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Dynamic Mechanical Properties of a TiO_2-Filled Crosslinked Epoxy Resin from 20–90°C.

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Synopsis

Dynamic mechanical measurements were made with a torsional pendulum of a TiO_2-filled epoxy polymer (crosslinked with hexamethylene diamine) over a temperature range from 20–90°C., at filler concentrations of 0–40 wt.-%. The second-order transition temperature (T_g) was raised as the filler content increased. The behavior of TiO_2 filler results in a long-range immobilization of the highly crosslinked system with resultant increases in shear modulus (higher G') as well as decreased capacity for energy dissipation (lower damping factor). The out-of-phase modulus (G'') increased with filler content as well. The magnitudes of the slope parameters H_T (representing G' data above T_g) and H_g (representing G' data below T_g) decreased with greater filler content. The possibility is set forth that the TiO_2 filler causes a different distribution of mobility around the nitrogen junction as well as a change in the effective number of CH_2 units between crosslinks.

Introduction

A number of investigations have been made on the effect of filler on the physical properties of polymers. Increases were observed in the glass transition temperature (T_g) of polyurethane and polyisobutylene which were filled with glass beads.[1] Glass powder filled poly(methyl methacrylate) and polystyrene also showed increases in T_g.[2] The ultimate tensile properties of these filled polymers can be represented by master curves with a WLF equation which is near universal function of the glass temperature. The increase in T_g apparently depends on volume fraction of filler and could be due to the immobilization of polymer segments near the filler surface.[3] The change in T_g when TiO_2 was added to poly(vinyl chloride–acetate) copolymer was also indicated by the changes in temperature coefficients of gas diffusion through the polymer at T_g.[4] Correspondingly, carbon black-filled polyisobutylene, acrylonitrile rubber, and *cis*-polybutadiene[5] did not exhibit changes in the glass transition temperature.

Experimental

Dispersion of titanium dioxide (Rutile 610, DuPont Corp., average size 0.2 μ) in 4,4′-bisglycidylphenyl 2-2′-propane (EPON-828 from Shell Chemical Co.) was achieved with a three roll mill. Both TiO_2-filled and un-

filled and 4,4′-bisglycidylphenyl 2-2′-propane and 1,6-hexanediamine (m.p. 39–41°C., Matheson, Coleman and Bell Co.) were mixed in stoichiometric amounts at the melting point of the diamine. The mixture was heated in molds at 60°C. for 24 hr. to prepare torsional pendulum specimens. After this, the samples were placed in a dessicator for at least 24 hr. before use. TiO_2 filler levels used ranged from 0–40 wt.-%.

Dynamic mechanical measurements were made with a torsional pendulum (Plas-Tech. Corp.) employing a linear differential transformer coupled to a high-speed recorder (Sanborn No. 296). Sample size ranged from 25 to 35 mil thickness. Temperatures employed were from 20 to 90°C.

Results and Discussion

The damping factor (Δ) decreased as the filler content increased. This is shown in Figure 1 where Δ is plotted against the amount of TiO_2 filler present for different temperatures from 20–90°C. Generally, at a given temperature the decrease in Δ was asymptotic with greater TiO_2 content, with less of a decrease above 30 wt.-% TiO_2.

Shear modulus (G') values remained fairly constant from 20°C. to about 40°C. and then dropped sharply in the transition temperature region, becoming fairly level beyond the glass transition region. The amount of decrease in G' was less pronounced as the filler content increased. The constraining and stiffening effect of TiO_2 tends to reduce the decrease in G' with temperature. Shear modulus vs. temperature relationships for 0 and 40 wt.-% TiO_2 are shown in Figure 2.

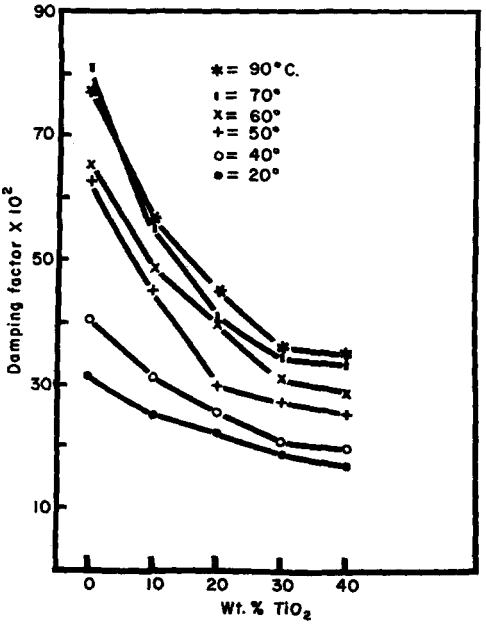

Fig. 1. Effect of filler on damping.

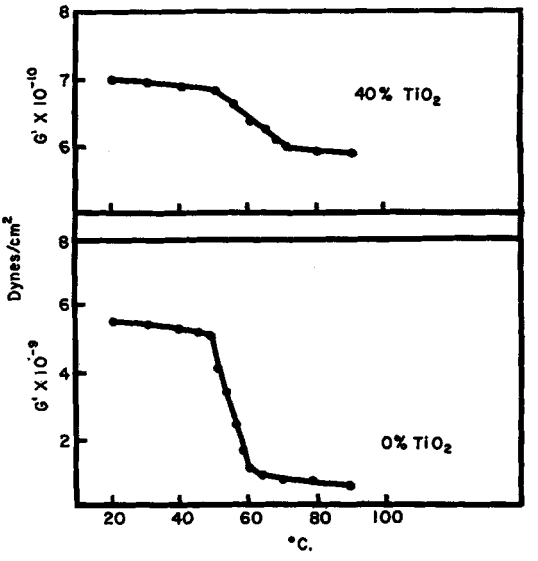

Fig. 2. Change in G' with temperature.

From damping factor maxima and the change in G' with temperature, glass transition temperatures were estimated. The T_g values were found to increase with filler content (Fig. 3). The TiO_2 appears to effectively increase system potential energy (higher stiffness) and this immobilizes the system so that more energy is needed to achieve the glass transition with a resultant rise in T_g.

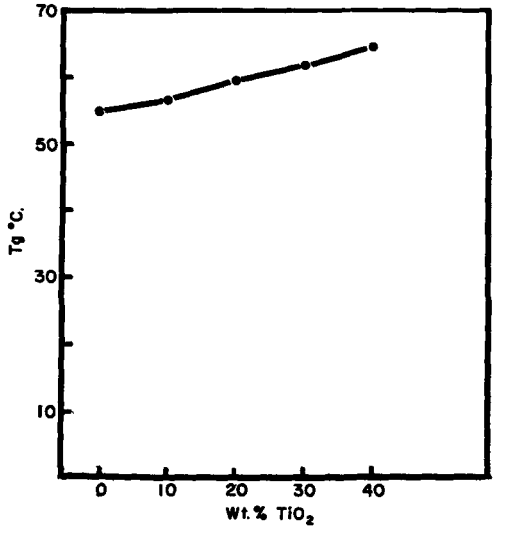

Fig. 3. Effect of filler on T_g.

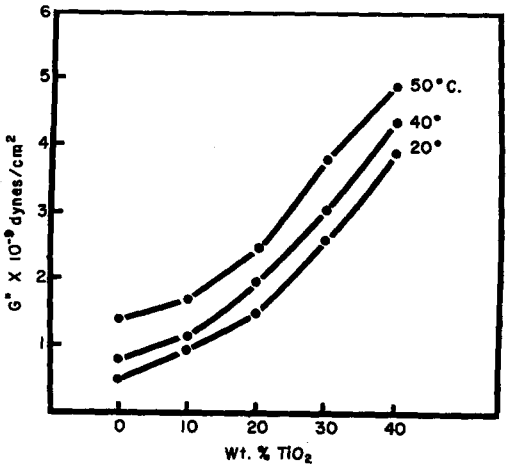

Fig. 4. Change in G'' with filler content.

The out-of-phase modulus (G'') is related to the kinetic energy content of the system and G'' generally increased with greater TiO_2 content at a given temperature (Fig. 4). The rate of increase of G'' was greater at higher filler content. G' must be increasing at a greater rate than the damping factor is decreasing with higher filler content for G'' to increase

$$\Delta = \pi(G''/G')$$

The suggestion was made[6,7] that the frequency dependence of the dynamic modulus may be fitted by an empirical normalization equation (1):

$$\log G' = {}^1/_2[\log G_1'G_2' + \log G_1'/G_2' \text{ erf } H \log (W/K)] \quad (1)$$

This equation is analogous to one used by Tobolsky for the relaxation modulus,[8]
or

$$\log (G'/G_2')/\log G_1'/G_2') = {}^1/_2[1 + \text{erf } H \log (W/K)] \quad (2)$$

where G_1' and G_2' are the upper and lower plateau values of the dynamic shear modulus, H is the parameter representing the steepness of frequency dispersion, W is the angular frequency, and K is the frequency at which $G' = (G_1'G_2')^{1/2}$, and erf is the error function.

It has been proposed[9] that since the frequency range is limited in a torsional pendulum and since modulus values are very insensitive to frequency changes in the range of 1 cps, the free oscillation values may be considered as essentially constant frequency values. Then eq. (3) obtained by replacing temperature for frequency in eq. (2) may be used to describe the experimental data:

$$\log (G'/G_2')/\log (G_1'/G_2') = {}^1/_2\{1 + \text{erf } H[(1/T) - (1/T_0)]\} \quad (3)$$

where T_0 is the temperature at which $G' = (G_1'G_2')^{1/2}$. A plot of the left-hand side of eq. (3) vs. $(1/T) - (1/T_0)$ on normal probability paper should yield a straight line from the slope of which H can be calculated.[10] Also steep dispersion curves correspond to large H values.[6]

Modulus data from a study of creep and relaxation of epoxy polymers when plotted according to eq. (2) resulted in straight lines.[10] Also, plots of shear modulus data according to eq. (3) for epoxy systems crosslinked with different diamines yielded data represented by two intersecting straight lines.[9] The slope parameter H_g (representing shear modulus data below T_g) was lowered when the number of CH_2 units between crosslinks was reduced. In addition, the slope parameter H_r (representing shear modulus data above T_g) was higher for crosslinking with a triamine than crosslinking involving diamines.

Plots of our data according to eq. (3) yielded curves represented by two straight lines intersecting at or near $(1/T) - (1/T_0) = 0$. The data obtained above and below the transition temperature for the different TiO_2 contents are described by the slope parameters H_r and H_g in Figures 5 and 6. The H_r value decreased at a greater rate at 10 and 20 wt.-% TiO_2 than at 30 and 40% TiO_2. The lower values of H_r for the filled polymers suggest the possibility of a different distribution of local mobility around the nitrogen junction as a result of TiO_2 presence. The magnitude of H_g decreased with higher TiO_2 content with a greater rate of decrease in H_g resulting at higher filler level. The possibility exists that the number of CH_2 units between crosslinks in the amine portion of the polymer has been effectively reduced by TiO_2 filler.

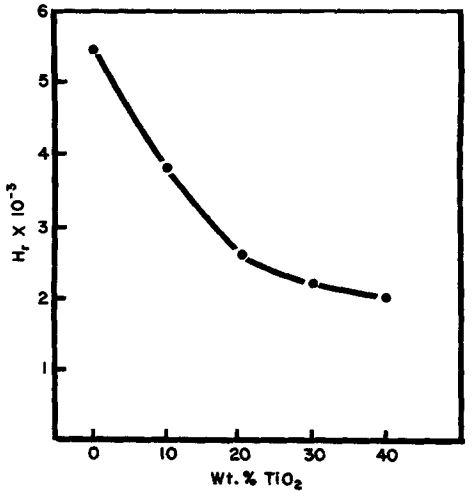

Fig. 5. Variation in H_r with filler content.

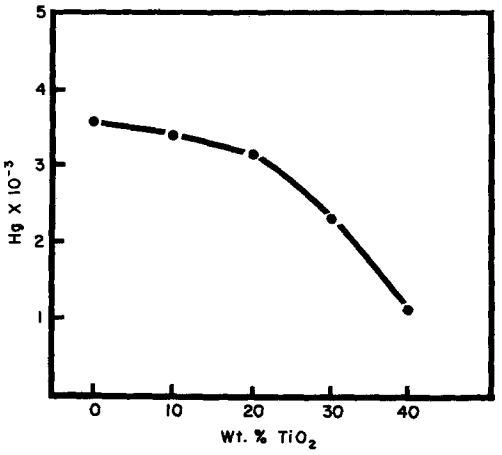

Fig. 6. Variation in H_g with filler content.

Conclusions

(*1*) The TiO_2 filler brought about a significant immobilization of the crosslinked epoxy system with greater stiffness (G') and higher potential energy. This long-range immobilization by filler resulted in increased energy necessary for a glass transition (higher T_g with greater filler content).

(*2*) Damping capacity was decreased with greater filler content (lower damping factor) resulting in a decrease in system capability for releasing energy upon distortion. Since the out-of-phase modulus (G'') increased with filler content, G' must increase at a greater rate than the damping factor is decreasing.

(*3*) The magnitude of the slope parameter H_r (representing G' data above T_g) was reduced by TiO_2 filler. The lower filler contents had a greater effect on the rate of decrease of H_r. A different distribution of local mobility around the nitrogen junction is possible due to the filler.

(*4*) The slope parameter H_g (representing G' data below T_g) also decreased with greater filler content. Higher TiO_2 contents resulted in a greater effect on H_g. A change in the effective number of CH_2 units between crosslinks may take place as a result of TiO_2 filler presence.

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Résumé

Des mesures dynamiques mécaniques ont été effectuées avec un pendule de torsion sur un polymère époxy chargé au TiO_2 (ponté au moyen d'hexaméthylène diamine) sur un domaine de température allant de 20 à 90°C, avec des concentrations de charge de 0 à 40% en poids. La température de transition de second ordre (T_g) décroissait à mesure que la teneur en charge croissait également. Le comportement de la charge TiO_2, entraîne une immobilisation à longue distance du système fortement ponté avec accroissement résultant du module de cisaillement (G' plus grand) de même qu'une diminution de l'énergie de dissipation (le facteur d'amortissement plus faible). Le module hors de phase (G'') croissait avec la teneur en charge. Les grandeurs des paramètres de tangentes H_r (représentant G' au-dessus de T_g) et H_g (représentant les résultats de G' en-dessous de T_g) décroissaient avec une teneur en charge croissante. La possibilité que la charge TiO_2 cause une distribution différente de mobilité autour de la jonction azotée aussi bien qu'un changement dans le nombre effectif d'unités méthyléniques entre les points est avancée.

Zusammenfassung

Dynamisch mechanische Torsionspendel-Messungen wurden an einem TiO_2-gefüllten Epoxypolymeren (mit Hexamethylendiamin vernetzt) in einem Temperaturbereich von 20–90°C und bei Füllstoffkonzentrationen von 0–40 Gew.% ausgeführt. Die Umwandlungstemperatur zweiter Art (T_g) stieg mit zunehmendem Füllstoffgehalt an. Der Einfluss des TiO_2-Füllstoffes führt zu einer Weitbereichs-Immobilisierung des hochvernetzten Systems, was eine Zunahme des Schubmoduls (höheres G') und eine Abnahme der Energiedissipations-Kapazität (niedrigerer Dämpfungsfaktor) bedingt. Auch der Ausser-Phase-Modul (G'') nahm mit dem Füllstoffgehalt zu. Die Grösse des Neigungsparameters H_r (für G'-Daten oberhalb T_g) und H_g (für G'-Daten unterhalb T_g) nahm bei höherem Füllstoffgehalt ab. Es besteht weiterhin die Möglichkeit, dass der TiO_2-Füllstoff sowohl eine verschiedene Beweglichkeitsverteilung um die Stickstoffverknüpfung als auch eine Änderung der effektiven Zahl der CH_2-Bausteine zwischen den Vernetzungsstellen verursacht.

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