

## Tensile Properties of TiO<sub>2</sub>-Filled Poly(vinyl Acetate) in the Transition Region

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### Synopsis

The stress-strain properties of TiO<sub>2</sub>-filled poly(vinyl acetate) have been studied at filler percentages of 0, 10, 20, 30, and 40% TiO<sub>2</sub> over a strain-rate range of 100-5000%/min at 24°C. Tensile strength, Young's modulus, and offset yield strengths all were found to increase with higher strain rates and higher TiO<sub>2</sub> contents. Ultimate elongations decreased with greater TiO<sub>2</sub> content and higher strain rates. Shift factors for volume fraction of filler were estimated for tensile properties as function of test rate. Stress-relaxation studies have shown a reduction in relaxation times with increasing TiO<sub>2</sub> content. Calculations of the out-of-phase Young's modulus were made as a function of filler content employing a box-type of distribution of relaxation times. A possible explanation for the stress-strain behavior observed is that introduction of TiO<sub>2</sub> changes the internal viscosity of the system, similar to the effect of temperature. This would also mean that the ultimate properties would be dependent on filler content and strain rate because viscous resistance to chain deformation would be altered. The effect of filler on stress relaxation could be thought of being due to an increase in short-range chain motion.

### Introduction

The glass transition of poly(vinyl acetate) has been reported over a range of 15°C. with values reported from 17 to 32°C.<sup>1</sup> The density of filled poly(vinyl acetate) calculated by using volume additivity is higher than observed experimentally.<sup>2</sup> In addition, thermal expansion coefficients for filled polymer are lower experimentally than calculated values. This suggests that filler particles may alter the close packing of polymer chains.

The purpose of this work was to investigate the tensile behavior of poly(vinyl acetate) for TiO<sub>2</sub> filler concentrations of 0-40 wt.-% (0-16 vol.-%) at a temperature in the transition region (24°C.).

### Experimental

The poly(vinyl acetate) employed was commercial AYAT (Union Carbide Corp.). The intrinsic viscosity in cyclohexanone was 0.69 dl./g. (20°C.). TiO<sub>2</sub> used was Rutile 610 (duPont Co.) with an 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 gauge from solutions of poly(vinyl acetate) in 2-butanone. Films were dried for 48 hr. at 60°C. and then

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allowed to stand in a desiccator for an additional 48 hr. at room temperature. The thickness of test samples was 2–4 mils. Tensile properties were obtained with an Instron tensile tester equipped with a high-speed recorder (Sanborn #301). The use of a high-speed recorder allowed more reliable recording of tensile properties under the short test times involved (less than 0.2 sec.). Films were tested at strain rates of 100–5000%/min. (test rates of 1–50 in./min., 1-in. samples).

### Discussion

Young's modulus increased with filler content in an exponential manner (Fig. 1). As the strain rate increased, the rise in Young's modulus became much larger with increase in filler content. Variation of Young's modulus with filler content is predicted for noninteracting spheres in an elastic matrix to be<sup>3</sup>

$$E = E_0(1 + 2.5\phi + 14.1\phi^2)$$

where  $\phi$  is the volume fraction filler. This equation was not followed for TiO<sub>2</sub>-filled poly(vinyl acetate). Equations for variation in Young's modulus with filler content are given as a function of strain rate in Table I.

Along with chain stiffening for higher filler content, ultimate elongations were reduced. Fractional decrease in elongation with filler content is given in Figure 2 at different strain rates. With higher strain rates, the

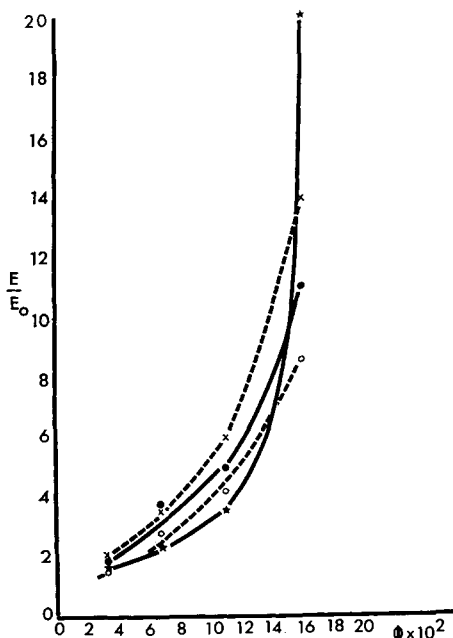


Fig. 1. Variation of Young's modulus with filler content: (O) 1 in./min.; (●) 10 in./min.; (X) 20 in./min.; (★) 50 in./min.

TABLE I  
Equations for Change in Young's Modulus for TiO<sub>2</sub> Filler Content

Strain rate, %/min.	Young's modulus equation <sup>a</sup>
100	$E = E_0(1 + 11.25\phi + 195.6\phi^2 + 12.6\phi^3)$
1000	$E = E_0(1 + 13.9\phi + 179.4\phi^2 + 652.5\phi^3)$
2000	$E = E_0(1 + 12.5\phi + 278\phi^2 + 784\phi^3)$
5000	$E = E_0(1 + 16\phi + 379\phi^2 + 356\phi^3)$

<sup>a</sup>  $E$  = Young's modulus at a filler content, volume fraction  $\phi$ ;  $E_0$  = Young's modulus at  $\phi = 0$ .

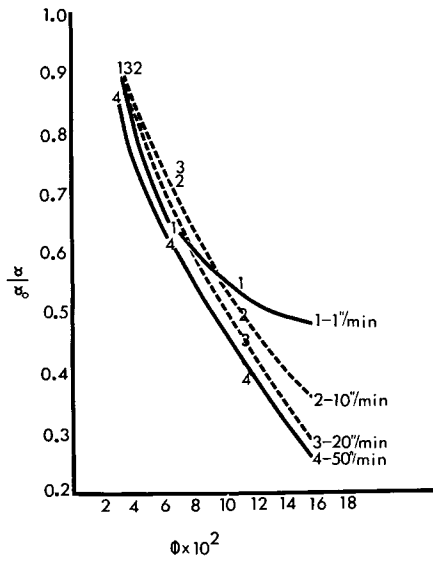


Fig. 2. Variation of ultimate elongation with filler content.

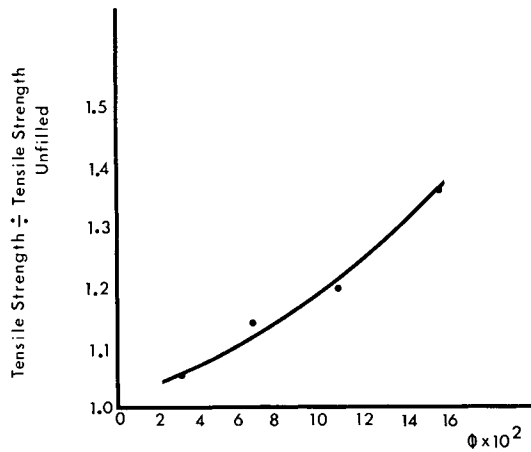


Fig. 3. Variation of tensile strength with filler content at 50 in./min.

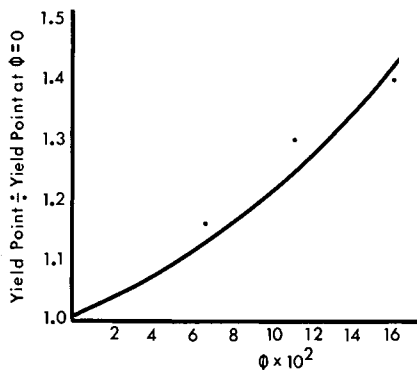


Fig. 4. Fractional increase in yield point with filler content at 50 in./min.

elongation decrease was greater.  $\text{TiO}_2$  acted as a reinforcing agent here with higher strengths resulting from greater filler content (Fig. 3). However, the rise in tensile strength with filler content was not nearly as great as the increase in Young's modulus. Offset yield points (initial change in slope of stress-strain curve) were determined for filled poly(vinyl acetate) and increased with filler content, following a similar increase in tensile strength. The fractional increase in offset yield points for filled poly(vinyl acetate) were higher with greater filler content (Fig. 4).

In order to compare the variation in tensile properties with filler content and strain rate, plots were made of the logarithm of tensile properties (tensile strength, Young's modulus, and ultimate elongation) versus the logarithm of strain rate. A typical relationship is shown in Figure 5 where the logarithm of tensile strength versus the logarithm of strain rate is given at different  $\text{TiO}_2$  levels. From this, tensile strength shift factors ( $A_\phi$ ) were defined for volume fraction filler in terms of strain rate.  $A_\phi$  values were also determined for elongation and Young's modulus. Reduced variable-type plots were then made of the logarithm of tensile properties versus the logarithm of  $1/(\text{strain rate})$  ( $A_\phi$ ) (Fig. 6). This allowed tensile strengths to be predicted up to eight times greater in strain

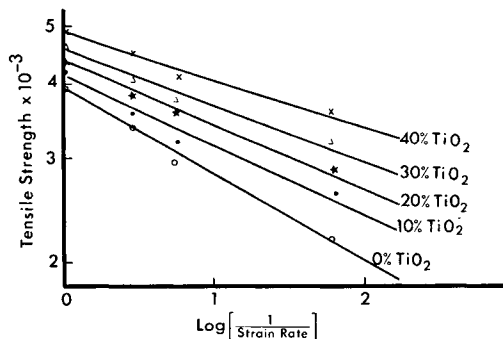


Fig. 5. Reduced variable plot of tensile strength.

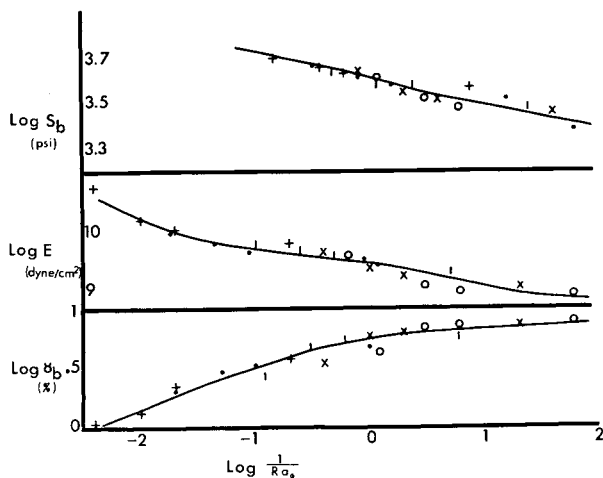


Fig. 6. Shift factor-strain rate plot of tensile properties: (O) no TiO<sub>2</sub>; (X) 10% TiO<sub>2</sub>; (I) 20% TiO<sub>2</sub>; (●) 30% TiO<sub>2</sub>; (+) 40% TiO<sub>2</sub>.

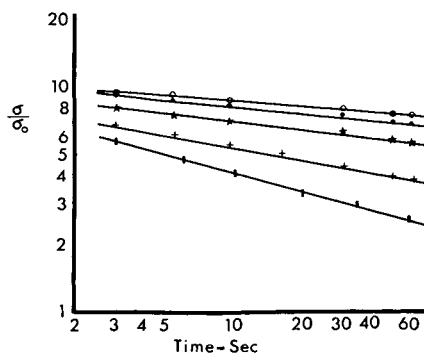


Fig. 7. Stress vs. time for various filler contents: (O) no TiO<sub>2</sub>; (●) 10% TiO<sub>2</sub>; (★) 20% TiO<sub>2</sub>; (+) 30% TiO<sub>2</sub>; (■) 40% TiO<sub>2</sub>. Strain rate = 100 %/min.; 1% extension.

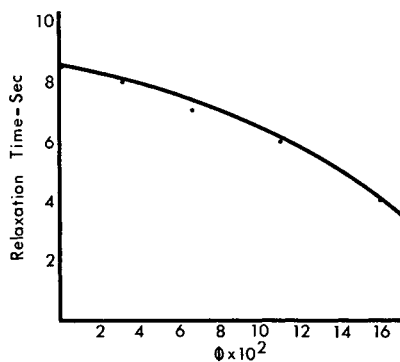


Fig. 8. Relaxation time vs. filler content; maxwell model; 1 in./min.; 1% extension.

rate than observed. Young's modulus and ultimate elongations were estimated up to 300 times higher in strain rate than found experimentally.

The rate of stress relaxation was found to increase with filler content as shown in Figure 7, where the logarithm of fractional decrease in stress is plotted against the logarithm of time. The 10 wt.-% TiO<sub>2</sub>-poly(vinyl acetate) was found to be closer in stress-relaxation rate to clear poly(vinyl acetate) than to the samples with a higher percentage of TiO<sub>2</sub>. This is also shown in a reduction in relaxation times (using a Maxwell model) with higher TiO<sub>2</sub> content (Fig. 8). Calculations of the out-of-phase modulus  $E''$  were made (Table II) as a function of filler content by employing a box type of distribution for stress relaxation:<sup>4, 5</sup>

$$E'' = -(\pi/2E_0 \log e^{10}) (d\sigma/d \log t)$$

TABLE II  
Stress-Relaxation Calculation of Out-of-Phase Modulus by  
Using Box-Type Distribution

TiO <sub>2</sub> %	$E''$ calculated. dynes/cm. <sup>2</sup>	$G''$ observed (torsional pendulum) dynes/cm. <sup>2</sup>
0	$7 \times 10^7$	$4.4 \times 10^7$
10	$8 \times 10^7$	$4.8 \times 10^7$
20	$2 \times 10^8$	$6 \times 10^7$
30	$4.8 \times 10^8$	$1.8 \times 10^8$
40	$6 \times 10^8$	$2.2 \times 10^8$

where  $\sigma$  is the stress,  $t$  is time, and  $E_0$  is extension.

In Table II, the  $E''$  calculated values are compared with  $G''$  (out-of-phase shear modulus) values obtained with a torsional pendulum apparatus.<sup>6</sup> The out-of-phase modulus,  $E''$ , increased with filler content, that of the 10 wt.-% TiO<sub>2</sub>-poly(vinyl acetate) again being very close in magnitude to that of clear poly(vinyl acetate). Thus, we see an increase in kinetic energy as a result of greater filler content.

A possible explanation for the stress-strain behavior observed with TiO<sub>2</sub>-poly(vinyl acetate) systems is that the introduction of TiO<sub>2</sub> changes the internal viscosity of the system, similar to the effect of temperature. This would mean that the ultimate tensile properties would be affected by filler content very much like strain-rate dependence because viscous resistance to chain deformation would be altered. Temperature may be very important here, since the experimental temperature of 24°C. represents a temperature within the second-order transition region for poly(vinyl acetate). Also, the filler would then act as a viscous drag on the polymer system, resulting in lower elongation. Increases in yield and tensile strength are indicative of filler-polymer reinforcement interaction.

The increase in kinetic energy for higher filler content as evidenced by greater rates of stress relaxation is indicative of more short-range chain motion as a result of filler presence, possibly due to movement involving

C—O bond rotation.<sup>1</sup> Increases in Young's modulus with higher filler content indicates that the polymer chains as a whole are stiffened. This long-range immobilization of polymer chains effectively increases potential energy for the system. By reducing the degrees of freedom for the polymer chains as a whole as a result of pigmentation, the close packing of polymer chains could enter into a more ordered state (decrease in total entropy). In this more ordered state of chain packing, side-chain groups or possibly chain ends may be more free to move on a short-range basis, resulting in increased kinetic energy for the system.

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### Résumé

Les propriétés de tension élongation d'acétate de polyvinyl chargé d'oxyde de titane ont été étudiées avec des pourcentages de charge de 0, 10, 20, 30, et 40% de TiO<sub>2</sub> sur un domaine de vitesse de tension de 100 à 5000% par minute à 24°C. La force de tension (module de Young) et les forces au rendement ont toutes été trouvées croissantes avec des vitesses de tension plus élevées et des teneurs en TiO<sub>2</sub> croissantes. Des élongations finales décroissaient avec une teneur croissante de TiO<sub>2</sub> et des vitesses de tension plus élevées. Les facteurs de glissement de la fraction de volume de la charge ont été estimés pour des propriétés de tension en fonction de la vitesse du test. Des études de tension-relaxation ont montrés une réduction des temps de relaxation avec une teneur croissante en TiO<sub>2</sub>. Les calculs du module de Young ont été faits en fonction de la teneur en charge en utilisant un type de distribution des temps de relaxation. Une explication possible du comportement tension-élongation observé consiste en ce que l'introduction de TiO<sub>2</sub> change la viscosité interne du système de façon semblable à l'effet de la température. Ceci signifierait également que les propriétés finales seraient dépendantes de la teneur en charge et de la vitesse de tension par suite de la résistance visqueuse à la déformation des chaînes. L'effet d'une charge sur la relaxation à la tension pourrait donc être dû à un accroissement de la mobilité d'une chaînes à petites distance.

### Zusammenfassung

Die Spannungs-Dehungeigenschaften von TiO<sub>2</sub>-gefülltem Polyvinylacetat wurden bei einem Füllstoffgehalt von 0, 10, 20, 30, und 40% TiO<sub>2</sub> in einem Verformungsgeschwindigkeitsbereich von 100–5000%/min bei 24°C. untersucht. Zugfestigkeit, Youngmodul und Elastizitätsgrenze nahmen mit höherer Verformungsgeschwindigkeit und höherem TiO<sub>2</sub>-Gehalt zu. Die Reissdehnung nahm mit höherem TiO<sub>2</sub>-Gehalt und höherer Verformungsgeschwindigkeit ab. Verschiebungsfaktoren für den Volumbruchteil un Füllstoff wurden für die Zugeigenschaften als Funktion de Test geschwindigkeit bestimmt. Spannungsrelaxationsuntersuchungen zeigten eine Herabsetzung der Relaxationszeit mit steigendem TiO<sub>2</sub>-Gehalt. Der Phasenverschiebungs-Youngmodul wurde als Funktion des Füllstoffgehalts mit einer Rechtecksverteilung der Relaxationszeiten berechnet. Eine mögliche Erklärung des beobachteten Spannungs-Dehnungsverhaltens liegt in der Annahme, dass die Einführung von TiO<sub>2</sub> die innere Viskosität des Systems ähnlich wie der

Temperatureinfluss verändert. Dies würde auch bedeuten, dass die Grenzeigenschaften von Füllstoffgehalt und Verformungsgeschwindigkeit abhängen, da der viskose Widerstand gegen Kettendeformation verändert ist. Der Einfluss des Füllstoffs auf die Spannungsrelaxation könnte auf eine Zunahme der Kettenbewegung in kleinen Bereichen zurückzuführen sein.

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