vinyl chloride copolymers containing 5% (Vinnol H/P5/65), 10% (vinnol H/P10/65), and 15% (Vinnol H/P15/50) of vinyl acetate were used (Wacker Chemie). The silicas were dispersed in the

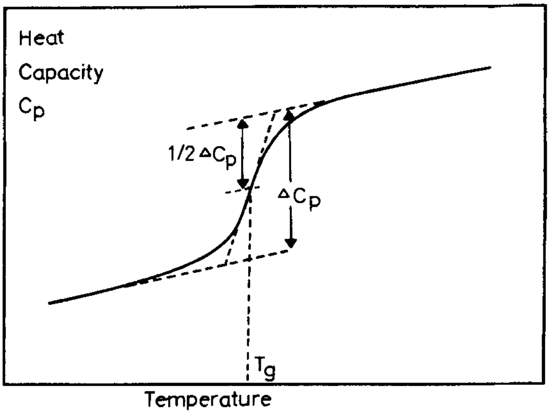

FIG. 3. Determination of T_g.

polymer solutions using an ultrasonic mixer. Aerosil silicas (Degussa) of surface area 300 m^2/g (10 nm particle diameter) and 50 m^2/g (50 nm) were used. A trimethylsilylated sample of Aerosil 300 was also used. The dispersions were spread on glass to provide films which were left to dry overnight at room temperature and then heated to 50° C in an oven under vacuum.

Measurements were made on a Perkin-Elmer DSC2 instrument using a heating rate of 10° C/min and a sample size of about 10 mg. Specimens were usually heated above T_g to 177° C and cooled to 42° C at 40° C/min before determining T_g. Some samples were annealed at 52° C in a vacuum oven before calorimetry. T_g was taken as the temperature at which the change in heat capacity was half the change for the transition (Fig. 3).

Determination of enthalpy of relaxation was performed by extrapolating the base line after T_g and cutting out and weighing the peak. Calibration of the DSC was performed using an indium standard.

RESULTS AND DISCUSSION

T_g measurements were made in duplicate for each of the three fillers at three levels (5, 20, and 40% by mass) in each of the three copolymer compositions. The error in the results arose mainly due to the difficulty in dispersing the filler to the same extent even though conditions and dispersion time were carefully reproduced. The statistical approach was designed to overcome this difficulty so that error in any one result would not mask overall conclusions. Data listed in Table 1 show the mean of duplicate measurements. The results of a factorial analysis of this data are summarized in Table 2. These results show a significant effect at the 99% confidence limit for each of the variables or combinations of variables.

The most important factor in determining a change in T_g was shown to be the level of vinyl acetate. This is a well-established relationship for copolymers. A curve is obtained from a plot of T_g versus vinyl acetate content (Fig. 4). This dependence serves as a reference for assessing the effects of the other variables.

The type of filler is the next most important determinant of T_g. This produced 13.8% of the total deviation which is about one-third the effect of varying vinyl acetate composition. In each case the trimethylsilylated silica increases T_g by the largest amount when changes in T_g are summed for other variables. Next in magnitude is the small particle size silica (Aerosil 300) and least the large particle size silica (Aerosil OX50). Trimethylsilylation decreases interactions between the silica particles, thus enabling better dispersion and hence more surface area for polymer adsorption. The smaller particle size also has a larger surface area for polymer adsorption.

Filler level caused 9.4% of total deviation. In general, the greater the level of filler, the larger the increase in T_g, when changes in T_g are summed for other variables. The relatively high levels of filler in this experiment may have underestimated the importance of filler level since a large surface was available for polymer adsorption in most cases.

The interaction between variables is significant and was one of the reasons necessitating the qualitative statistical approach of this work. It may also be one of the reasons for the conflict of results of previous work [3, 4]. Interactions between vinyl acetate level and filler type produced 11.5% of total deviation. Vinyl acetate units can hydrogen bond with the silica surface. For low vinyl acetate levels, Aerosil 300 gives a large increase in T_g whereas for the other filler types only small increases were observed.

For 10 and 15% vinyl acetate levels the trimethylsilylated Aerosil 300 gave equally large increases in T_g. Though an increased vinyl acetate level will provide an increased ability to hydrogen bond, the nature and availability of the surface to accept the hydrogen bonds is also important. This depends on trimethylsilation and degree of dispersion of the filler.

Interaction of filler type with filler level produced 10.4% of total deviation. Aerosil 300 and trimethylsilylated Aerosil 300 each have their greatest effect at highest concentration, whereas Aerosil OX50 has its greatest effect at the 20% level. This interaction may be due

TABLE 1. Glass Transition Temperatures

Level of filler (mass %)	Level of vinyl acetate in poly(vinyl chloride-co-vinyl acetate)								
	5% (T_g = 69.3)			10% (T_g = 62.5)			15% (T_g = 56.5)		
	Aerosil 300	Aerosil 300-TMS	Aerosil OX50	Aerosil 300	Aerosil 300-TMS	Aerosil OX50	Aerosil 300	Aerosil 300-TMS	Aerosil OX50
5	75.0[a]	73.0	71.0	63.0	68.5	68.0	56.5	60.0	55.6
	76.0[a]	75.5	69.0	61.8	68.5	66.5	56.0	59.0	52.0
	75.5[b]	74.3	70.0	62.4	68.5	67.3	56.3	59.5	53.8
20	76.0	69.5	73.0	62.0	67.2	68.0	55.5	60.2	58.5
	76.0	69.5	72.0	62.0	68.9	66.4	56.3	59.5	59.5
	76.0	69.5	72.5	62.0	68.1	67.2	55.9	59.9	59.0
40	80.0	76.5	68.0	64.3	69.0	64.3	59.2	70.6	55.0
	81.0	76.0	67.0	65.6	72.0	63.8	62.0	69.2	55.0
	80.5	76.3	67.5	65.0	70.5	64.1	60.6	69.9	55.0

[a] Duplicate measurements.
[b] Means, temperatures in °C.

TABLE 2. Analysis of Variance of Glass Transition Temperatures[a]

	Degree of freedom	Mean square	Variance ratio, F	Standard deviation	% SD of total SD
Factor					
Vinyl acetate level	2	930.67	830.96	30.5	44.8
Filler level	2	40.66	36.30	6.4	9.4
Filler type	2	88.92	79.39	9.4	13.8
Interactions					
Vinyl acetate/filler level	4	14.80	13.21	3.9	5.7
Vinyl acetate/filler type	4	61.43	54.85	7.8	11.5
Filler type/filler/level	4	50.09	44.72	7.1	10.4
Vinyl acetate/filler type/ filler level	8	4.24	3.78	1.9	2.8
Residual	27	1.12		1.1	1.6
Totals	53			68.1	

[a] From statistical tables: $F_{0.01}^{2,27} = 5.49$, $F_{0.01}^{4,27} = 4.11$, $F_{0.01}^{8,27} = 3.26$

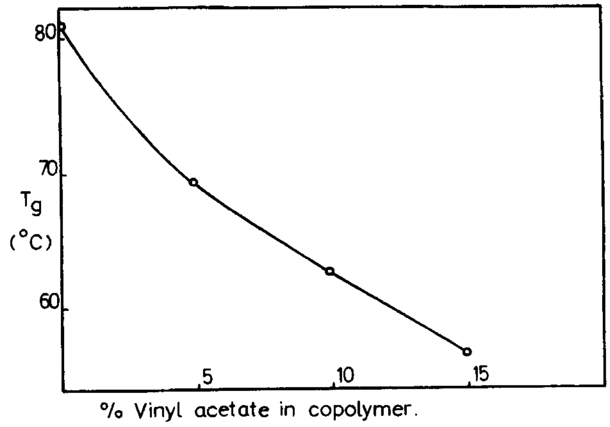

FIG. 4. T_g vs copolymer composition.

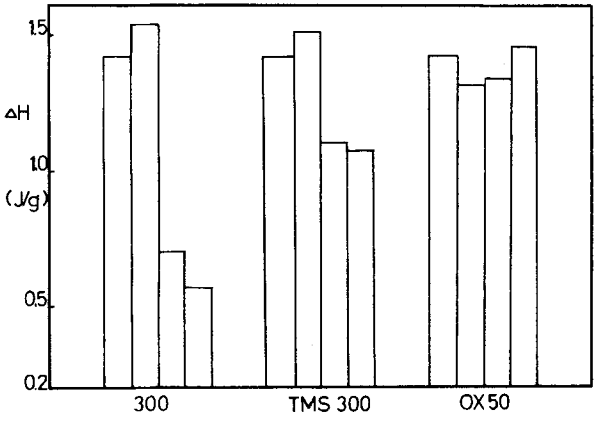

FIG. 5. Relaxation enthalpy change at T_g (96 h annealing: 0. 7. 25. and 44% Aerosil).

to the tendency of the silica particles to form aggregates to varying degrees.

A lesser interaction was found between vinyl acetate level and filler level. A high level of silica produces a large effect for all levels of vinyl acetate, whereas a low level of silica has an expected minimal effect with the highest vinyl acetate composition.

The results are further complicated by a tertiary interaction between all three factors which caused 2.8% of the total deviation.

The precision of the measurements is such that a residual of 1.6% of the total deviation was obtained. This shows that the results are reliable though quantitative correlations between the variables are not evident because of the multitude of interactions.

Annealed samples of polymers exhibit a relaxation enthalpy peak at the inflection of the T_g on a DSC scan. Measurement of the relaxation enthalpy was made after long annealing times for samples with 5% vinyl acetate. The results are shown in Fig. 5. The results for Aerosil 300 and trimethylsilylated Aerosil 300 showed similar effects although the latter produced the lesser relaxation. In each case a small level of silica decreased the enthalpy greatest while the larger concentrations slowed the relaxation process. It would be expected that adsorption of polymer onto the silica should reduce the mobility of the molecules and hence impede relaxation. The reason for the reversed effect of the low concentration is not apparent. Aerosil OX50 showed a smaller effect but with enthalpy decreasing most with largest filler concentration, indicating that an increased level of this filler aided relaxation.

CONCLUSION

The results of this statistical analysis of the effect of filler on the mobility of polymer molecules, as reflected in changes in glass transition temperature, showed that each of the variables studied was significant at the 99% confidence limit. In order of decreasing importance, the factors studied were vinyl acetate level, filler type, and filler level. Interactions between the variables were significant. The interactions in order of decreasing effect were vinyl acetate level–filler type, filler type–filler level, vinyl acetate level–filler level, and finally a tertiary interaction between all three variables. The causes of the changes in glass transition observed in this work require further investigation to establish quantitative relationships between the variables, though the interactions between variables will make this approach difficult.

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