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Effect of Moisture on Hammer-Milled Glass-Fiber-Reinforced Polyurethane

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The effect of moisture on the dynamic properties of hammer-milled glass-fiber-reinforced polyurethane was investigated. Similar investigations were also made on an unfilled polyurethane matrix for comparison. Moisture was found to increase the shear modulus at lower temperatures due to the formation of ice. At higher temperatures, however, shear modulus decreased due to the plasticizing effect of water. Moisture also modified the damping properties of the material.

Keywords
dynamic properties, effect of moisture, fiber-reinforced polyurethane, shear modulus

1. Introduction

REINFORCED polymeric materials, often used for engineering applications, may be exposed to moisture during service. This can modify their dynamic properties, such as the storage modulus and the damping factor (Ref 1-6). These defects are produced by the plasticizing effect of the absorbed water. This paper presents the results of a study on the effect of moisture on the dynamic properties of hammer-milled glass-fiber-reinforced polyurethane. Results of a similar study on an unfilled polyurethane matrix are also presented for comparison.

2. Experimental Method

Polyurethanes can be prepared by a number of methods. The most widely used technique involves the reaction of a hydroxyl compound, based on either polyester or polyether, with a polyfunctional isocyanate (Ref 6). Raw materials selected for polyurethane matrix preparation were the industrial tetrol UGI 3310 (supplied by Produits Chimiques Ugine Kuhlmann, Tour Manhattan-Palace de l'Iris Cedex 21-92087, Paris La Defense 2) and Suprasac VM-10 (supplied by ICI Americas, Inc., Wilmington, DE). The ratio of (NCO) to (OH) was kept equal to 1 for determining the concentration of the reactants. The tetrol was weighed directly into a 250 mL round-bottom three neck flask. The flask was provided with a stirrer gland and a steel stirrer with a polytetrafluoroethylene (PTFE) blade. The preparation of polyurethane specimens (fiber diameter, volume fraction, etc.) is detailed in Ref 7.

The reaction mixture was poured into a stainless steel rectangular mold that was preheated to 40 °C with inner dimensions of 160 by 120 by 4.50 mm^3. The mixture was allowed to reach the gel point in a vacuum oven at 40 °C. The temperature of the oven then was increased to 150 °C and the gel allowed to cure for 4 h. Test pieces (130 by 12.5 by 3.5 mm^3) were milled from the cured molded sheets. Each test piece was visually inspected using an optical traveling microscope; pieces with visible defects such as large voids were rejected.

For the filled samples, the calculated amount of hammer-milled E-glass fibers was weighed into a three-neck round-bottom flask along with the tetrol. The slurry of tetrol and fibers was continuously stirred to achieve homogeneity. Filled molded sheets were examined similarly under the microscope to determine whether any fibers had separated from the matrix. The rest of the procedure was the same as that described for the unfilled specimens. The volume fraction of fibers (φ_f) was determined by burning off the matrix. The density of the E-glass fibers was 2.54 g/cm^3, with average diameter of 5 μm, as determined by scanning electron microscopy (Ref 7). A value of 76 GN/m^2 was used as the modulus of E-glass fibers. Fiber-length distribution measurements were also carried out by dispersing them on a glass slide and measuring their lengths. A histogram plotted by measuring the length of each fiber is given in Ref 7.

All samples were dried in a vacuum oven, maintained at approximately 120 °C to constant weight, and kept in a dessicator over silica gel until required for testing. Water-saturated "wet" samples were prepared by immersing the previously dried and weighed samples in boiling water until constant weight was achieved. The samples were then immersed in water at room temperature for at least 2 weeks. By this process it was assumed that the maximum amount of water (2.6%) had been absorbed, and the moisture content was expressed as a percentage of dry weight.

The dynamic properties of these samples were studied via a torsional free decay experiment. The torsion pendulum was designed on principles similar to those used by Heijboer et al. (Ref 8). To study the effect of temperature on the dynamic properties, the specimens were mounted in an environmental chamber having double walls of stainless steel. The walls were adequately insulated with glass wool. The temperature of the chamber was lowered to −180 °C by pouring liquid nitrogen between the walls and then raised to 200 °C at the rate of 1 °C/min by controlled heating with the aid of built-in heaters. The frequency of oscillation was kept at 1 Hz, and the readings were recorded at 10 °C intervals. The experiments were carried out for dry and wet samples with filler (hammer-milled glass fiber) volume fractions of $\varphi_f = 0.0$ and 0.158, which is the maximum fiber volume fraction achieved.

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3. Results and Discussion

Values of storage modulus (G'), loss modulus (G''), and damping ($\tan \delta = G''/G'$) were obtained for dry and wet samples at various temperatures. Each value represents the average obtained from the results of three separate tests. Figure 1 shows plots of tan δ against temperature for unfilled ($\varphi_f = 0.0$) dry and wet polyurethane samples. Both types of samples show three distinct peaks, labeled α, β, and γ in order of decreasing temperature. The α peak represents the glass transition temperature of the polyurethane. The dynamic behavior of the polyurethane matrix is typical of those of amorphous polymers. The glassy modulus is ~2.0 GN/m^2 and drops slowly until the vicinity of T_g, when there is a sharp fall in value to 10 MN/m^2 with temperature. Therefore, the effect of moisture on the T_g or α peak, which is due to the motion of main chain segments between crosslinks, could not be correctly estimated. However, the extrapolated peak shows an increase in its magnitude due to moisture. There is also a downward shift of about 12 °C in the glass transition temperature due to moisture.

The β peak can be attributed to the restricted motion of either urethane or phenyl group (Ref 9) in the vicinity of an aliphatic group. Moisture has increased the peak height slightly and broadened it to some extent. A possible reason could be that moisture, through its plasticizing effect, helps increase the mobility of network chains.

The lower end of the γ peak is assigned to the methyl side groups (Ref 10), whereas the high-temperature end can be assigned to the motion of hydrogen-bonded species (Ref 11-13). The effect of moisture on this peak is most pronounced. The intensity of the peak increases markedly in the presence of moisture. This effect may be explained by the fact that the presence of water facilitates the motion of hydrogen-bonded polyurethane groups by weakening the intermolecular bonds. This fact can be supported by the broadening effect of moisture on this peak. The lower end or high-temperature maxima of this peak is around –80 °C, the region where hydrogen-bonded urethane groups are believed to be operative in the presence of moisture (Ref 11-13).

Figure 2 shows plots of tan δ versus temperature for dry and wet reinforced ($\varphi_f = 0.158$) polyurethane composite. Apart from lower actual numerical values of tan δ, the effects of moisture on the reinforced polyurethane samples are similar to those observed in Fig. 1 for unfilled samples. Figure 3 shows plots of G' against temperature for dry and wet polyurethane matrix. Similar plots for reinforced dry and wet samples ($\varphi_f = 0.158$) are shown in Fig. 4.

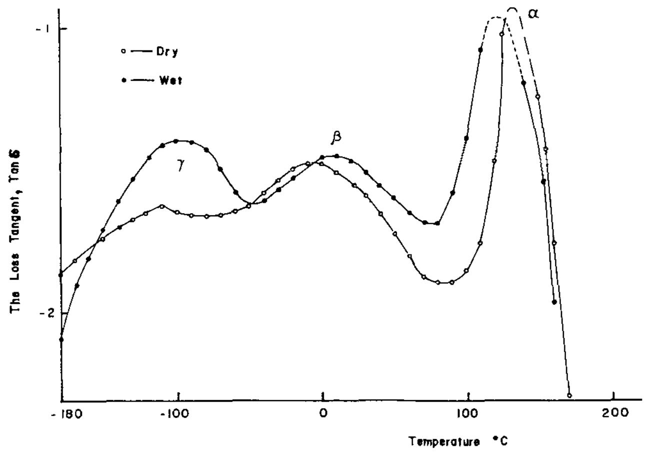

Fig. 1 Effect of moisture on tan δ of the unfilled matrix

It is apparent that the effect of moisture on the unfilled and reinforced samples is nearly the same. A small increase in the shear modulus of wet samples over dry samples in the lower temperature range can be attributed to the formation of ice, which has a shear modulus greater than that of the polymer; that is, ice has a reinforcing effect. This effect decreases with increasing temperature. From 0 °C onward, the shear modulus of the wet sample is less than that of the dry samples, and this trend continues throughout the rubbery region. The shear modulus of both unfilled and reinforced wet samples is found to be less than that of the dry samples in the rubbery region.

Figure 5 is a plot of relative shear modulus (shear modulus of the composite G'_c/shear modulus of the matrix G'_m) against temperature for the wet composite along with the theoretical

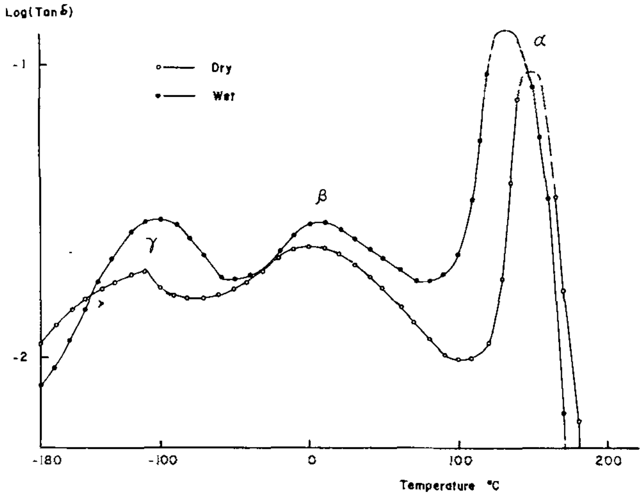

Fig. 2 Effect of moisture on tan δ of the reinforced polyurethane ($\varphi_f = 0.158$)

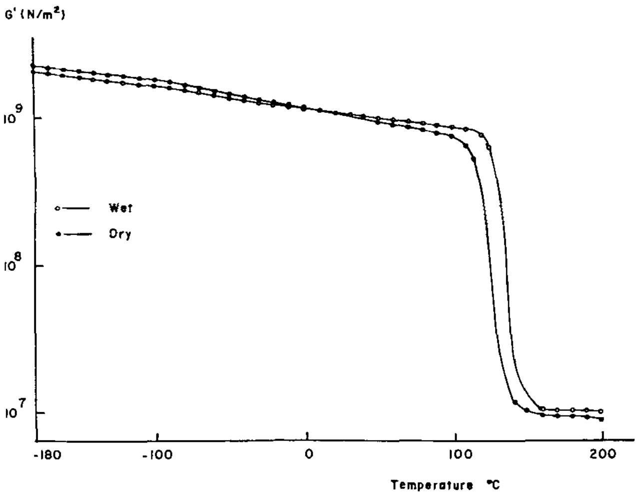

Fig. 3 Effect of moisture on G' of the unfilled matrix

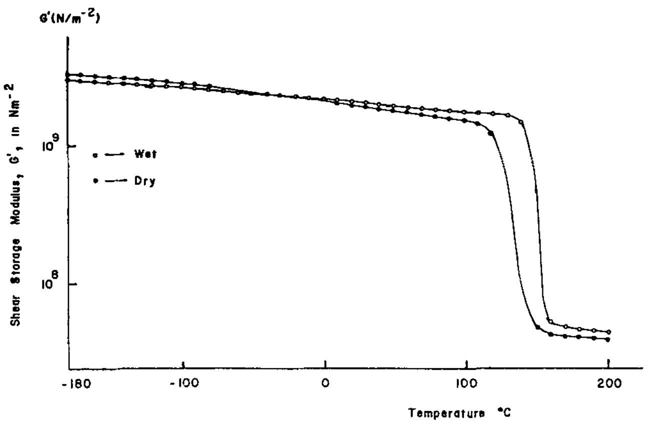

Fig. 4 Effect of moisture on G' of the reinforced polyurethane ($\varphi_f = 0.158$)

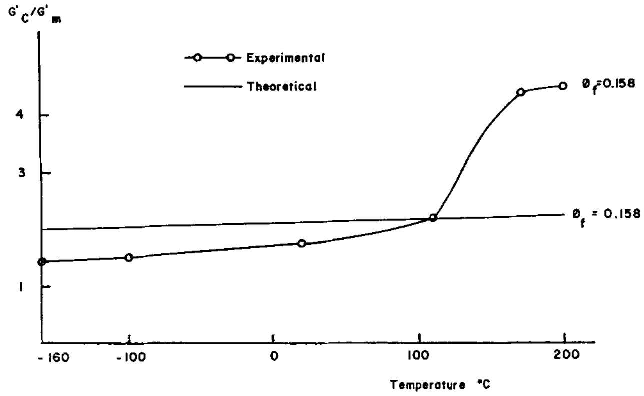

Fig. 5 Plot of relative modulus versus temperature for the wet composite ($\varphi_f = 0.158$)

curve due to Neilsen's equation (Ref 14, 15). At lower temperature the experimental values are lower than the theoretical values. As the temperature is increased above the glass transition temperature, the experimental values become much higher than the theoretical values. The decrease in relative values at lower temperatures can be attributed to the introduction of stresses in the polymer matrix due to mismatch of the coefficients of thermal expansion of the polymer and the filler. The modulus of a strained polymer is lower than that of an unstrained polymer. When the temperature is increased, stresses are relieved and a substantial improvement in the matrix modulus results, leading to a gradual increase in the relative modulus.

4. Conclusions

Moisture acts as a plasticizer, bringing about a downward shift of about 12 °C in the α (glass transition) peak. In the presence of moisture, the intensity of all three peaks is increased. This effect is more pronounced in the case of the γ peak.

Incorporation of hammer-milled glass fibers has led to an increase in glass transition temperature (around 12 °C in the case of $\varphi_f = 0.158$). It has also been observed that the increase in temperature is not a linear function of filler volume fraction. The increase in glass transition temperature with the filler concentration can be explained by the adsorption of the polymer on the filler surface, which restricts the mobility of the polymeric chains.

The effect of moisture on the shear storage modulus is similar to its effect on tensile modulus; above room temperature, the shear storage modulus decreases slightly. It has also been observed that below the glass transition region, the generalized equation of Neilsen can be successfully applied to predict the theoretical values of shear storage moduli of hammer-milled glass-fiber-reinforced polyurethane composites. Any change in the glass transition temperature of the polymeric materials directly affects their mechanical and physical properties. The practical implications of lowered T_g values due to moisture are a decrease in shear modulus and an increase in impact properties.

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