

## The Effect of Humidity on the Tensile Properties\* of TiO<sub>2</sub>-Filled Poly(vinyl Acetate)

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### Synopsis

The tensile properties of TiO<sub>2</sub>-filled poly(vinyl acetate) were studied at strain rates of 100%/min. to 5,000%/min. at 25°C. after exposure to relative humidities of 10, 25, 51, 70, and 90% for 160 hr. Filler concentrations studied were 0, 10, 20, 30, and 40 wt.-% TiO<sub>2</sub>. The change in tensile properties with greater humidity was dependent on filler content. As the filler content increased, strength was lowered, elongation increased, and stiffness decreased with greater humidity. Generally, changes in tensile properties with humidity were less pronounced at higher strain rates. A mechanism is proposed where H<sub>2</sub>O alters the packing of polymer chains and affects the interaction of filler with polymer.

### INTRODUCTION

Poly(vinyl acetate) is glass-like at room temperature with reported glass transition temperatures ranging from 17–32°C. An explanation of the wide range reported for the glass transition temperature has been made on the basis of marked thermal expansivity changes over a temperature interval of 15°C.<sup>1</sup> The calculated density of filled poly(vinyl acetate) is higher than observed experimentally.<sup>2</sup> In addition, thermal expansion coefficients are lower experimentally than calculated values. This suggests that filler particles may alter the close packing of polymers. The out-of-phase shear modulus,  $G''$ , has been found to increase with TiO<sub>2</sub>-filled poly(vinyl acetate).<sup>3</sup> It has been proposed that with TiO<sub>2</sub>-filled poly(vinyl acetate) the side chain groups rotate at a greater rate. In addition, tensile properties of TiO<sub>2</sub>-filled poly(vinyl acetate) conditioned at low relative humidity were found to result in greater stiffness, higher strength and lower ultimate elongation than unfilled poly(vinyl acetate).<sup>4</sup> The clustering capability of water in poly(vinyl acetate) is high, particularly at high relative humidity.<sup>5</sup> The effect of higher humidity on a TiO<sub>2</sub>-filled crosslinked epoxy system was to raise tensile strength and stiffness.<sup>6</sup>

The purpose of this work was to study the effect of humidity conditioning on the tensile properties of TiO<sub>2</sub>-filled poly(vinyl acetate) in a range of relative humidity from 10 to 90%.

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## EXPERIMENTAL PROCEDURE

The poly(vinyl acetate) employed was commercial AYAT (Union Carbide Corp.). Intrinsic viscosity in cyclohexanone was 0.69 dl./g. (20°C.). The TiO<sub>2</sub> used was Rutile 610 (Du Pont Co.) with average particle size of 0.2 μ. TiO<sub>2</sub> was incorporated into the polymer by two-roll melt mixing. Films were made with a Gardner gage from solutions of poly(vinyl acetate) in 2-butanone. Films were dried for 48 hr. at 60°C. and then exposed to a specific humidity for 160 hr. before testing. Thickness of test samples was 2-4 mil. Films were tested with an Instron tensile tester at strain rates from 100%/min. to 5,000%/min. (test rates of 1 in./min. to 50 in./min. on 1-in. length samples). Tensile properties were obtained with a high-speed recorder (Sanborn No. 301). TiO<sub>2</sub> concentrations used were 0-40 wt.-% (0-16 vol.-%). The temperature was 25°C.

## EXPERIMENTAL RESULTS AND DISCUSSION

### Effect of Humidity on Tensile and Yield Strength

The tensile strengths at a given filler concentration are given, relative to the tensile strength of unfilled poly(vinyl acetate) at each conditioning relative humidity, in Figure 1. At 10% relative humidity, the tensile strength of filled poly(vinyl acetate) was greater than unfilled poly(vinyl acetate), and this difference increased with TiO<sub>2</sub> content. However, with increasing relative humidity, the tensile strength became less than that of unfilled poly(vinyl acetate).

The effect of increasing humidity on unfilled poly(vinyl acetate) was to raise tensile strength. This is shown in Figure 2 where tensile strength at

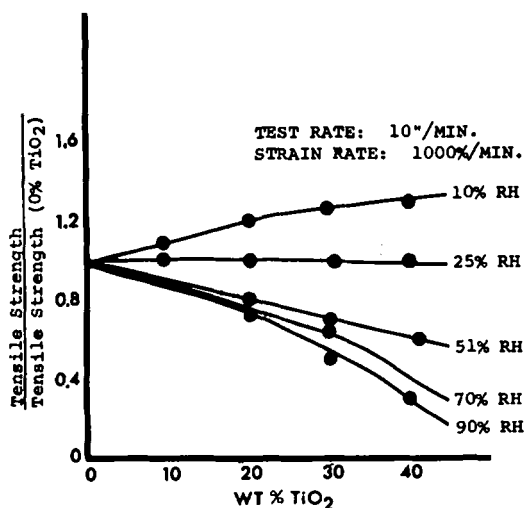


Fig. 1. Change in tensile strength with TiO<sub>2</sub> content at different humidities.

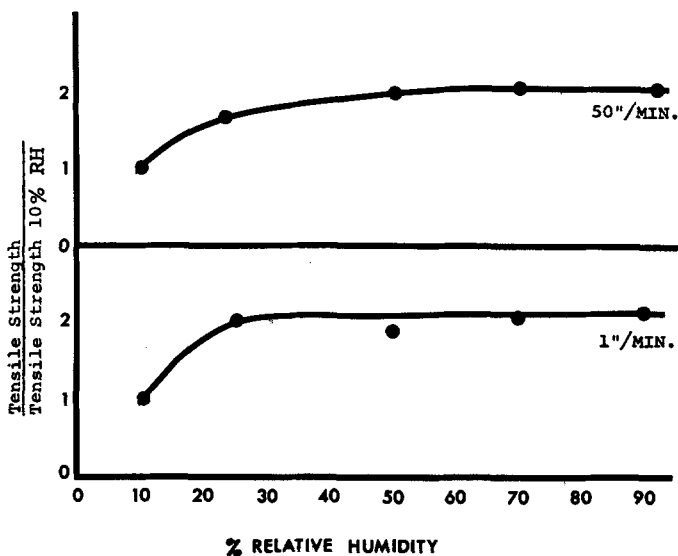


Fig. 2. Effect of humidity on tensile strength of unfilled poly(vinyl acetate).

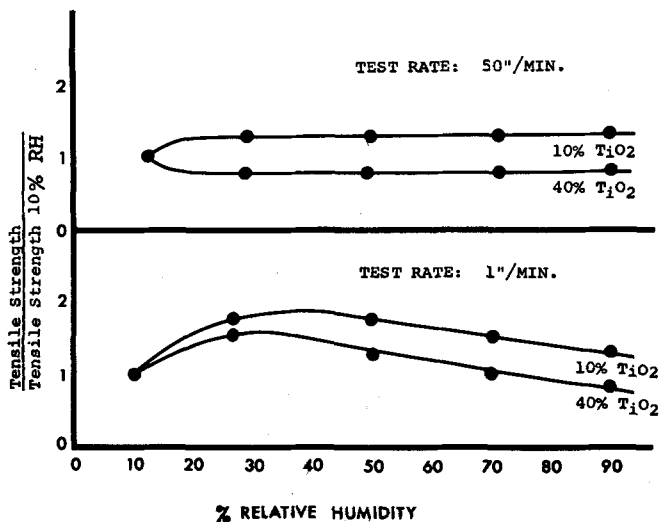


Fig. 3. Change in tensile strength with humidity for TiO<sub>2</sub>-filled poly(vinyl acetate).

a given humidity compared to tensile strength at 10% relative humidity is plotted against per cent relative humidity. This rate of increase in tensile strength became less with greater relative humidity and higher strain rate.

At low strain rates, the tensile strength of filled poly(vinyl acetate) decreased in the region from 25% relative humidity to 90% relative humidity, with an increase from 10% relative humidity to 25% relative humidity (Fig. 3). At higher strain rates, the tensile strength was constant above

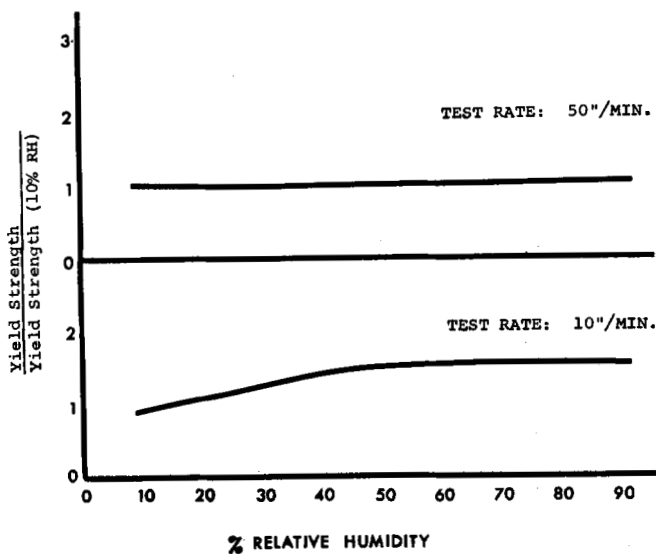


Fig. 4. Variation in yield strength for unfilled poly(vinyl acetate) with humidity.

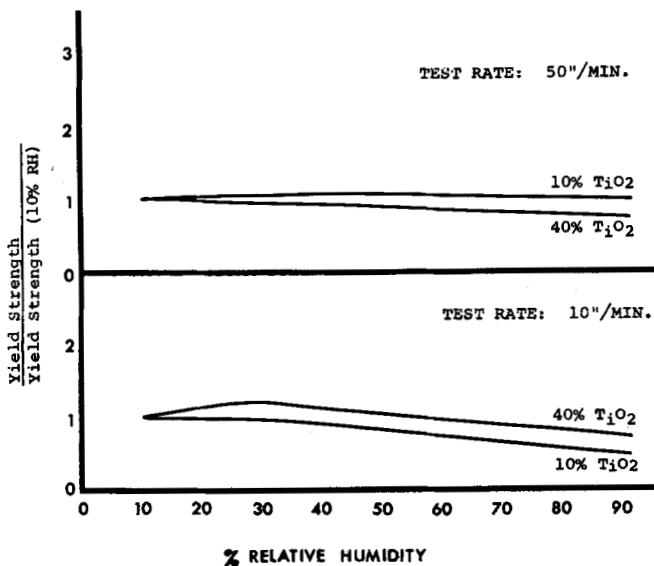


Fig. 5. Change in yield strength with humidity for TiO<sub>2</sub>-filled poly(vinyl acetate).

25% relative humidity. There was a slight overall increase in tensile strength for 10 wt.-% TiO<sub>2</sub> poly(vinyl acetate), but higher TiO<sub>2</sub> concentration samples showed an overall decrease in tensile strength.

The yield strength for unfilled poly(vinyl acetate) at low strain rates showed an increase with higher humidity, leveling off above 50% relative humidity (Fig. 4). However, at 50 in./min. test rate, yield strength did

not vary with humidity. With filled poly(vinyl acetate), yield strength dropped off at higher TiO<sub>2</sub> contents (Fig. 5). Again at greater strain rates, the yield strength became less sensitive to humidity for filled polymers.

### Ultimate Elongation and Young's Modulus

At low strain rates, ultimate elongation for filled poly(vinyl acetate) was lower than ultimate elongation of unfilled polymer at 10% relative humidity; and this decrease in elongation became greater with higher TiO<sub>2</sub> content (Fig. 6). At 10% TiO<sub>2</sub> content, the ultimate elongation was less than for unfilled poly(vinyl acetate) at all humidities. But with greater TiO<sub>2</sub> content, the decrease in ultimate elongation compared to unfilled poly(vinyl acetate) became less; until at 40% TiO<sub>2</sub> content under conditions at 70 and 90% relative humidity, the ultimate elongation was greater than that of unfilled poly(vinyl acetate). For test rates of 50 in./min., ultimate elongations at 10% relative humidity were also lower than unfilled polymer. As the relative humidity was increased, ultimate elongation rose, becoming greater than unfilled polymer with a maximum at 10% TiO<sub>2</sub> and a leveling off above 20% TiO<sub>2</sub> content.

The ultimate elongation of unfilled poly(vinyl acetate) decreased at higher per cent relative humidity with a slight rise in the region from 10–25% relative humidity (Fig. 7). The ultimate elongation of TiO<sub>2</sub>-filled

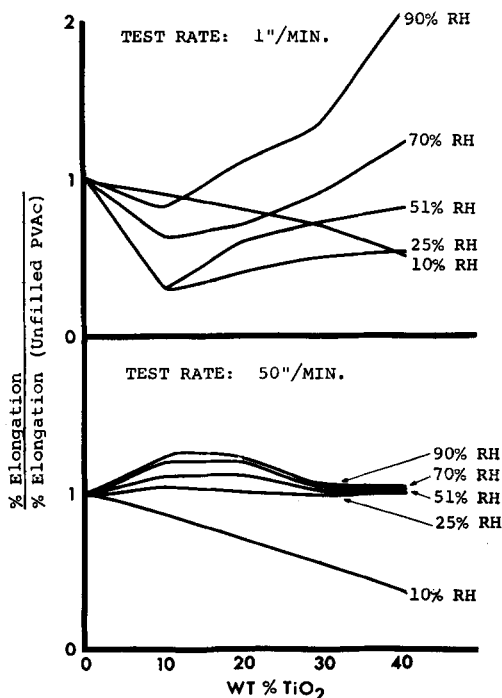


Fig. 6. Change in ultimate elongation with TiO<sub>2</sub> content for different humidities.

poly(vinyl acetate) increased with higher humidity, the rate of increase being greater with higher filler content.

At 50 in./min. test rate, the unfilled poly(vinyl acetate) elongation was less dependent on humidity (Fig. 8). With filled polymer, the elongation

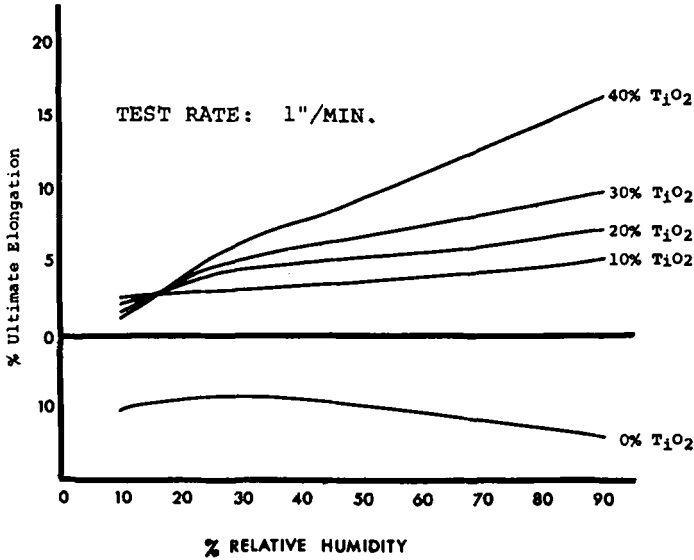


Fig. 7. Effect of humidity on ultimate elongation of  $\text{TiO}_2$ -filled poly(vinyl acetate) at 1 in./min.

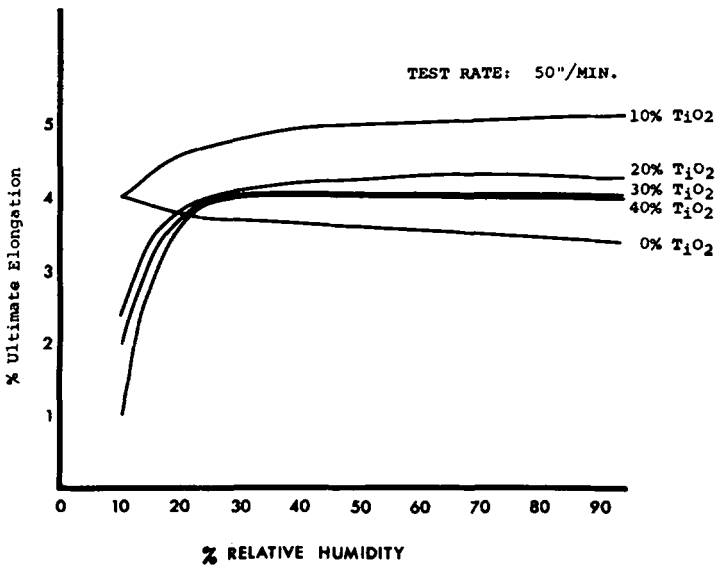


Fig. 8. Effect of humidity on ultimate elongation of  $\text{TiO}_2$ -filled poly(vinyl acetate) at 50 in./min.

increased in the region from 10–25% relative humidity and then remained nearly constant as the humidity was raised further.

Young's modulus rose for unfilled poly(vinyl acetate) with higher relative humidity (Fig. 9). Young's modulus leveled off above 70% relative humidity here. As relative humidity increased, Young's modulus decreased for TiO<sub>2</sub> filled poly(vinyl acetate) with, again, a leveling off at above 70% humidity (Fig. 10).

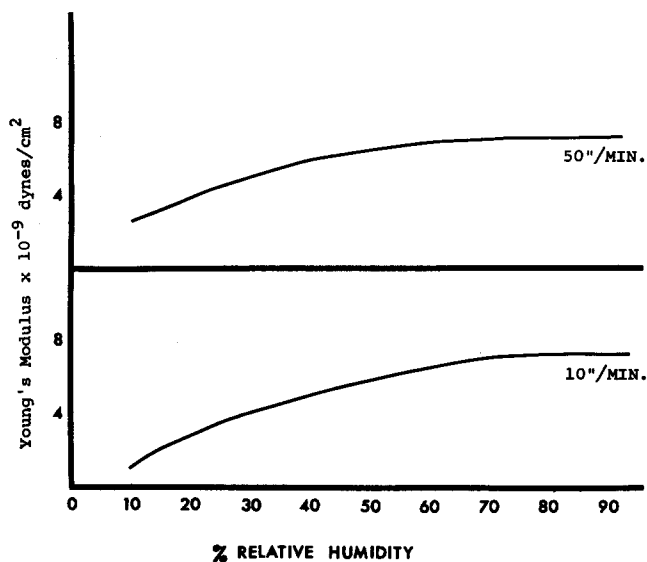


Fig. 9. Effect of humidity on Young's modulus for unfilled poly(vinyl acetate).

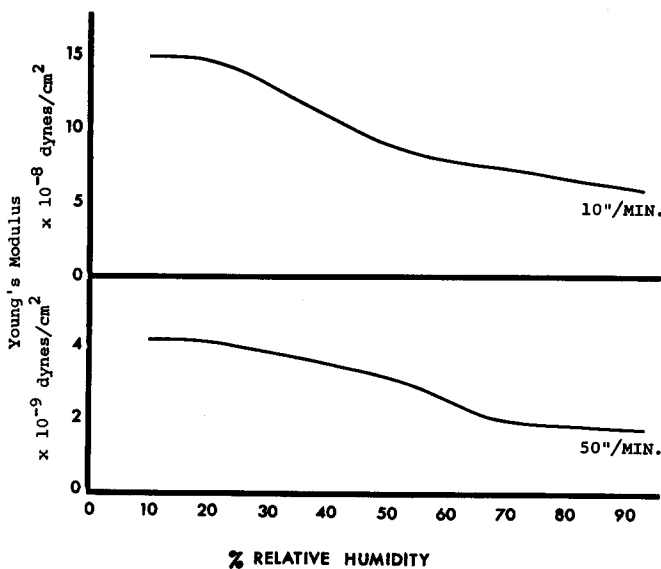


Fig. 10. Effect of humidity on Young's modulus for 10 wt.-% TiO<sub>2</sub> poly(vinyl acetate).

### Work of Breaking

The work of breaking, as measured by stress-strain curve area, is a measure of material toughness. The work of breaking for unfilled poly(vinyl acetate) showed an increase with greater humidity, leveling off at

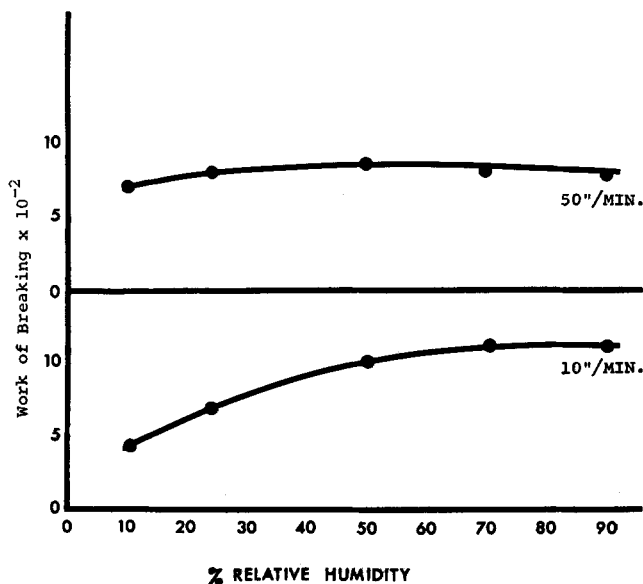


Fig. 11. Change in work of breaking for unfilled poly(vinyl acetate) with humidity.

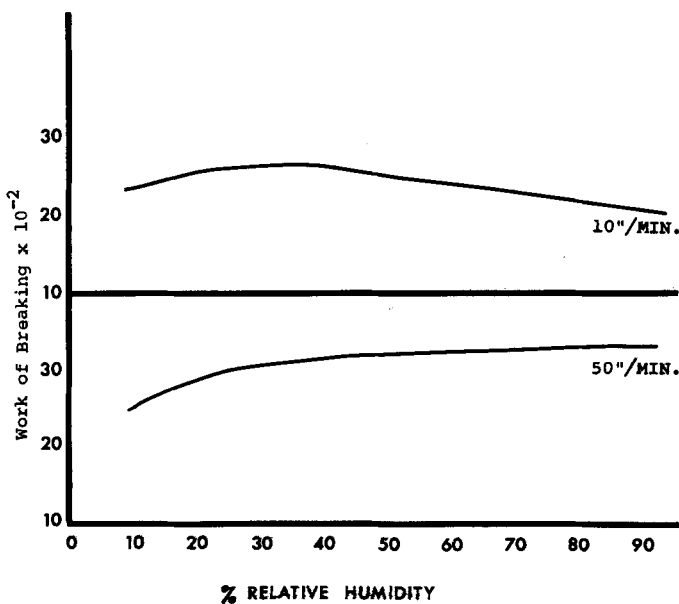


Fig. 12. Variation in work of breaking for 10 wt.-%  $\text{TiO}_2$  poly(vinyl acetate).



90% relative humidity. This increase in work of breaking was not as great at 50 in./min. compared to lower test rates (Fig. 11). There was a decrease in work of breaking with higher humidity for filled polymer at low strain rates (Fig. 12). A maximum existed at 25% relative humidity. However, at 50 in./min., the work of breaking increased up to 50% relative humidity. Above 50% relative humidity, the work of breaking was almost constant.

### Stress Relaxation

The rate of stress relaxation for unfilled poly(vinyl acetate) decreased with greater humidity. The greatest decrease in stress-relaxation rate took place from 10–25% relative humidity. This is shown in Figure 13 where relaxation times are given as a function of relative humidity. TiO<sub>2</sub>-filled polymer also had a decrease in stress-relaxation rate as a result of conditioning at higher humidity (Fig. 13). The rate of stress relaxation

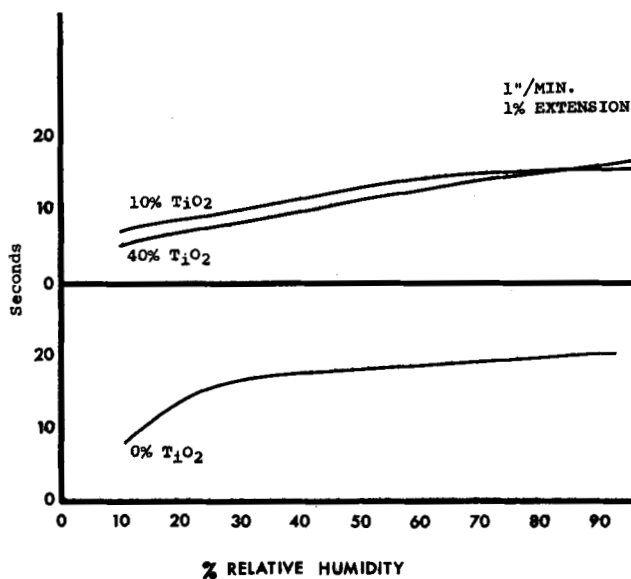


Fig. 13. Relaxation times for unfilled and filled poly(vinyl acetate). Maxwell model.

was reduced with greater humidity for TiO<sub>2</sub>-filled poly(vinyl acetate), but the rate of stress relaxation still remained higher than for unfilled poly(vinyl acetate).

Previously,<sup>4</sup> it was found that the rate of stress relaxation of TiO<sub>2</sub>-filled poly(vinyl acetate) conditioned at low humidity was greater than with unfilled poly(vinyl acetate). This was correlated with increase in out-of-phase modulus and in turn with greater side chain motion. Poly(vinyl acetate) filled with TiO<sub>2</sub> appears to have more side chain motion than unfilled poly(vinyl acetate) at all the humidities studied.

### Proposed Mechanism

For unfilled poly(vinyl acetate), the packing of polymer chains was altered by water, thereby, changing intermolecular forces with resultant changes in tensile properties, perhaps by affecting the movement of acetate side-chain groups. In the case of TiO<sub>2</sub> filled poly(vinyl acetate), the interaction of filler with polymer chains is affected as well by H<sub>2</sub>O with resultant differences in resistance to deformation and ultimate rupture.

### CONCLUSIONS

The effect of conditioning at greater humidity on unfilled poly(vinyl acetate) was to increase overall chain stiffness and in turn to raise system potential energy. Along with this, tensile strength was increased and ultimate elongations decreased. Overall chain stiffness was decreased by higher humidity conditioning for TiO<sub>2</sub>-filled poly(vinyl acetate), thereby, lowering system potential energy. The change in tensile properties with increased humidity was dependent on filler concentration. As the filler content increased, strength was reduced and ultimate elongation rose. Generally, for filled and unfilled polymer, changes in tensile properties were less pronounced at higher strain rates.

The work of breaking for unfilled poly(vinyl acetate) was increased with greater humidity. For filled polymer at low strain rates, work of breaking decreased with greater humidity. At high strain rates, work of breaking increased for TiO<sub>2</sub>-filled polymer with higher humidity.

The rate of stress relaxation was reduced for both filled and unfilled poly(vinyl acetate) with higher humidity. However, the rate of stress relaxation was still greater for filled polymer. At all humidities studied, TiO<sub>2</sub>-filled poly(vinyl acetate) appears to have greater side chain motion than unfilled polymer.

The time (strain rate) dependence of the humidity effect on tensile properties indicates that the times needed for complete water-polymer interaction may be longer than the test times (<0.2 sec. at 5000%/min.) at higher strain rate.

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### Résumé

Les propriétés de tension d'acétate de polyvinyle chargé de dioxyde de titane ont été étudiées à des vitesses de tension de 100%/min. à 5.000%/min à 25° après exposition à des humidités relatives de 10, 25, 51, 70 et 90% durant 160 heures. Les concentrations en charge étudiées étaient de 0, 10, 20, 30 et 40% en poids de TiO<sub>2</sub>. Le changement des propriétés de tension à humidité plus grande était dépendant de la teneur en charge. Lorsque la teneur en charge croît, la force diminue, l'élongation croît et la rigidité décroît avec une humidité plus grande. Généralement, les changements de propriétés de tension avec l'humidité sont moins prononcés à des vitesses de tension plus élevées. Un mécanisme est proposé suivant lequel l'eau modifie l'empaquettement des chaînes polymériques et affecte l'interaction de la charge avec le polymère.

### Zusammenfassung

Die Zugeigenschaften von TiO<sub>2</sub>-gefülltem Polyvinylacetat wurden bei Dehnungsgeschwindigkeiten von 100 bis 5000%/min bei 25°C nach Einwirkung einer relativen Feuchtigkeit von 10, 25, 51, 70 und 90% durch 160 h untersucht. Die Füllstoffkonzentrationen lagen bei 0, 10, 20, 30 und 40 Gew.% TiO<sub>2</sub>. Die Änderung der Zugeigenschaften bei grösserer Feuchtigkeit war vom Füllstoffgehalt abhängig. Mit zunehmendem Füllstoffgehalt wurde bei höherer Feuchtigkeit die Festigkeit erniedrigt, die Dehnung nahm zu und die Steifigkeit ab. Im allgemeinen war die Abhängigkeit der Zugeigenschaften von der Feuchtigkeit bei höheren Dehnungsgeschwindigkeiten weniger stark ausgeprägt. Als Mechanismus wird eine Änderung der Packung der Polymerketten und eine Beeinflussung der Wechselwirkung des Füllstoffes mit dem Polymeren durch H<sub>2</sub>O angenommen.

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