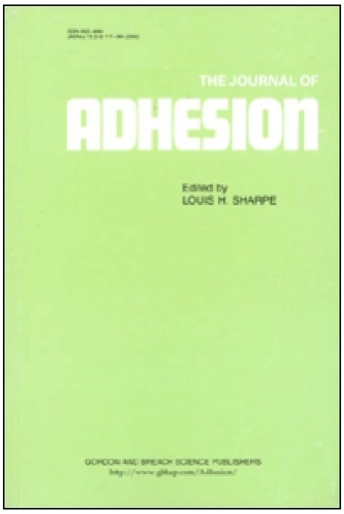

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Interfacial Contact and Bonding in Autohesion II-Intermolecular Forces

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Interfacial Contact and Bonding in Autohesion

II-Intermolecular Forces

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ABSTRACT

The second stage of autohesion involves bond formation after contact is established by elastic, viscous, or viscoelastic deformation of the surfaces. The interfacial bonding for polystyrene is mainly through van der Waals intermolecular forces. Molecular repeat units across the interface interact to yield an attractive force. The intermolecular forces are derived from a 6-12 Lennard-Jones potential. The two unknown constants for this potential are determined from the equilibrium distance and comparison of the computed lattice energy with the cohesive energy.

INTRODUCTION

A VISCOELASTIC contact theory has been developed that controls the first stage of autohesion [1]. The second stage of interfacial bonding will be developed in this paper and the one that follows.

Wherever contact is established, interfacial bonding takes place due to primary or secondary bond forces. In case of non-polar polymers such as polystyrene. the intermolecular attraction is mainly due to van der Waals forces. Molecular repeat units on the two sides of the interface interact with each other to result in a net attractive force.

The strength of the secondary bonds is not known for polystyrene. They consist of an attractive and a repulsive component. The long range attractive component is a London dispersion force [2], the potential governing this is proportional to the inverse sixth power of the distance up to about 2000 Angstroms. Beyond this distance the variation is to the inverse seventh power of the distance due to electromagnetic retardation [3]. The repulsive force due to the overlap of electron clouds is a short range force decreasing exponentially with distance. The potential for this may be approximated by an inverse twelfth power [4]. Thus, the net potential between molecules may be given by the well-known 6-12 Lennard-Jones potential.

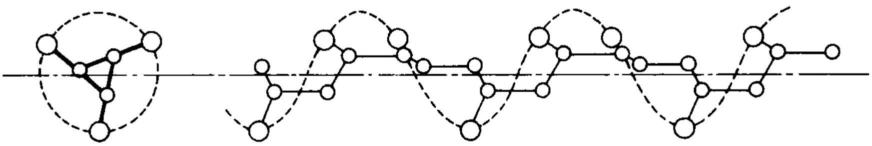
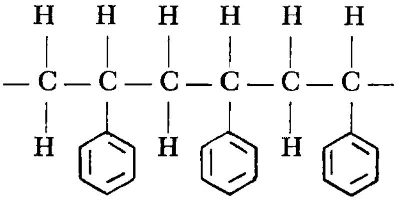


Figure 1. Type I helical conformation of isotactic polystyrene. Small circles represent the backbone units such as —CH or —CH$_2$; the large circles represent

This potential involves two unknown constants. The values of these constants are determined from a knowledge of the single crystal lattice structure of isotactic polystyrene and its cohesive energy density. The procedure followed is similar to the one developed for polyethylene [5].

POLYSTYRENE CRYSTAL STRUCTURE

Configuration of isotactic polystyrene is



which shows three chemical repeat units. The molecule has type I, 3-fold helical conformation as shown in Figure 1 and 2.

The crystal structure is rhombohedral [6] with cell constants $a = b = (21.9 \pm 0.1)$ Å, and $c = (6.65 \pm 0.05)$ Å. The axis c is along the polymer

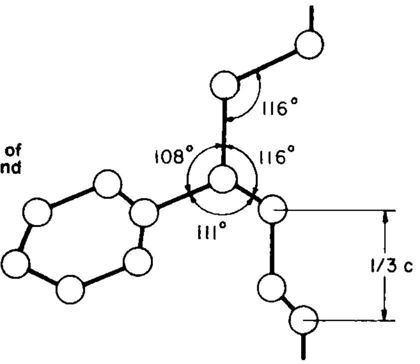


Figure 2. Conformation of a unit of polystyrene showing the C—C bond angles involved.

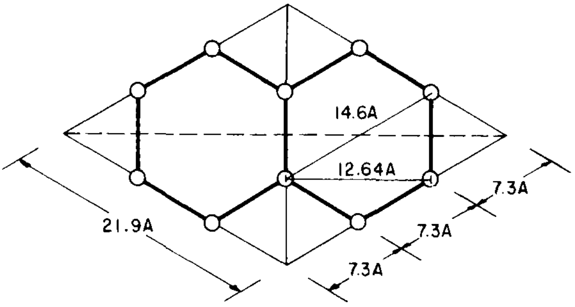


Figure 3. Molecular packing showing the hexagonal unit cell structure.

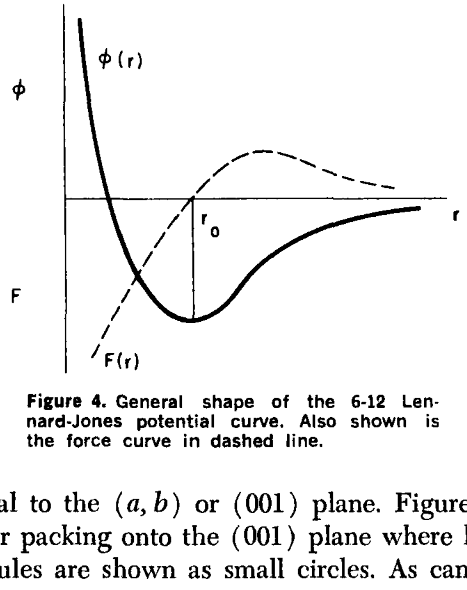


Figure 4. General shape of the 6-12 Lennard-Jones potential curve. Also shown is the force curve in dashed line.

chain and is normal to the (a, b) or (001) plane. Figure 3 shows the projection of molecular packing onto the (001) plane where lattice points occupied by the molecules are shown as small circles. As can be seen, the unit cell or the molecular packing is hexagonal in nature with lattice parameter $a' = 7.3$ Å.

LENNARD-JONES POTENTIAL

A chain lying along the c-axis may be considered to consist of repeat units $(—CH_2—CH\ C_6H_5—)$ without loss of generality. The force between these units is determined by the intermolecular potential. The latter may be approximated by a 6-12 Lennard-Jones curve, as shown in Figure 4. If r is the distance and $\phi(r)$ the potential, we may write

$$\phi(r) = \frac{A}{r^{12}} - \frac{B}{r^6} \tag{1}$$

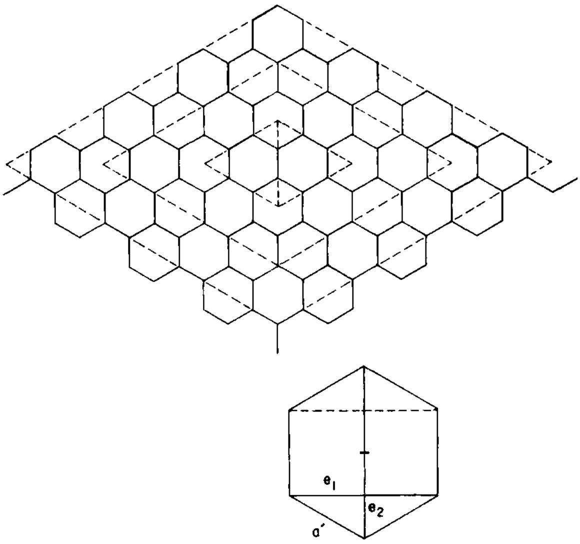


Figure 5. Lattice structure in the (a,b) plane used for computation of lattice energy.

where A and B are the unknown Lennard-Jones constants. Gradient of $\phi(r)$ gives the force $F(r)$ as

$$F(r) = -\frac{d\phi}{dr} = \frac{12A}{r^{13}} - \frac{6B}{r^7} \tag{2}$$

Figure 4 also shows the $F(r)$ curve. The force $F(r)$ being zero at the equilibrium distance, r_o, for polystyrene of

$$r_o = 7.30\ \text{Å}$$

determines the ratio

$$p = \frac{A}{B} = \frac{1}{2}(r_o)^6 \tag{3}$$

Thus, one need obtain only one of the Lennard-Jones constants, since their ratio is fixed.

It is possible to determine the constants by computing the crystal potential or lattice energy and comparing it with the experimentally determined value of cohesive energy.

Figure 5 shows the lattice structure in the (a, b) plane that will be used for computation of the lattice energy U. Letting

$$\begin{aligned} e_1 &= a'\sqrt{3}/2 = 6.32\ \text{Å} \\ e_2 &= a'/2 = 3.65\ \text{Å} \\ e_3 &= c/3 = 2.22\ \text{Å} \end{aligned} \tag{4}$$

The distance r_{lmn} of a point $(l,m,n,)$ from the origin $(0,0,0)$ is

$$r_{lmn} = [(le_1)^2 + (me_2)^2 + (ne_3)^2]^{1/2} \tag{5}$$

It may be observed that when l is odd, m has the values $3 + 6i$ and $-1 + 6i$, and when l is even, m has the values $+ 6i$ and $2 + 6i$, where i is a positive or negative integer. Also, all the units for which both l and m are zero should be excluded since they belong to a single chain and do not count in the cohesive energy.

It follows from (1) which gives the energy of a pair of units that the lattice energy U of a unit $(0,0,0)$ is

$$\begin{aligned} U &= \frac{1}{2} \sum_{lmn=-\infty}^{\infty} \phi_{lmn}(r) \\ &= \frac{1}{2} \sum \left(\frac{A}{r_{lmn}{}^{12}} - \frac{B}{r_{lmn}{}^{6}} \right) \\ &= \frac{1}{2} \left[\sum \left(\frac{p}{r_{lmn}{}^{12}} - \frac{1}{r_{lmn}{}^{6}} \right) \right] B \end{aligned} \tag{6}$$

This reduces the problem to one of calculating sums of the type

$$A_s = \sum_{l,m,n=-\infty}^{\infty} r_{lmn}{}^{-s} \tag{7}$$

for $s = 12$ or 6 and with l, m, and n taking values discussed above.

We may rewrite U in the form

$$U = \frac{1}{2} B \, (pA_{12} - A_6) \tag{8}$$

LATTICE AND COHESIVE ENERGY COMPARISON

If M is the molecular weight of the repeat unit occupying the lattice points, then M gms. of polystyrene will contain N_A such units where N_A the Avogadro number $= 6.0249 \times 10^{23}$. Thus, the crystal potential energy E is

$$E = N_A \, U \tag{9}$$

The cohesive energy per mole Δ is

$$\Delta = \frac{M\delta^2}{\rho} \tag{10}$$

where δ^2 the cohesive energy per cm^3 is [7]

$$\begin{aligned}\delta^2 &= 74 \text{ cal/cm}^3\\ &= 3.09 \times 10^{-15} \, erg/A^3\end{aligned}$$

The value of M is

$$M = 104$$

and the density ρ is [6]

$$\rho = 1.12 \times 10^{-24} \text{ gm}/A^3$$

Comparing (9) and (10), we get

$$B = \frac{2M\delta^2.}{N_A\rho(pA_{12} - A_6)} \tag{11}$$

A computer program has been written to evaluate the sums A_{12}, A_6, and compute the values of the *L-J* constants A and B. The series sums are very fast converging and only a few terms have to be included.

Substitution of the numerical values of the various factors in (11) and (3) yields the value of the constants as

$$\begin{aligned}B &= 1.428 \text{ dynes } A^7\\ A &= 1.080 \text{ dynes } A^{13}\end{aligned}$$

DISCUSSION

Values of the Lennard-Jones potential constants determined here have the same order of magnitude as for rare gases. This is to be expected because the lattice energy is of the same order of magnitude [8].

The intermolecular forces of polystyrene arise from the interaction between the hydrogen atoms which are attached to the carbon atoms by covalent bonds formed by sharing a pair of electrons. Thus, the valence electron of hydrogen spends most of the time between the carbon and hydrogen atoms and very little time outside this region. The result is that the dispersion type of van der Waals forces, which arise from the time varying instantaneous electron configurations, are very weak—a condition existing in rare gases too.

The Lennard-Jones potential determined here is used to compute the bond strength of two flat plates of polystyrene in self-adhesion. This forms the subject of the next paper. The values compare well with those experimentally determined value of the yield stress of polystyrene.

NOMENCLATURE

a, b, c, a' = Lattice parameters
ϕ = Potential
F = Force
r, r_o = Distance
A, B = Lennard-Jones constants
p = Ratio of A to B
e_1, e_2, e_3 = Units of distances along the three axes a, b, and c
l, m, n, i = Integers
r_{lmn} = Distance of the unit (l, m, n) from $(0, 0, 0)$
U = Lattice energy
Σ = Summation
A_s = Summation for power s
E = Crystal potential energy
N_A = Avogadro number
Δ = Cohesive energy per mole
δ = Solubility parameter
M = Molecular weight of the repeat unit
ρ = Density

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