

Polymer-Filler Interaction: Vapor Sorption Studies

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Synopsis

The effect of pigments on the vapor sorption characteristics of a noncrosslinked polymer [poly(vinylacetate)] and a highly crosslinked polymer (epoxy type) were investigated. The fillers used in this study were a polar surface (titanium dioxide) and a nonpolar surface (copper phthalocyanine blue). With both polar and nonpolar fillers, a marked decrease in the sorption of organic vapors was noted at low relative pressures, even with very low filler content. At high vapor pressures, the sorption isotherm of the filled polymer approaches that of the unfilled polymer. It was also noted that the shape of the sorption isotherm of the filled polymer closely resembles that of the pure polymer below its glass transition temperature. The experimental results are discussed in terms of the partial immobilization of the polymer segments in the presence of fillers, as a result of the reduced number of possible configurations of the polymer chains.

I. INTRODUCTION

The effect of filler incorporation on the physical and mechanical properties of polymers has been the subject of many investigations. For example, the incorporation of glass beads into polyisobutylene and polyurethane leads to increases in the glass transition temperatures (T_g) of the polymers.¹ The storage and loss modulus, the small deformation and ultimate tensile properties of these filled polymers can be represented by master curves along with a WLF-type equation which is a near-universal function of the glass temperature.¹ The increase in T_g appears to be dependent on the volume fraction of the filler in the system and is probably due to the immobilization by adsorption of the polymer segments close to the surface of the filler particles. Additional examples of increases in T_g have been reported for polystyrene and poly(methyl methacrylate) filled with glass powder.² The observed changes in T_g of poly(vinyl chloride-acetate) copolymer upon incorporation of titanium dioxide were also reflected in the changes in the temperature coefficients of gas diffusion through the polymer at T_g .³ On the other hand, gum rubber,⁴ polyisobutylene,⁵ acrylonitrile rubber,⁵ and *cis*-polybutadiene⁵ filled with carbon black do not exhibit changes in glass transition temperatures.

Several questions remain unanswered. (1) Is the immobilization effect present in filled polymer systems where increases in T_g are not observed? How can the effect be demonstrated? (2) Is there any method one can use to estimate the degree of immobilization?

In this laboratory, we have attempted to study solid-polymer interaction by the vapor sorption method. Poly(vinyl acetate), Epon-amine polymer (crosslinked) filled with titanium dioxide, and copper phthalocyanine were studied. To minimize the complication of higher order particle-particle interaction, low filler contents (volume fraction 1-10%) were used. For each system, the T_g of the filled polymer is within 2°C. of that of the corresponding unfilled polymer; the difference is probably within the range of experimental uncertainty. Nevertheless, differences in the vapor sorption isotherms of filled and unfilled polymers were observed.

II. EXPERIMENTAL

Materials

Poly(vinyl acetate) (AYAT from Union Carbide and Carbon Corporation) was dissolved in toluene. Dispersion of titanium dioxide (Rutile 610, Dupont, average size 0.2μ) or copper phthalocyanine (Interchemical Corporation, average size 0.05μ) in poly(vinyl acetate) solution was prepared by the use of a three-roller mill. Films were drawn on tin foil, allowed to stand in a desiccator overnight, and then dried at 60°C. for two days. 4,4'-Bisglycidylphenyl 2,2'-propane (Shell Chemical Company) and 1,6-hexanediamine (Matheson Coleman and Bell Company) were mixed in stoichiometric proportions to prepare the crosslinked epoxy films. The detailed procedure was described elsewhere.⁶ In the preparation of filled epoxy films, the filler was dispersed in a solution of 4,4'-bisglycidylphenyl 2,2'-propane. Reagent grade solvents were used in film preparation and vapor sorption experiments without further purification.

Glass Transition Temperatures

The glass transition temperatures of the two polymers were determined by a dilatometric method.

Vapor Sorption Experiments

The vapor sorption of the polymer film was measured by means of a quartz helix microbalance described by Prager and Long.⁷ The final pressure and the amount of vapor sorption by the sample were recorded when the weight gain was less than 0.005 mg. (for a polymer sample of 50-100 mg.) overnight.

III. RESULTS AND DISCUSSION

The glass transition temperatures of poly(vinyl acetate) and the epoxy polymer were determined to be 22 and 54°C. respectively. Within the range of pigment volume concentration used in the present study (1-12%), no change in the T_g of the polymer was observed.

Typical sorption isotherms for acetone in poly(vinyl acetate) are shown in Figure 1. At temperatures above the T_g of PVAc, the isotherms appear

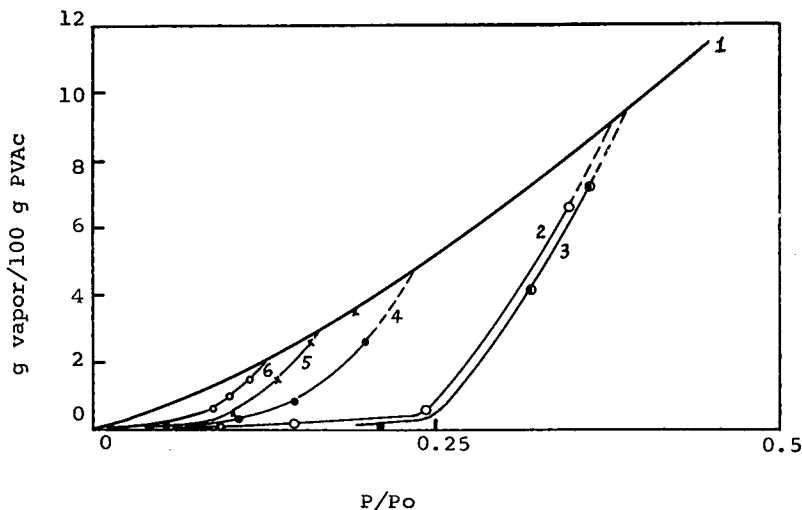


Fig. 1. Sorption of acetone by poly(vinyl acetate): (1) unfilled, 40°C.; (2) unfilled, 20°C.; (3) filled, 12.1% TiO₂, 20°C.; (4) filled, 12.1% TiO₂, 30°C.; (5) filled, 12.1% TiO₂, 40°C.; (6) filled, 12.1% TiO₂, 50°C.

to obey the solution theory of Flory and Huggins.⁸ The temperature coefficient of equilibrium sorption is slightly negative.⁸ In the glassy state, at 20°C., poly(vinyl acetate) sorbs practically no acetone at low vapor pressures; in addition, desorption hysteresis is noticed. It is possible that within the time scale of our experiments, the system is not at its equilibrium state at low vapor pressures. Sorption of acetone by PVAc at 20°C. becomes noticeable at $P/P_0 = 0.20$ and increases sharply thereafter. The acetone-PVAc isotherm at 20°C. bears great resemblance to that of chloroethane sorption by poly(vinyl chloride) glass and to that of ethylbenzene sorption by low molecular weight polystyrene compact glass, as reported by Kargin.⁹ According to Kargin, the sharp rise in vapor sorption by a glassy polymer occurs when the concentration of the sorbed vapor in the polymer is sufficient to "melt" or "plasticize" the glass.

The sorption isotherms of acetone by TiO₂-filled PVAc at 30, 40, and 50°C. (Fig. 1) resemble the isotherm for acetone sorption by the unfilled polymer below its T_g . While the amount of acetone sorbed by the unfilled polymer was reported⁸ to decrease very slightly with increasing temperature, the sorption by the filled polymer shows a positive temperature coefficient at low vapor pressures. The difference in the temperature dependence of acetone sorption may be construed as evidence suggesting different mechanisms of sorption. The isotherms for the filled and the unfilled PVAc tend to become identical above P/P_0 of 0.23, 0.17, and 0.12 at 30, 40, and 50°C., respectively.

The isotherm for acetone sorption by TiO₂-filled PVAc at 20°C. does not differ greatly from the corresponding isotherm for the unfilled polymer.

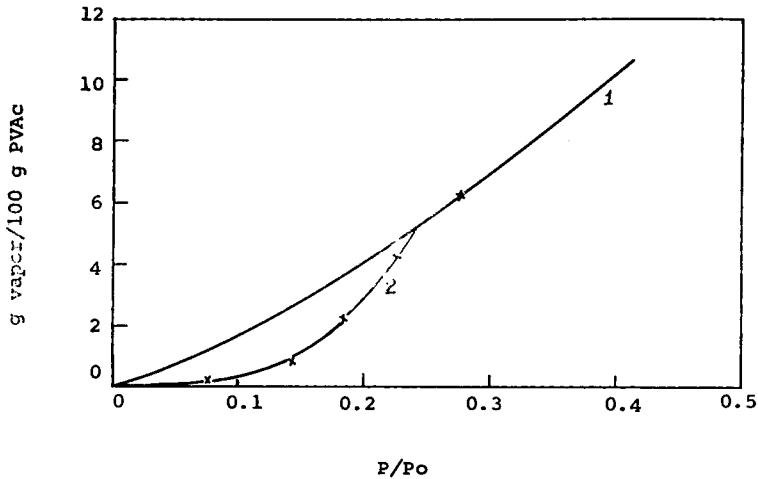


Fig. 2. Sorption of acetone by poly(vinyl acetate): (1) unfilled, 30°C.; (2) filled, 19.5% copper phthalocyanine, 30°C.

Figure 2 shows the sorption of acetone by PVAc filled with 19.5% by volume of copper phthalocyanine. The general characteristics of the isotherm are similar to those found in the sorption by the TiO_2 -filled polymer.

The sorption isotherms of chloroform by the unfilled and the filled epoxy polymers are shown in Figures 3 and 4. The isotherm at 50°C., below the T_g of the polymer, again shows desorption hysteresis in the low vapor pressure region. The reduction in sorption is noticeable at low vapor pressures even when the volume fraction of the filler is as low as 1%. In addition, the decrease in vapor sorption at low vapor pressures is proportional to the amount of the filler incorporated.

The application of Bueche's theory¹⁰ of filler reinforcement to our experimental data results in the untenable conclusion that there are 100 times more polymer segments attached to the filler than can possibly be accommodated on the filler surface. It may be postulated that the reduction in the number of possible configurations of the polymer chains upon absorption onto the filler surface imparts effectively glasslike properties to the polymer, although the filled polymer may have the same dilatometric T_g as the unfilled polymer. It is conceivable that the theory of rubber elasticity may be inapplicable, under the experimental conditions, to the polymer-vapor mixture which is in the glassylike, nonequilibrium state at low vapor pressures. The vapor pressure at which the concentrations of acetone sorbed by the filled and the unfilled polymer become identical may have similar significance as the critical volume concentration¹¹ in a polymer-diluent system at which the diffusion of the diluent becomes Fickian.

For the filled polymer to exhibit glasslike properties, the influence exerted by the filler particles probably is not limited to the immediate vicinity of the particle surface. The mechanism by which the adsorption of poly-

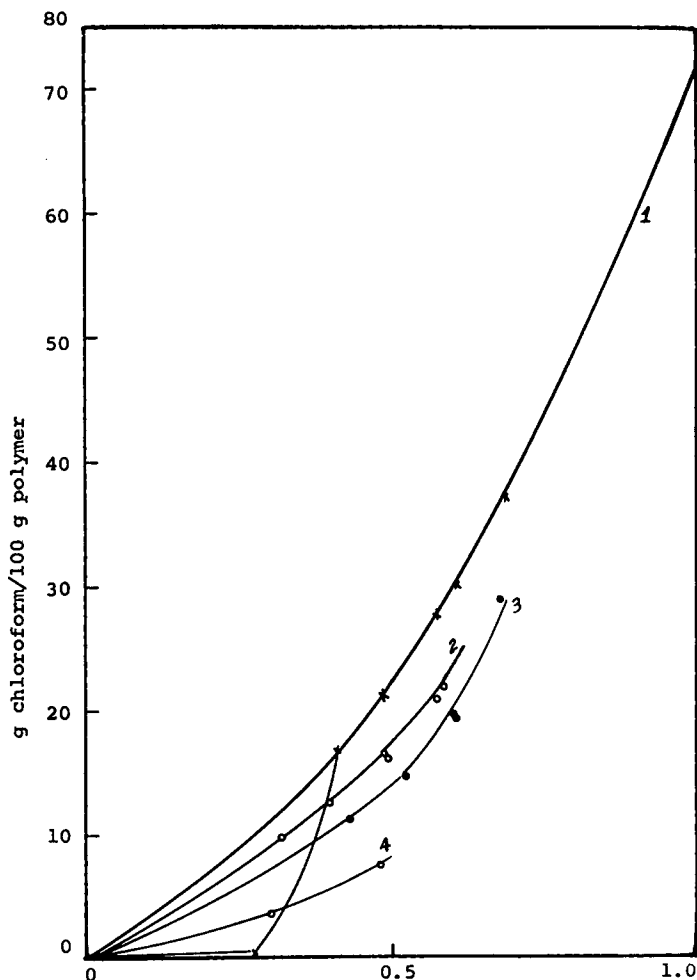


Fig. 3. Sorption of chloroform by epoxy polymer: (1) unfilled, 60°C.; (2) filled, 1.06% TiO₂, 60°C.; (3) filled, 2.37% TiO₂, 60°C.; (4) filled, 4.41% TiO₂, 60°C.; (5) unfilled 50°C.

mer molecules on the filler surface reduces the number of possible configurations of the polymer molecules in a substantial portion of the polymer sample is admittedly not clear. It may be likened to a mechanical chain with two ends anchored on two filler particles, each polymer coil being depicted as a link in the chain. The mobility of such a mechanical chain is greatly reduced. It should also be mentioned that recent viscosity studies of dilute polymer solutions by Öhrn,¹² Takeda,¹³ Hugue,¹⁴ and Tuijnam and Hermans¹⁵ led to the interpretation that the adsorbed polymer layer on glass capillary had an "apparent" thickness of the order of 1000 Å. Stromberg and co-workers¹⁶ obtained the thickness of adsorbed polystyrene on chrome plate by ellipsometry to be about 200 Å. While the

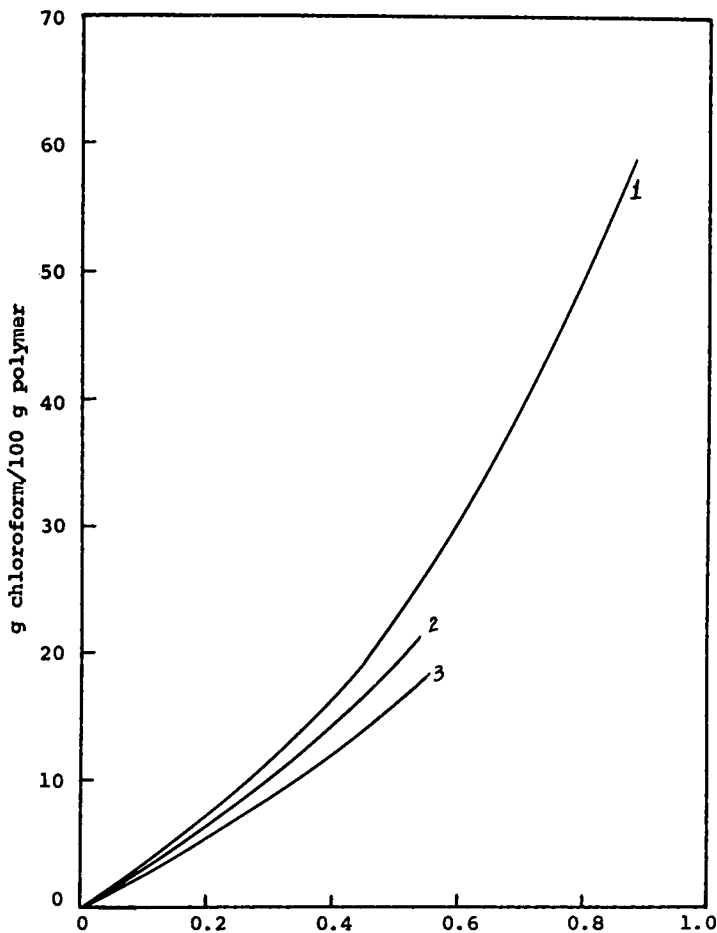


Fig. 4. Sorption of chloroform by epoxy polymer: (1) unfilled, 60°C.; (2) filled, 1.26% copper phthalocyanine, 60°C.; (3) filled, 3.43% copper phthalocyanine, 60°C.

physical significance of the thickness of the adsorbed polymer layer on solid surfaces is still clouded, it seems reasonable to conclude that the polymer molecules at a distance up to $\sim 10^3$ A. from a solid surface may possess properties different from the unfilled polymer. It is our postulate that these polymer molecules near the solid surface have sorptive properties analogous to those of glassy polymers. An increase in the number of permissible configurations of the polymer chains appears to occur when a critical concentration of the sorbed vapor in the filled polymer is reached. The plasticization of the filled polymer by the solvent vapor and the weakening of the polymer-filler interaction due to possible competitive adsorption of the solvent molecules on the filler surface may both be operative in bringing about the increase in the number of possible configurations of polymer molecules near the filler surfaces.

If the sorptive properties of polymer molecules near filler surface may be regarded as analogous to those of glassy polymers, the following method is proposed to estimate the extent of immobilization of polymer molecules in a filler-polymer mixture. Let A_0 be the amount of vapor sorbed by the unfilled polymer above its T_g at a given vapor pressure P , A_g be the amount of vapor sorbed by the unfilled polymer below its T_g at P , and A be the amount sorbed by the filler polymer at P . The three quantities are related by equation:¹

$$A = (1 - f)A_0 + fA_g \quad (1)$$

where f is the fraction of the polymer in a filled sample that possessed glasslike sorptive properties. At low vapor pressures, A_g is negligible compared to A_0 ; one may write:

$$A \cong (1 - f)A_0 \cong (1 - \alpha x)A_0 \quad (2)$$

where x is the weight of the filler particle per unit weight of the polymer in the filler sample and α is the weight of the "glasslike" polymer induced by a unit weight of the filler. A plot of A/A_0 versus x will yield a straight line with a slope of $-\alpha$. The sorption results of chloroform in TiO₂-filled epoxy polymer agrees with eq. (2) well for data obtained at P/P_0 less than 0.3. The value of α is about 4.1. The α value for copper phthalocyanine filled epoxy polymer is about 5. The thickness t of the glasslike layer of epoxy polymer near the filler surface may be estimated from α , the density, and the particle size of the filler. The values of t are 1500 and 500 Å for TiO₂ and copper phthalocyanine, respectively. The magnitude of t is of the order of the diameter of the filler particle.

In principle, α may be used as a measure of the immobilization effect caused by the filler particles. It is premature at present, however, to assess the general validity of our postulate and the relation of α to the physical constants of the filler and the polymer. A study of the effect of surface area and surface forces of the filler is in progress.

References

1. Landel, R. F., and T. L. Smith, *Am. Rocket Soc. J.*, **31**, 599 (1961); *Rubber Chem. Technol.*, **35**, 291 (1962).
2. Lipatov, Yu. S., *Dokl. Akad. Nauk SSSR*, **143**, 1142 (1962).
3. Kumins, C. A., and J. Roteman, *J. Polymer Sci.*, **A1**, 527 (1963).
4. Mason, P., *J. Appl. Polymer Sci.*, **4**, 212 (1960).
5. Baccaredda, M., and E. Butta, *J. Polymer Sci.*, **57**, 617 (1962).
6. Kwei, T. K., *J. Polymer Sci.*, in press.
7. Prager, S., and F. A. Long, *J. Am. Chem. Soc.*, **73**, 407 (1951).
8. Kokes, R. J., A. R. DiPietro, and F. A. Long, *J. Am. Chem. Soc.*, **75**, 6319 (1953).
9. Kargin, V. A., *J. Polymer Sci.*, **23**, 47 (1957).
10. Bueche, A. M., *J. Polymer Sci.*, **25**, 139 (1957).
11. Kokes, R. J., F. A. Long, and J. L. Hoard, *J. Chem. Phys.*, **20**, 1711 (1952).
12. Öhrn, O. E., *J. Polymer Sci.*, **17**, 137 (1955).
13. Takeda, M., and R. Endo, *J. Phys. Chem.*, **60**, 1202 (1956).
14. Hugue, M. M., M. Fishman, and D. A. I. Goring, *J. Phys. Chem.*, **63**, 766 (1959).

15. Tuijnam, C. A. F., and J. J. Hermans, *J. Polymer Sci.* **25**, 385 (1957).
16. Stromberg, R. R., E. Passaglia, and D. J. Tutas, paper presented at 144th National American Chemical Society Meeting, Los Angeles, April 1963.

Résumé

On a étudié l'effet des pigments sur les caractéristiques de sorption de vapeur d'un polymère non-réticulé (acétate de polyvinyle) et d'un polymère fortement réticulé (type époxy). Les charges utilisées dans cette étude sont une surface polaire (dioxyde de titane) et une surface non polaire (bleu de cuivre phthalocyanine). Avec les charges polaires et non polaires, on note une diminution marquée dans la sorption des vapeurs organiques à pression relativement faible, même avec de très faibles teneurs en charges. À pressions de vapeur élevées, l'isotherme de sorption des polymères chargés tend vers celle d'un polymère non chargé. On note aussi que la forme de l'isotherme de sorption du polymère chargé ressemble fortement à celui du polymère pur en-dessous de sa température de transition vitreuse. On discute les résultats expérimentaux sur la base d'une immobilisation partielle des segments de polymère en présence de charges, comme résultant du nombre réduit de configurations possibles des chaînes de polymère.

Zusammenfassung

Der Einfluss von Pigmenten auf die Dampfsorptionscharakteristika eines nicht vernetzten Polymeren (Polyvinylacetat) und eines hoch vernetzten Polymeren (Epoxytyp) wurde untersucht. Die bei dieser Untersuchung benützten Füllstoffe besaßen eine polare (Titandioxyd) und eine nicht polare (Kupferphthalocyaninblau) Oberfläche. Sowohl mit dem polaren als auch mit dem nicht polaren Füllstoff wurde bei niedrigem relativen Druck, sogar bei sehr geringem Füllstoffgehalt, eine deutliche Abnahme der Sorption von organischen Dämpfen festgestellt. Bei hohen Dampfdrücken näherte sich die Sorptionsisotherme des gefüllten Polymeren derjenigen des ungefüllten. Ausserdem wurde festgestellt, dass die Gestalt der Sorptionsisotherme des gefüllten Polymeren der des reinen Polymeren unter halb seiner Glasumwandlungstemperatur äusserst ähnlich ist. Die Versuchsergebnisse werden im Hinblick auf die teilweise Immobilisierung der Polymersegmente in Anwesenheit von Füllstoffen als ein Ergebnis der geringeren Zahl von möglichen Konfigurationen der Polymerkette diskutiert.

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