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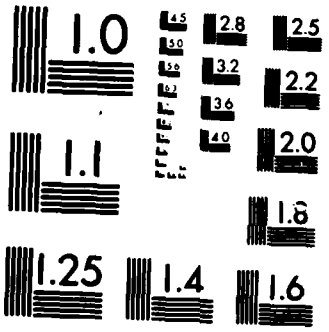

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This research was concerned with determination of the effects of static tensile and cyclic tensile (fatigue) mechanical deformations on the sorption, diffusion, and permeation of selected gases, vapors, and liquids in representative elastomers, glassy polymers, and semicrystalline polymers. The project also considered apparent effects of the sorbed and diffusing penetrant on polymer structure in so far as those effects lead to concurrent changes in sorption and transport behavior.

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ARO 19240.2-MS

The Effects of Mechanical Deformation on Sorption and Diffusion in Polymers

FINAL REPORT

24 February 1986

U.S. Army Research Office
DAAG29-82-K-0172
(Proposal # 19240-MS)

Case Western Reserve University
Cleveland, Ohio 44106

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FINAL REPORT

A. Statement of the Problem Studied

This research project was concerned with determination of the effects of static tensile and cyclic tensile (fatigue) mechanical deformations on the sorption, diffusion, and permeation of selected gases, vapors, and liquids in representative elastomers, glassy polymers, and semicrystalline polymers. The project also considered apparent effects of the sorbed and diffusing penetrant on polymer structure in so far as those effects lead to concurrent changes in sorption and transport behavior.

The polymers chosen for this study were: blends of different modulus silicone rubber (kindly provided by the General Electric Company), synthetic natural rubber (Natsyn, Goodyear Rubber Company), biaxially oriented polystyrene (Trycite, Dow Chemical Company), bisphenol-A-polycarbonate (Lexan, General Electric Company), polyethylene (densities of 0.92 and 0.96 g/cc, DuPont Company), polypropylene (Hercules), and polybutene-1 (Northern Petrochemical Co.). The penetrant gases, vapors, or liquids were: helium, nitrogen, argon, carbon dioxide, methanol, acetone, benzene, and dichloropentane. Not all penetrants were used with all polymer samples; the penetrant was selected for each experiment on the basis of the information desired.

The observed effects of deformation are interpreted in terms of the magnitude and distribution of defects introduced by irreversible deformations, changes in free volume, changes in morphology (crystalline domain modification, chain orientation, etc.) due to deformation and subsequent relaxations. The effects of sorbed and diffusing penetrant on polymer structure and properties are considered in terms of site or hole (defects, excess free volume) filling (dual-mode sorption, quasiporous flow) concurrent with localized diffusion/relaxation swelling. Temporal changes of sorption and transport behavior in either deformed or undeformed samples are considered in terms of relaxation-controlled structural changes (including a redistribution of free volume) which may be enhanced by a swelling, plasticizing action of the sorbed penetrant.

B. Summary of the Most Important Results

1. The study of methanol sorption and transport in silicone rubber blends showed that the permeability ($\underline{P}$) and diffusion (D) coefficients decrease with increasing strain. The solubility coefficient (S) increases with increasing strain. An increase in filler (fumed silica) loading gave an increase in stiffness and modulus such that: a) S increased faster with strain increase as the loading level decreased, b) D decreased faster with strain increase as the loading decreased, and c) $\underline{P}$ decreased faster with strain increase as the loading decreased.

These results are attributed to a decrease in the network chain segmental mobilities. An "entropy correlation theory" was applied to the diffusion data which indicated diffusion was occurring through strain induced cavities in addition to the diffusion through the rubber matrix. This hypothesis is substantiated by the departure of the system from a linear free energy relationship (the enthalpy of activation is not linearily related to the entropy of activation) thereby indicating that the overall mechanism of transport is changing as strain deformation increases.

In the case of the increase in solubility with strain, an increase was predicted based on the solution thermodynamic theory of Flory-Huggins as modified by Treloar and others to account for the effect of imposed strain on solubility. However, the theory, which has been successfully applied to several different rubber-solvent systems, markedly underestimates the sorption mangitudes found in this study for methanol in filled silicone rubber blends. The additional sorption is attributed to methanol adsorbed onto filler surfaces and clustered in voids caused by the imposed strain.

It is proposed that the strain induced cavities or voids are primarily due to dewetting of the filler by the matrix. There is a pronouced "stress-whiting" upon straining the samples past a certain strain range. This effect is apparently nearly completely reversible upon decreasing the strain since there is little, if any, change in mass transport or other properties of the sample in the no-strain state after straining.

The dependence of mass transport on filler loading level is attributed to the increased cavitational flow for the higher filled blends which act to increase the overall diffusivity and permeability. The increase in solubility as loading level decreases is tentatively attributed to immobilization of methanol clustered in the strain -induced voids. These clusters are active in the transport process but cannot be detected by the methods used up until recently. Methanol, a nonsolvent for silicone rubber, would be expected to undergo this type of partial phase separation upon sorption (entropic vs enthalpic effects). The nature of this mode-of-sorption effect could be studied using other techniques.

2. The study of benzene sorption and transport in synthetic natural rubber (Natsyn) showed that D decreased by 20% up to a deformation of 50% and then remained essentially constant up to a deformation of 200%. S decreased by nearly 40% up to the deformation of 50% after which it increased with increasing strain until, at 200% elongation, it was only 10% below the value of S for the undeformed sample. The value of $\bar{P}$ likewise decreased nearly 50% up to the deformation of 50% after which it increased until, at 200%

elongation it was 35% below the value for the undeformed sample.

The determined swelling of the sample followed the general dependence on strain observed for the solubility. Again, the effect of strain on S and swelling did not follow the thermodynamic prediction (Flory-Huggins, Treloar) at strains below 50%. Above that strain, the rate of change of S and swelling did agree fairly well with the thermodynamic prediction.

The overall results are interpreted in terms of an initial decrease in segmental motion due to constraints imposed during an isofree volume deformation (a theoretical description of this effect is being developed in cooperation with Professor D. Perchak). Above a certain deformation (here about 50%), the increase in S and swelling with increasing elongation provides for enough enhanced segmental mobility so that there is little further change in D, but there is an increase in $\underline{P}$ since $\underline{P}$ = DS.

3. The results of these studies on two different elastomers suggest that the a priori prediction that elongation should have little, if any, effect on transport since there is no change in free volume (Poisson Ratio $\sim$ one half) must be viewed with caution. It appears that there are other factors and/or Poisson's ratio is a function of elongation. A semiempirical relationship has been developed and, as mentioned, a more rigorous theoretical basis is being developed to represent this behavior.

4. The transport properties of dichloropentane (DCP) have been determined for silicone rubber. Its value of D is about two orders of magnitude lower than that of methanol, S is two orders of magnitude higher than that of methanol, so that the value of $\underline{P}$ is about the same as that of methanol. This is of significance for the selection of simulants to represent sorption and transport behavior of DCP and other simulants in other polymers is continuing (investigators are CWRU undergraduates working on a research project as a curriculum degree requirement).

5. A relationship between free volume and elongation has been modified to account for the formation of non-thermodynamic volume (voids, defects, etc.) and an elongation dependence of the material's Poisson Ratio. This approach is to be further revised by consideration of craze initiation fracture mechanics to describe precursor damage leading to crazing.

A method for estimation of the Poisson Ratio, ν, for a wide range of polymeric materials can be made using the expression:

$$\ell n(B/p) = 8.3 - 4\nu$$

where B is the bulk modulus and p is the density. It has been shown (D. W. van Krevelen, Properties of Polymers, 2nd Ed., Elsevier Sci. Publ. Co., 1976, Chap. 13) that $B/p = (U/V)^6$ where U is the Rao Function (related to molar sound velocity) and V is molar volume. Both U and V can be calculated by the method of group contributions.

6. Studies of the effects of mechanical fatigue on gas and vapor permeation in elastomers indicates that accumulated damage within the material strongly affects the transport of gases, such as helium and carbon dioxide, with lesser effects on vapors such as methanol. For example, for a silicone rubber sample cycled fifty times as a stress of 38 psi, $\underline{P}(CO_2)$ increased by a factor of 1.5 while $\underline{P}$(methanol) decreased by a factor of 0.9. The decrease in D(methanol)(factor of 0.66) overcame the increase in S (factor of 1.4) to determine the relative change in $\underline{P}$.

Fatigue of glassy polymers under much lower cyclic strain magnitudes gave generally comparable trends, but with considerable experimental scatter under the conditions used. A revised procedure has been developed which is giving much better reproducibility (undergraduate investigators). The dependence of detection of fatigue damage on the size distribution of damage and its temporal evolution may be obtained by permeation studies to elucidate crazing and other fatigue damage mechanisms.

7. The decrease in carbon dioxide $\underline{P}$ over time periods long as compared to the time of $\underline{P}$ value measurement in glassy polymers (Lexan, Trycite, cellulose acetate) has now been shown to be of lesser magnitude than previously reported. An instrumental difficulty magnified the effect. Correction of the experimental procedure has confirmed that slow relaxation of the polymer structure in the presence of a sorbed condensible vapor (e.g., carbon dioxide) leads to a decrease in permeation rate. The behavior has the characteristics of a relaxation process and also can be related to aspects of both Case II sorption behavior and dual-mode sorption behavior. There also are comparable changes in other properties, e.g., a progressive decrease in tensile modulus with time under exposure to CO_2. These studies are continuing on both the experimental and theoretical levels.

C. Publications and Presentations

1. Presentations

a. C. E. Rogers, "Sorption, Diffusion, and Permeation in POlymers", AMMRC, Marcj 2 and 3, 1983.

b. C. E. Rogers, "Effects of Deformation on Sorption and Transport in Polymers", 1983 Sci. Conf. on Chem. Def., Aberdeen Proving Gd., Nov. 1983.

c. C. E. Rogers, "Transport through Membranes", International Symposium on Synthetic Membranes, MMI, Midland, MI., August 1984 (in part).

d. C. E. Rogers, N. Mitchell and T. Goodman, "Effects of Deformation and Fatigue on Sorption and Transport in Polymers", 1984 Sci. Conf. on Chem. Def., Aberdeen Proving Gd., Nov. 1984.

e. C. E. Rogers, "Deformation, Degradation and Diffusion in Polymers"

   i. Department of Macromolecular Sci. Sponsor's Symposium, Nov. 1984

   ii. The Dow Chemical Company, Midland, MI, Dec. 1984

   iii. Sohio Research Center, Jan. 1985.

   iv.

f. N. F. Mitchell and C. E. Rogers, "Deformation and Mass Transport in Elastomers", Amer. Phys. Soc., Div. of High Polym. Physics, Baltimore, March 1985

g. T. W. Goodman and C. E. Rogers, "Effects of Exposure to Gases on the Transport Properties of Glassy Polymers", Amer. Phys. Soc., Div. of High Polym. Phys., Baltimore, March 1985

h. (Authors and titles as in f. and g.), ACS Regional Meeting, Akron, June 1985.

2. Publications

a. C. E. Rogers, "Effects of Deformation on Sorption and Transport in Polymers", Proc. 1983 Sci. Conf. Chem. Def. Res., CRDC-SP-84014, Oct. 1984, pp. 793-798.

b. C. E. Rogers, N. Mitchell, and T. Goodman, "Effects of Deformation and Gatigue on Sorption and Transport in Polymers", Proc. 1984 Sci. Conf. Chem. Def. Res., CRDC-85006, June 1985, pp. 555-560.

c. C. E. Rogers and N. Mitchell, "Deformation and Mass Transport in Elastomers", to be submitted to Rub. Chem. Tech.

d. N. Mitchell, S. N. Mohammad and C. E. Rogers, "Effects of Fatigue on Mass Transport in Elastomers", to be submitted.

e. T. W. Goodman, S. N. Mohammad and C. E. Rogers, "Effects of Exposure to Gases on the Transport Properties of Glassy Polymers", to be submitted to Polym. Engr. Sci.

f. C. E. Rogers, T. Goodman and S. N. Mohammad, "Experimental Correction Procedures for Using the Linde Permeation Test Cell", to be submitted to ASTM.

g. C. E. Rogers, T. Goodman and S. N. Mohammad, "A Permeation Model for Continuous Feed Batch Reactors", to be submitted. (Note: This paper is based on data obtained during the CO_2-glassy polymer study before correction of the experimental procedure was made).

D. Participants

Professor C. E. Rogers, Principal Investigator

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M.S. Degree in Macromolecular Science

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The following personnel were involved in some aspects of the study but were not supported by ARO funds:

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