

The Application of Limited Swelling in the Studies of the Cohesive Energy Density of Polyethylene Thin Film

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Synopsis

The mechanism and growth of limited swelling of linear high-density polyethylene (LHDPE) in some selected commonly used industrial solvents have been studied. The equilibrium solvent uptake has been used to determine its cohesive energy density. The data obtained during the course of these investigations fits a mechanistic growth model that predicts solvent uptake. This method offers a suitable and alternative way of determining the structural strength and resistance of polymers in contact with common solvents.

INTRODUCTION

The ability of polymeric materials to imbibe solvents and thus swell has long been a subject of several investigations.^{1,4,8,9} Limited swelling of polymer in a solvent could be used to estimate the extent of crosslinking, molecular conformation, coil dimension, and thermodynamic flexibility among other factors.^{1,2,7,8} This method has been used extensively in the dyeing of synthetic fibers where a suitable solvent is used as a carrier to transport the dye into the fiber structure. Swelling studies could also provide a suitable alternative method for elucidating the mechanism of chemical degradation of polymers. Hitherto, thermal, and to some extent, photochemical degradation have been emphasized in the studies of polymer degradation mechanisms and characterizations to the utter neglect of other methods.

This paper focuses on the limited swelling of polyethylene film with a view to elucidating important chemical properties. This is accomplished by using the measured limited swelling of linear high-density polyethylene (LHDPE) in some selected common solvents to estimate its cohesive energy density. The plot of measured solvent uptake against time is also shown to fit a mechanistic swelling growth kinetic model. The basic equation relating solubility and the mixing energy is given by^{2,4}

$$\Delta H_m = \Delta V_m \left[\frac{(\Delta E_1)^{1/2}}{v_1} - \frac{(\Delta E_2)^{1/2}}{v_2} \right]^2 \Phi_1 \Phi_2$$

Where V_i = molar volume of component i and Φ_i = volume fraction of component i . The quantity $\Delta E_i/V_i$ is the cohesive energy density and its square root is the solubility parameter, δ_i .

TABLE I
 Physical Properties of Solvents^{4,6}

Solvent	Mol. wt	Density (g/ml)	Molar/Volume (ml)	Solubility parameter δ cal/ml
Diethylether	72.12	0.708	104.69	7.40
Methanol	32.04	0.797	40.92	14.50
Benzene	46.07	0.789	58.39	9.15
Acetone	58.08	0.791	73.43	10.00
<i>n</i> -Hexane	86.00	0.659	130.50	7.30
Toluene	92.14	0.866	106.39	—
Tetrahydrofuran	72.11	0.888	81.21	9.90

EXPERIMENTAL

A thin polyethylene film (density 0.943 g/ml thickness 0.075 mm) and seven different organic solvents as given in Table I were obtained from E. Merck of Darmstadt, West Germany. The film was cut into small rectangular pieces of flat sheets. Each piece was washed and thoroughly rinsed with distilled water, blot dried with filter paper, and then dried for 24 hours in an oven at 40°C. The samples were further kept overnight in a dessicator.

Each film sample was accurately weighed and transferred into the respective solvent in a 50-cc conical flask and stoppered. The solvent uptake with respect to time was obtained by periodically removing a sample from its solvent, quickly blot drying, and reweighing. The measurements were conducted at room temperature of 27°C. Calculations of volumes and concentrations of solvents in the polymer were carried out using the method of Collings et al.³

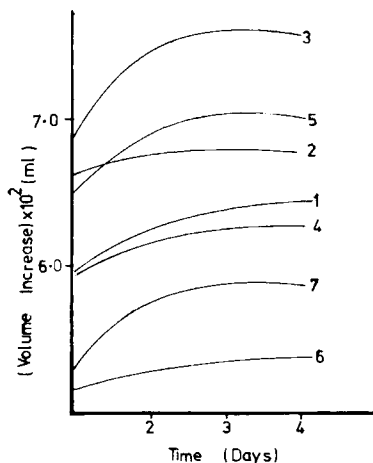


Fig. 1. Polyethylene Thin Film Swollen Volume Characteristics In Different Solvents: 1. Diethylether; 2. Methanol; 3. Benzene; 4. Acetone; 5. *n*-Hexane; 6. Toluene; 7. Tetrahydrofuran.

RESULTS AND DISCUSSIONS

In Figure 1, all the solvents showed similar behavior during the first 24 hours of limited swelling of the polyethylene sample. A closer observation indicates a rather steeper rate of volume increase for benzene, *n*-hexane, and tetrahydrofuran solvents. This phenomenon is attributable to the closeness of their respective solubility parameters given in Table I to that of the polyethylene. The volumetric swelling curves uniformly remained stable after attaining the equilibrium volume. However, small variations at this point can be observed if the volume ratio or the degree of swelling is plotted against time as shown in Figure 2. Furthermore, in Figure 2, the degree of swelling of polyethylene in diethylether, *n*-hexane, and tetrahydrofuran reached positions of maxima. This is attributable to the ability of the solvents to diffuse rapidly into the polymer structure. This diffusion created some strains in the chain molecules and the strains themselves tended to oppose further solvent uptake.

This was followed by solvent exudation from the polymer until the structural strain energy equalled the cohesive energy. It is inferred that the positions of maxima were indicative of the maximum structural strength of the polymer with respect to the solvents beyond which further solvent uptake would lead to molecular chain breakdown. This phenomenon was not observable while using toluene, acetone, and methanol as solvents. The latter showed steep but irreversible solvent uptake until they attained equilibrium. The equilibrium solvent uptakes were then plotted against the respective solubility parameter of the solvents as shown in Figure 3.

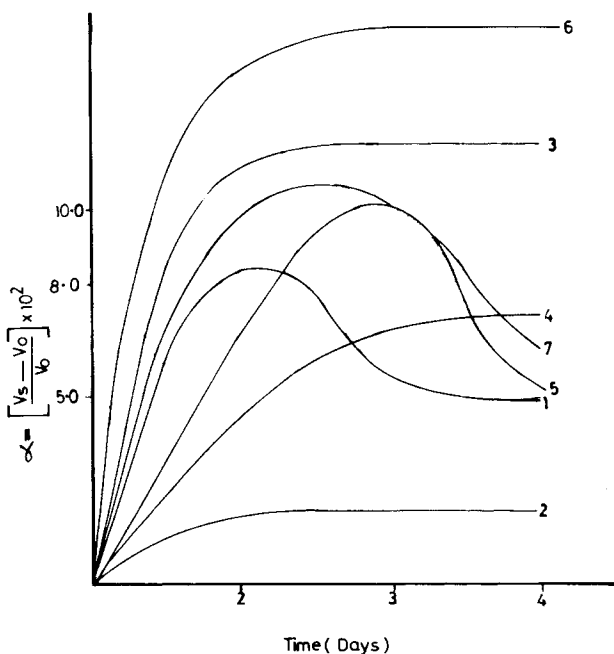


Fig. 2. Volumetric Degree Of Swelling Of Polyethylene Thin Film: 1. Diethylether; 2. Methanol; 3. Benzene; 4. Acetone; 5. *n*-Hexane; 6. Toluene; 7. Tetrahydrofuran.

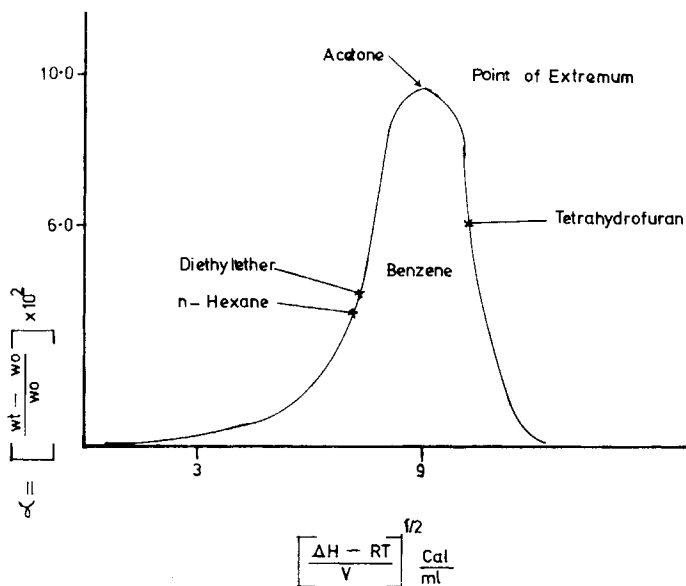


Fig. 3. Dependence of limited swelling on the cohesive energy density a case of polyethylene thin film.

Also in Figure 3 a point of extremum close to the solubility parameter of 9.7 is observed. This point lies between the positive and negative values of the rate of increase in solvent equilibrium uptake against solubility parameters of the solvents. This value gives the cohesive energy density of the linear high-density polyethylene sample to be 94.09 Cal/ml as against 63.04 Cal/ml reported for the low-density polyethylene.^{4,9}

The failure of the sample to dissolve in any of the solvents is an indication of lack of specific interaction between the functional groups of the solvents and polyethylene. This made polyethylene solvent miscibility impossible. It also strengthened the idea that similarity in solubility parameters alone is not enough of a criterion for selecting polymer solvents. To further understand the fundamental reasons behind the observed differences in the rates of limited swellings in each solvent, a kinetic investigation was conducted.

KINETICS OF LIMITED SWELLING

One of the most recent attempts to explain the nature and mechanism of solvent imbibed into a high-molecular weight polymer is that of Smith and Fisher² who related solvent uptake to its diffusivity in the polymer structure. The effect of polymer porosity has also been reported by Poinescu et al.¹ There has, however, not been a precise quantitative method of solvent uptake prediction and the effects of polymer stress relaxation rate on the mechanism of solvent uptake into a polymer.

Based on the above reported works and that of Blow,⁹ the mechanism of limited swelling is essentially a first order phenomenon that can be math-

ematically described thus;

$$\frac{dw}{dt} = K(m - w) \quad (2)$$

which when integrated yields

$$W_t = m(1 - \beta \exp(-Kt)) \quad (3)$$

where m is the initial weight of polymer, W_t is time-dependent weight of polymer, K is the swelling rate constant, and β is the characteristic stress relaxation rate.

Equation (3) could further be simplified into the form:

$$\alpha = (1 - \beta \exp(-Kt)) \quad (4)$$

where $\alpha = \frac{W_t}{m}$

The data given in Table II has been fitted to the exponential Eq. (3) using the standard least-squares method to obtain for toluene⁵ the expression;

$$W_t = 0.04(1 - \beta \exp(-8.0 \times 10^{-2}t)) \quad (5)$$

Equations (3), (4), and (5) therefore constitute the working models. Equation

TABLE II
Mechanistic Swelling Growth Model for Different Stress Relaxation Rates
 $W_t = 0.04[1 - \beta \exp(-8.0 \times 10^{-2}t)] \times 10^2$ (g)

β \ Time (days)	0	1	2	3	4
0.1	3.60	3.63	3.66	3.69	3.71
0.3	2.80	2.89	2.98	3.06	3.13
0.6	1.60	1.78	1.95	2.11	2.26
0.8	0.80	1.05	1.27	1.48	1.68
1.0	0.00	0.31	0.59	0.85	1.10

TABLE III
Kinetic Parameters of Limited Swelling of Polyethylene Thin Film in Different Solvents at 27°C

Solvent	$m \times 10^2$ (g)	$k \times 10^3$ (day ⁻¹)	(δ^2) ⁴
Diethylether	6.0	1.56	0.39
Methanol	6.0	0.97	0.07
Benzene	6.0	4.54	0.78
Acetone	6.0	2.98	0.94
<i>n</i> -Hexane	4.0	50.00	0.07
Toluene	5.0	3.81	0.78
Tetrahydrofuran	5.0	2.57	0.43

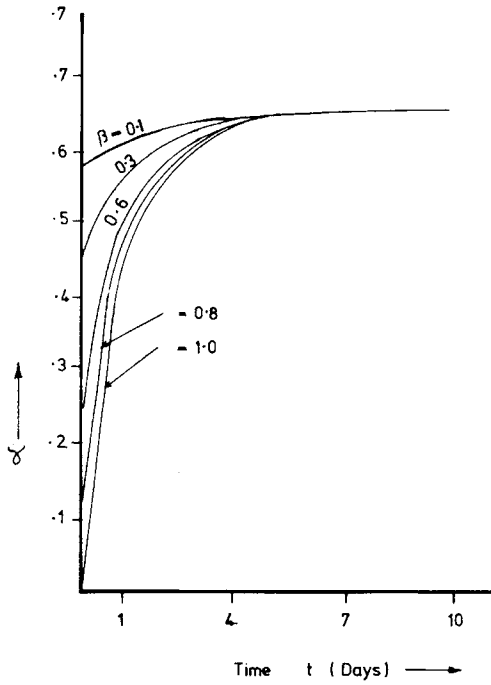


Fig. 4. Theoretical Curves Of The Model $\alpha = 1 - \beta \exp(-kt)$.

(4) predicts the swelling behavioral pattern of the polymer in the solvent while Eq. (5) describes the observed characteristics from the actual investigations conducted. Equations (4) and (5) have been plotted for various possible stress relaxation rate β as shown in Figures 4 and 5, respectively. The mechanistic growth model represented by Eq. (4) and shown in Figure 4 indicates a rather rapid rate of convergence to equilibrium value when

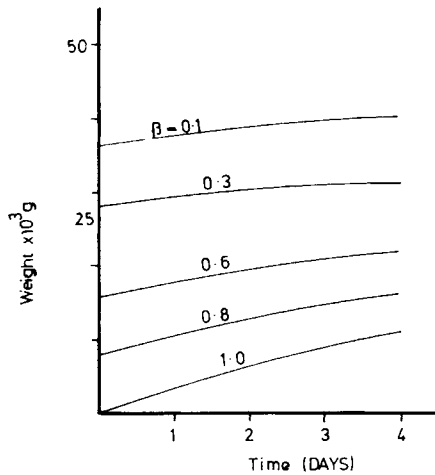


Fig. 5. Observed Curves of Mechanistic Swelling Growth Model. For Polyethylene in Toluene $w = 0.04(1 - \beta e^{-8.0 \times 10^{-2}t})$ $w = 0.04(1 - \beta e^{-8.0 \times 10^{-2}t})$.

the swelling rate constant is unity. This is the highest expected value for limited swelling process. Equation (5) which has been plotted as shown in Figure 5, is characterized by a slower rate of equilibrium attainable in practice for the same values of stress relaxation rate. As would be expected, Figure 5 shows different values of equilibrium, for each solvent as a result of the deviation of the swelling rate constant from unity. It could be inferred that limited swelling mechanism is dependent, to a large extent, on the rate constant and the stress relaxation rate. The latter is a direct consequence of the viscoelastic memory of the polymer.

CONCLUSIONS

Benzene, *n*-hexane, and tetrahydrofuran showed a rapid polymer uptake. The observed solvent exudation was due to the strain imposed on the polymer chains by the solvent and the equilibrium level measured the structural cohesive energy. The mechanistic swelling growth model has described the limited swelling of polyethylene film in the selected solvents used in this investigation. It seems the swelling rate constant and the viscoelastic properties of the polymer greatly influenced the swelling mechanism.

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