

Dynamic Mechanical Properties of Titanium Dioxide-Filled Poly(vinyl Acetate) at 0-40°C.

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Synopsis

The dynamic mechanical properties of titanium dioxide-filled poly(vinyl acetate) have been studied at filler concentrations of 0, 10, 20, 30, and 40 wt.-% TiO_2 by using a torsional pendulum. The damping factor was found to increase with higher temperatures. At 40°C., the damping factors for the different TiO_2 concentrations were estimated to be the same. Damping factors above 40°C. were difficult to obtain due to the rubbery nature of the TiO_2 -poly(vinyl acetate) systems. From 24 to 35°C., 10 wt.-% TiO_2 -poly(vinyl acetate) was closer in damping factor increase to unfilled poly(vinyl acetate) than to the higher TiO_2 content polymers. At all temperatures, damping factors decreased with higher TiO_2 concentration. As the temperature decreased to 0°C., damping factors for the filled systems approached a common value. Potential energy of filled systems as indicated by shear modulus values is increased by higher TiO_2 concentrations and lower temperature. Kinetic energy for the filled systems, as shown by the out-of-phase modulus, is actually increased by larger filler concentration and higher temperature. A model is proposed where introduction of TiO_2 filler acts to increase general long-range polymer chain stiffening and at the same time enables short-range chain mobility to rise, possibly through greater side-chain motion.

Introduction

An investigation was made in this work of the dynamic mechanical behavior of poly(vinyl acetate) at TiO_2 filler concentrations of 0-40 wt.-% (0-16 vol.-%) at 0-40°C. Poly(vinyl acetate) is glasslike at room temperature with reported glass transition temperatures in the range of 17-32°C.¹ 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 about 15°C.¹ Densities of filled poly(vinyl acetate) films have been found to be less than calculated densities assuming volume additivity.² In addition, thermal expansion coefficients for filled poly(vinyl acetate) (above the glass transition temperature) were reported to be lower for the filled polymer than for unfilled polymer. It has been suggested that the presence of filler particles may alter the packing of polymer segments. Another transition for poly(vinyl acetate) was reported at 3°C.³ The possibility of short-range movement of polymer chain ends was set forth.

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Experimental

A commercial poly(vinyl acetate) (AYAT, Union Carbide Corp.) with an intrinsic viscosity of 0.69 dl./g. in cyclohexanone (20°C.) was used. TiO₂ was incorporated into the polymer by two-roll melt mixing. The TiO₂ was Rutile 610 (duPont Corp.) with an average particle size of 0.2 μ. Test samples were made in molds from 2-butanone solutions followed by drying at 60°C. for 48 hr. Test samples were then allowed to stand in a desiccator at room temperature for 48 hr. Sample thickness ranged from 10 to 20 mil.

Dynamic mechanical measurements were made with a torsional pendulum (Plas-Tech. Corp.) employing a linear differential transformer coupled to a high speed recorder, (Sanborn #296). Damping factors⁴ were calculated from the rate of decrease in torsional oscillation:

$$\Delta = \ln (A_1/A_2)$$

where A_1 , A_2 are successive amplitudes of oscillation. Shear modulus (G') calculations were made according to

$$G' = 38.5I / KP^2D^3C$$

where I is the system moment of inertia, P is the period of oscillation, K is a geometric constant, L is the sample length, D is specimen thickness, and C is sample width.

Results and Discussion

The damping factor (fractional loss in energy upon distortion) was found to increase with higher temperatures for the filled polymers, very much like the unfilled polymer (Fig. 1). A reduction in damping factor was

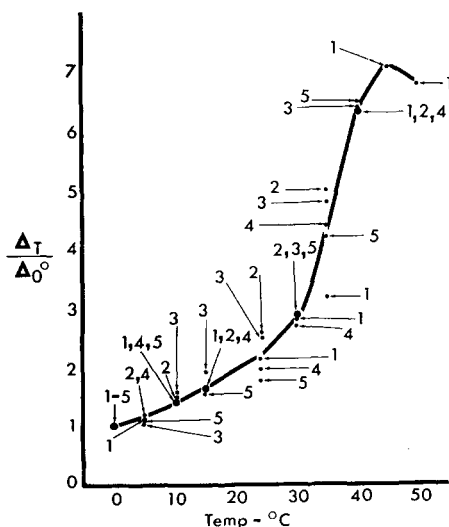


Fig. 1. Effect of temperature on damping factor change with filler content: (1) no TiO₂; (2) 10% TiO₂; (3) 20% TiO₂; (4) 30% TiO₂; (5) 40% TiO₂.

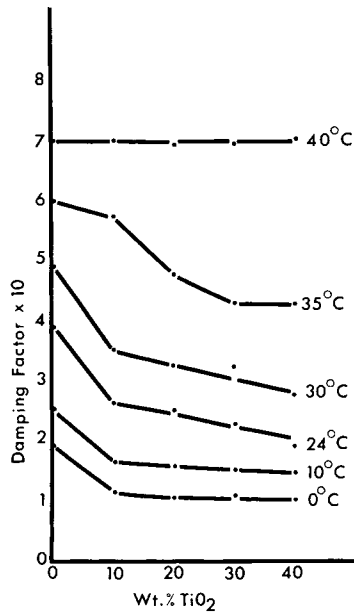


Fig. 2. Effect of filler on damping factor.

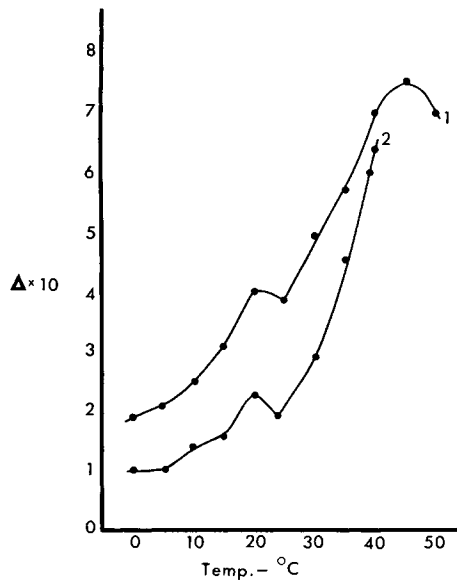


Fig. 3. Variation of damping factor with temperature: (1) no TiO₂; (2) 40% TiO₂.

found in TiO₂-filled poly(vinyl acetate) at 24°C., compared to unfilled polymer (Fig. 2). At 24°C., the largest drop in damping factor took place at 10 wt.-% filler content, with less of a decrease from 10 to 40 wt.-%. As the temperature was increased to 35°C., the 10% TiO₂-poly(vinyl

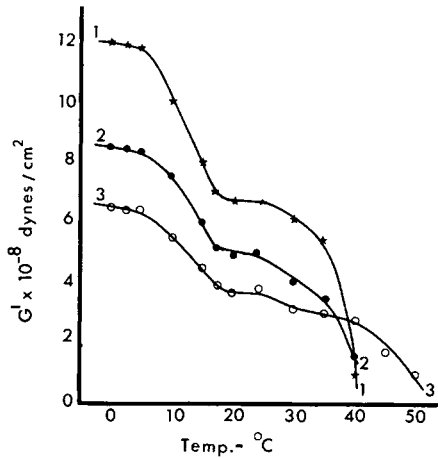


Fig. 4. Effect of temperature on shear modulus at various TiO₂ filler contents: (1) 20% TiO₂; (2) 10% TiO₂; (3) no TiO₂.

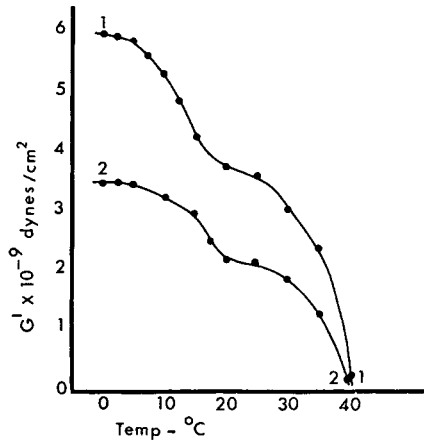


Fig. 5. Effect of temperature on shear modulus at various TiO₂ filler contents: (1) 40% TiO₂; (2) 30% TiO₂.

acetate) approached the unfilled poly(vinyl acetate) in damping factor value more rapidly than higher TiO₂ content samples. Damping factors for the different TiO₂ concentrations were estimated to be the same at 40°C. Above 40°C. the filled polymers became very rubbery, and data were difficult to obtain. With the unfilled polymer, the system was less rubbery above 40°C., and damping factors were obtained up to 50°C. with a definite peak existing at 45°C. (Fig. 3). When the temperature was decreased to 0°C., the damping factors were reduced, with the filled polymers approaching a common value. A small peak in damping factor was found in the region of 20°C., which is related to second-order transition effects.

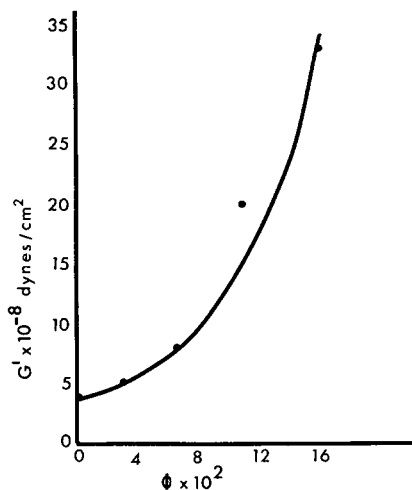


Fig. 6. Variation of shear modulus G' with filler content at 24°C.

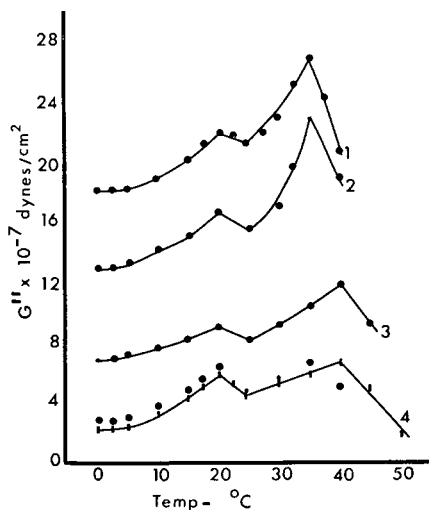


Fig. 7. Variation of out-of-phase modulus with temperature: (1) 40% TiO₂; (2) 30% TiO₂; (3) 20% TiO₂; (4) 10% (●) and 0% (◻) TiO₂.

The shear modulus G' is the in-phase modulus and represents the potential energy of the system as a whole per cycle. G' was found to drop with increasing temperature for the filled polymers as well as unfilled polymer (Figs. 4 and 5). The drop in G' was more regular as the TiO₂ content increased. A discontinuous region in the vicinity of 20°C. was seen for filled and unfilled polymers. This could be due to second-order transition effects. Also, a large drop in G' was found for the filled polymers above 35°C., which is due to first-order softening phenomena. The unfilled poly(vinyl acetate) showed no sharp drop in G' at 35°C., but G' decreased more

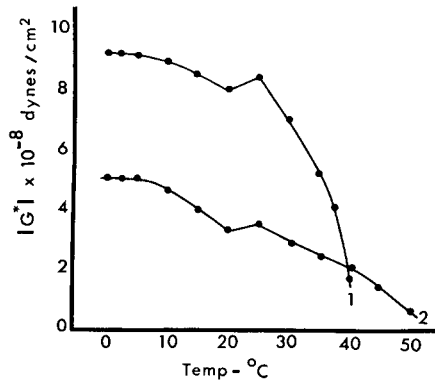


Fig. 8. Change in complex modulus $[G^*]$ with temperature: (1) 20% TiO_2 ; (2) no TiO_2 .

sharply above 40°C . This illustrates softening effects with temperature for filled and unfilled polymers. As the temperature was reduced, G' increased and in the region of 0 – 5°C , a plateau existed. This plateau may be due to transition effects like short-range chain-end motion.³ G' was found to increase exponentially with higher filler content (Fig. 6) at a given temperature.

The out-of-phase modulus G'' is related to the energy loss per cycle in the system and is the kinetic energy component of a system. G'' for clear poly(vinyl acetate) was found to have two peaks, one around 20°C , and another at 40°C . With the filled polymers, a peak existed in the region of 20°C , and around 35°C . The peaks observed around 20°C , again are due to second-order transition effects, while the second peak for unfilled poly(vinyl acetate) at about 40°C , for unfilled polymer and 35°C , for filled polymer are related to first-order softening effects (Fig. 7). G'' tended to level off as the temperature was reduced to 0°C . At a given temperature, G'' was found to increase with higher filler content. The 10 wt.-% TiO_2 -filled polymer had a G'' value which was very close to that of the unfilled resin.

The complex modulus G^* is a composite of G' and G'' and is really the sum of real and imaginary moduli:

$$G^* = G' + iG''$$

When the temperature was increased G^* decreased very much like G' with temperature for both filled and unfilled polymer. This is shown in Figure 8 for unfilled and 20 wt.-% TiO_2 -poly(vinyl acetate). A change in slope was found around 20°C . For the filled polymers a large reduction in G^* took place in the region of 40°C .

Conclusions

The TiO_2 filler acts to reduce the overall capacity of poly(vinyl acetate) to dissipate energy upon distortion (lower damping factor). At the

same time overall chain stiffening takes place with a very large increase in system in-phase modulus (shear modulus). Since both the out-of-phase modulus G'' and in-phase modulus G' increased with greater filler content with a resultant decrease in damping factor, G' must increase at a greater rate than G'' here.

The dynamic mechanical behavior of the 10 wt.-% TiO_2 system was closer to that of unfilled poly(vinyl acetate) than to that of higher TiO_2 content polymers. This is shown in the mechanical behavior of 10 wt.-% TiO_2 -poly(vinyl acetate) with temperature as well as the magnitude of G'' at a given temperature.

The complex modulus G^* varied with temperature in a similar manner as G' for a given filler content, because G' makes a much greater contribution to the complex modulus, since G'' is smaller than G' .

As the temperature was reduced to 0°C ., the filled samples were similar in dynamic mechanical behavior. G' and G'' for the different levels of TiO_2 approached common values as the temperature was lowered to 0°C . By lowering the thermal motion of the polymer chains (lower temperature), the effect of increasing filler content on dynamic mechanical properties was reduced.

The plateau from 0 to 5°C . for G' may also be due to secondary effects associated with the second-order transition.

Proposed Model

A model is proposed where the introduction of TiO_2 filler acts to increase general long-range polymer chain stiffening. This is shown by the increase in shear modulus with greater filler content. Consequently, the potential energy of the system is greatly increased by higher filler content. At the same time G'' increased with greater TiO_2 content, thereby, indicating a rise in short-range chain mobility. This short-range mobility may be due to greater side-chain motion with more rotation of the acetate group about the oxygen atom. This type of rotation has been proposed for unfilled poly(vinyl acetate).³ The 10 wt.-% TiO_2 -filled polymer appears to differ very little in short-range chain mobility compared to unfilled poly(vinyl acetate).

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Résumé

Les propriétés dynamiques mécaniques d'acétate de polyvinyle chargé de dioxyde de titane ont été étudiées à des concentrations de charges variant de 0, 10, 20, 30, et 40% en

pois de TiO_2 utilisant le pendule de torsion. Le facteur d'amortissement s'accroît avec des températures croissantes; à 40°C le facteur d'amortissement pour diverses concentrations de TiO_2 ont été estimées égales. Les facteurs d'amortissement au delà de 40°C , sont difficiles à obtenir par suite de la nature caoutchouteuse des systèmes d'acétate de polyvinyle TiO_2 . De 24 à 35°C , le facteur d'amortissement d'un acétate de polyvinyle contenant 10% de TiO_2 est plus voisin de l'acétate de polyvinyle non chargé que des polymères contenant une plus grande quantité de TiO_2 . A toutes les températures, les facteurs d'amortissement décroissent avec une concentration plus élevée en TiO_2 . Lorsque la température décroît à 0°C , les facteurs d'amortissement pour les systèmes chargés se rapprochent d'une valeur commune. L'énergie potentielle des systèmes chargés telle qu'obtenue au départ des modules de tension est accrue par des concentrations plus élevées en TiO_2 et par des températures plus basses. L'énergie cinétique pour des systèmes chargés, telle qu'on peut obtenir au départ du module, est actuellement accrue par des concentrations en charges plus importantes et par des températures plus élevées. Un modèle a été proposé suivant lequel l'introduction de charges de TiO_2 provoque une augmentation de la structure rigide des chaînes polymériques et en même temps rend la mobilité des chaînes plus grande, probablement par suite d'une mobilité plus élevée des chaînes latérales.

Zusammenfassung

Die dynamisch-mechanischen Eigenschaften von Titandioxyd-gefülltem Polyvinylacetat bei Füllstoffkonzentrationen von 0, 10, 20, 30, und 40 Gewichts% TiO_2 warden mit einem Torsionspendel untersucht. Der Dämpfungsfaktor stieg mit höheren Temperaturen an. Bei 40°C war der Dämpfungsfaktor für die verschiedenen TiO_2 -Konzentrationen gleich. Oberhalb 40°C konnten Dämpfungsfaktoren wegen der kautschukartigen Beschaffenheit des TiO_2 -Polyvinylacetatsystems nur schwierig erhalten werden. Von 24°C bis 35°C war das System 10 Gewichts% TiO_2 -Polyvinylacetat in bezug auf die Zunahme des Dämpfungsfaktors dem ungefüllten Polyvinylacetat ähnlicher als den Polymeren mit höherem TiO_2 -Gehalt. Bei allen Temperaturen nahmen die Dämpfungsfaktoren mit höherer TiO_2 -Konzentration ab. Bei Temperaturabnahme auf 0°C näherten sich die Dämpfungsfaktoren für die gefüllten Systeme einem gemeinsamen Wert. Wie die Schubmodulwerte zeigen, wird die potentielle Energie gefüllter Systeme durch höhere TiO_2 -Konzentrationen und niedrige Temperatur erhöht. Die kinetische Energie der gefüllten Systeme wird, wie der Phasenverschiebungsmodul zeigt, durch grössere Füllstoffkonzentration und höhere Temperatur tatsächlich erhöht. Ein Modell wird vorgeschlagen, bei welchem die Einführung von TiO_2 -Füllstoff eine Erhöhung der allgemeinen weitreichenden Polymerkettenversteifung bewirkt und gleichzeitig einen Anstieg der Kettenbeweglichkeit in kurzen Bereichen gestattet, möglicherweise durch starke Bewegung der Seitenketten.

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