The Influence of Filler Particles and Polymer Structure on the Mobility of Polymer Molecules

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Synopsis

The presence of carbon filler has been shown to cause a change in the glass transition temperature of polymers. For poly(vinyl chloride) and two of its copolymers with 10 and 15% vinyl acetate an increase in T_g was observed when Graphon C Carbon was added. The increase was greater when the proportion of vinyl acetate was greater. Polar vinyl acetate units allow stronger adsorption of polymer onto the carbon. Brittle polymers such as polystyrene and poly(methyl methacrylate) showed scattered T_g's when filled with carbon. The changes were not a function of concentration. It is postulated that the thermal stress of these polymers is increased in the presence of filler.

INTRODUCTION

Previous work[1] has shown that the glass transition temperature T_g of poly-(vinyl chloride-co-vinyl acetate) was increased in the presence of fillers. T_g increased with concentration of filler until a plateau was reached. The maximum increase depended on the nature of the filler. In the work described in this paper Graphon C carbon (Cabot) was chosen since it had previously produced a large increase in T_g and a smooth T_g versus concentration plot.

Torsional pendulum measurements[2] had shown that the T_g's of composites were shifted to higher temperatures and that this could be correlated with polymer–filler interaction energies. The shift in T_g was found to increase for strongly polar polymers.

Treatment of Fe_2O_3 powder with oleate to render its surface hydrophobic reduced the increase in T_g of polyurethanes filled with the powder.[3] The hydrophobic treatment had decreased the polar attractive forces between the surface and the polymer chains.

The increase in T_g of silica filled poly(vinyl chloride-co-vinyl acetate) was shown to depend qualitatively on the vinyl acetate, that is polar, content of the polymer.[4]

In some cases the presence of filler has been shown to decrease T_g.[5] This has been shown to be dependent on the thermal history of the specimen.

Relaxation of a polymer after adsorption onto a surface has been correlated with segmental motions in the polymer.[6] For plasticized poly(vinyl chloride), a lower activation energy and a larger rate of relaxation was found. This should also be true for thermal relaxation of filled polymers. The more flexible the

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polymer, the greater should be its rate of relaxation. Relaxation of a polymer onto a filler surface will minimize thermal stress and increase the influence of the filler on properties such as the glass transition.

EXPERIMENTAL

Samples were prepared from butarone 5–10% (m/v) solutions of the polymers, vinyl chloride polymers containing 0, 10, and 15% vinyl acetate, and poly(methyl methacrylate) (PMMA) were used. Polystyrene samples were prepared from a 10% (m/v) solution of the polymer in toluene. Graphon C carbon (Cabot) was dispersed in the polymer solutions using an ultrasonic mixer.

Pretreatment of the sample films and measurements were carried out as previously described.[4] Samples containing Aerosil 300 (Degussa) silica were prepared in a similar manner.

RESULTS AND DISCUSSION

Glass transition temperatures for the Graphon-C-filled polymers are listed in Table I. The data for poly(vinyl chloride) (PVC) and its vinyl acetate co-polymers (VAc) are plotted in Figure 1. The curves are similar in shape though the magnitude of the increase in T_g increases with the level of vinyl acetate. The maximum increase in T_g was 2.5°C for 0% VAc, 12.5°C for 10% VAc, and 15.5°C for 15% VAc. Vinyl acetate increases the polarity of the polymers and enables stronger adsorption of polymer molecules to the filler. The strength of adsorption had been related previously to polarity by using solubility parameters as a measure of polarity.[7] ESCA measurements have also shown a preferential adsorption of acetate groups of poly(vinyl chloride–vinyl acetate) onto metal substrates.[8] The preferential adsorption was detected as a concentration profile within the outer layer of polymer molecules.

The results for polystyrene are scattered, although an increase in T_g is observed in the presence of carbon. The results for poly(methyl methacrylate) are also scattered and a decrease in T_g is observed for carbon-filled samples. Repetition of measurements on samples from the same film preparation gave a standard deviation of 1.6°C compared with a standard deviation of 1.1°C for all the poly(vinyl chloride–vinyl acetate) results. Results obtained with Aerosil-300-silica-filled poly(methyl methacrylate) also produced scattered results but with an increase in T_g (Table I). The two sets of data were obtained from separately prepared samples. The first set has a mean of 110.6°C and standard deviation for duplicate measurements of 0.6°C; the second, 111.7 and 1.7°C, respectively. There is no significant difference between the means, indicating that samples' preparation was consistent in each case, though some values within each set are widely different.

It is proposed that, during cooling of the samples, thermal stresses cause crack formation around the filler particles. The polymer shrinks on cooling setting up these stresses. The high modulus filler does not distort, and therefore the brittle matrix cracks.

This will lower the surface adhesion of the polymer to the filler. The many voids created cause a lowering of T_g depending on the degree to which polymer-filled interactions have been disrupted. Polystyrene and poly(methyl

TABLE I
Glass Transition Temperatures of Filled Polymers

PVC with 15% VAc		PVC with 10% VAc		PVC		Polystyrene		PMMA		PMMA with Aerosil 300 silica (A)			
%C[a]	T_g[b]	%C	T_g	%C	T_g	%C	T_g	%C	T_g	%A	T_g	%A	T_g
0.0	56.5	0.0	62.5	0.0	75.5	0.0	94.0	0.0	105.4	0	107.0	0	107.5
0.2	65.3	0.5	67.8	1.1	76.2	0.6	97.5	0.2	84.0	0.2	110.0	0.2	112.5
0.8	72.0	1.6	70.4	2.1	76.5	1.4	97.0	0.3	87.8	0.6	110.0	0.5	111.5
2.2	69.8	3.5	72.0	3.9	77.3	3.2	98.6	0.6	81.5	1.2	103.0	1.0	112.4
4.3	70.4	7.5	73.5	7.5	77.9	7.1	95.6	1.1	84.0	1.6	110.0	1.8	113.3
8.2	68.0	13.3	74.5	13.7	77.7	12.3	96.4	1.9	83.5	4.1	108.0	4.5	108.4
14.0	68.5	19.7	75.0	21.9	77.5	19.1	94.5	3.8	94.2	7.8	117.0	8.6	112.0
21.4	71.2	31.5	74.0	30.5	78.0	33.1	97.0	9.4	86.0	14.2	118.0	15.8	113.0
37.7	67.0	45.6	74.0	47.7	77.2			17.2	91.0	23.4	115.0	24.5	111.8
										41.1	108.0	43.8	115.0

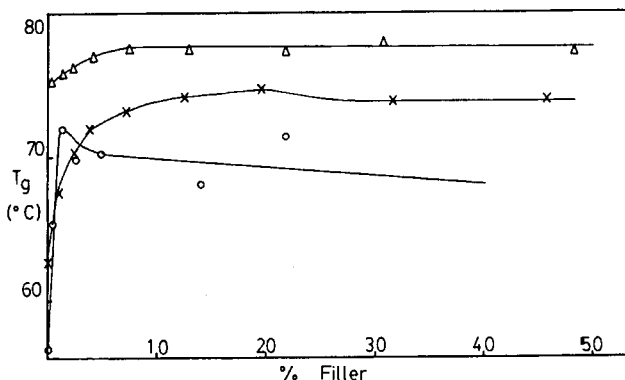[a] % by mass of Graphon C carbon.
[b] T_g in °C.

Fig. 1. T_g of Graphon-C-filled polymers. (△) PVC; (×) PVC—10% VAc; (○) PVC—15% Vac.

methacrylate) exhibit this behavior because they are brittle polymers. The vinyl chloride polymers are more flexible and so can relax onto the filler surfaces promoting good adhesion.

CONCLUSION

Adsorption of a polymer onto a filler can produce an increase in T_g due to restriction of the mobility of the polymer molecules. The magnitude of the increase in T_g will depend on the strength of adsorption; in general, greater polarity will produce stronger adsorption.

In the case of rigid polymers, thermal stresses will reduce adsorption by formation of cracks between the polymer and the filler. These cracks will give the polymer molecules increased volume for motion and will tend to reduce T_g.

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