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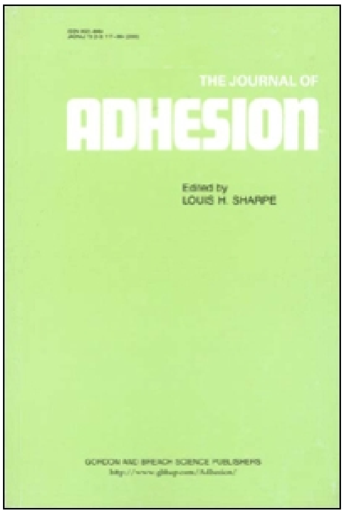

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On the Hysteresis of Polymer Wetting

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The reasons for the appearance of the hysteresis of wetting are considered. The model is proposed according to which the hysteresis is the result of the orientations of molecules of wetting liquids which is preserved due to the action of surface forces even after the flow ceases.

KEY WORDS: Wetting; advancing and receding contact angles; hysteresis; molecular orientation; surface heterogeneity; interfacial interactions; surface polarization; polymers.

1. INTRODUCTION

Most methods of estimation of the surface tension for polymeric bodies are based on the determination of the contact angles of wetting.[1,2] However, hysteresis of wetting appears during measurements of the contact angle. It is not clear what contact angle should be taken into account for estimating the interphase interactions: at the advancing contact boundary or at the receding one (advancing angle, θ_a, or receding, θ_r).

Although wetting hysteresis was mentioned for the first time more than 100 years ago[3], up to now its reasons are not clear. It is supposed that this phenomenon is connected with adsorption of wetting liquids at the interface or with adsorption of some admixtures.[4–9] Among other possible reasons, the probable orientation of polar groups at the interface with polymer,[10] roughness of the surface[1–15] and energetic nonuniformity of the surface[16–19] are mentioned.

However, no one of these factors has the determining role. Adsorption hysteresis is possible only for a definite length and shape of the molecules in the adsorption layer[20] and may be avoided when removing all admixtures from the wetting liquid. The same relates to the surface roughness—it is sufficient to diminish the height of roughness to 0.5 μm to avoid the hysteresis.[20,21]

Consider now the energetic nonuniformity. For the model of a heterogeneous surface both advancing and receding angles are important. These angles characterize the wetting of surface zones with different value of the surface tension γ' and γ'' (let $\gamma' > \gamma''$). This model predicts diminishing hysteresis with the increase in the vibration energy of

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the drop.[18] However, this statement contradicts the experimental data on dynamic hysteresis.

2. EXPERIMENTAL DATA ON THE WETTING HYSTERESIS

Experimental measurements of the dynamic hysteresis, *i.e.* at conditions of stationary liquid flow,[23-25] have shown that with increasing rate of advancing boundary (that is equivalent to increasing the vibration energy) the hysteresis increases as well. Simultaneously, it was shown that at low rates of the wetting liquid frontier (up to 1 mm/min), both advancing and receding contact angles are independent of the flow rate and are equal to the static contact angles. In such a way the reason for hysteresis again is not clear.

To establish the main reasons for hysteresis we can consider the following experimental data[26] on wetting of galena: for freshly split galena and its film sputtered onto a glass surface in vacuum, the same values, $\theta_a = 90° \pm 3$ and $\theta_r = 0°$, have been found for wetting with water. However, the surfaces in these two cases are distinctly different both in their roughness and heterogeneity. The crystalline surface has no polar groups capable of reorientation by wetting or dewetting, which excludes all three reasons mentioned as the sources of hysteresis.

Our own data on wetting hysteresis have been obtained using thin plates of polymers immersed vertically into a liquid.[27] The description of the film properties and their treatment are given in the Appendix.

The displacement of the vessel with wetting liquid was performed at a rate below 0.2 mm/min and measurements were done in the static regime. The following nomenclature is used:

γ_1 is the surface tension of wetting liquid, γ_2 is the same of a support, γ_{12} is the interfacial tension, $\Delta_w = \cos\theta_r - \cos\theta_a$ characterizes the hysteresis of wetting.

Figure 1 shows the wetting hysteresis for poly (tetra fluoroethylene) (fluoroplast). This polymer was chosen because it does not swell or dissolve in the large majority of liquids. The vertical dotted line denotes the transition through the value $\theta_a = 90°$. As by this transition the dependence of $\Delta_w = f(\gamma_1)$ does not change, the conclusion can be drawn that, in this case, the effect of the surface roughness on the hysteresis is absent. Really, in the region where θ_a already is $> 90°$ whereas θ_r has not yet reached 90°, the spreading along the furrows and trenches should markedly change the dependence of $\Delta_w = f(\gamma_1)$. However, the experimental data presented in Figure 1 for various wetting liquids show that such dependence is absent. We should like also to note that none of the theories describing the dependence of the hysteresis on the surface roughness predicts the growth of Δ_w with the surface tension of the wetting liquid.

It is seen that experimental points are rather well described by the equation:

$$\Delta_w = a\gamma_1 + b \qquad (1)$$

where coefficients a and b are equal to $(8.0 \pm 0.2) \times 10^{-3}$ and $-(0.106 \pm 0.008)$, respectively (the confidence half intervals are given for the level of confidence probability of 0.95). The systematic deviations from the dependence are observed for the mono methyl ether of ethylene glycol (MEG) and 2-acetophenone.

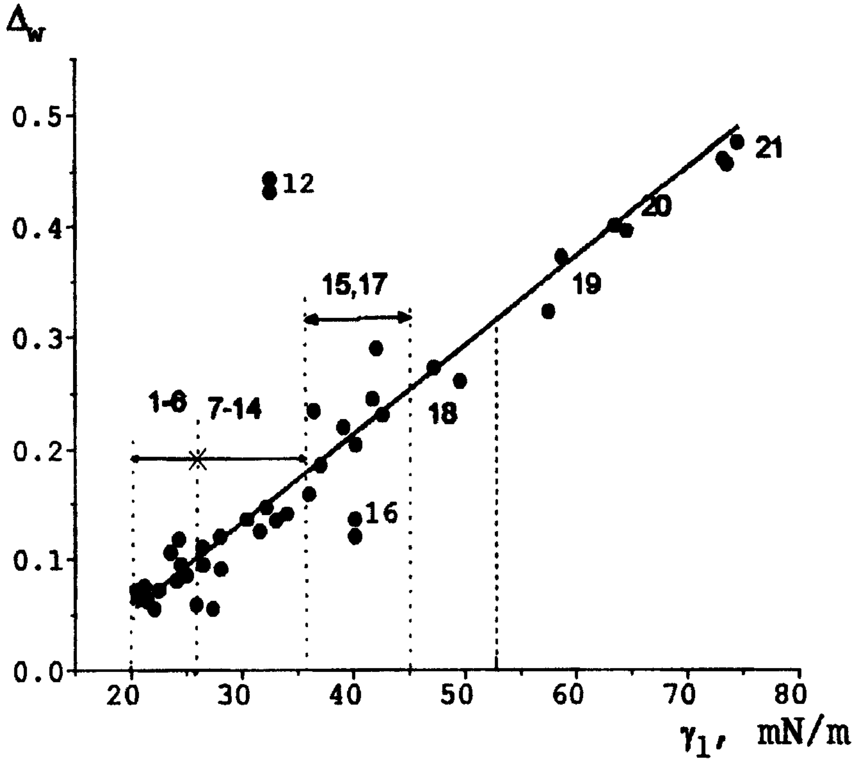

FIGURE 1 Dependence of hysteresis on the surface tension of wetting liquids, as follows: 1-heptane, 2-isopropanol, 3-octane, 4-decane, 5-dodecane, 6-*n*-amyl alcohol, 7-tetradecane, 8-hexadecane, 9-octanol-2, 10-tetrahydrofuran, 11-vaseline oil (liquid paraffin), 12-methylcellosolve (ethylene glycol monomethyl ether), 13-oleic acid, 14-castor oil, 15-dibromoethane, 16-acetophenone, 17-*o*-nitrotoluene, 18-ethylene glycol, 19-formamide, 20-glycerol, 21-water.

The same measurements have been done for polystyrene and cured epoxy resin ED-20. It was established that the dependence $\Delta_w = f(\gamma_1)$ is linear for these two polymers (Fig. 2). For polystyrene:

$$\Delta_w = 5.1 \times 10^{-3}\gamma_1 - 0.17; \quad \text{for epoxy polymer: } \Delta_w = 27.3 \times 10^{-3}\gamma_1 - 1.03.$$

3. THE SUBSTANTIATION OF THE NEW CONCEPT OF THE WETTING HYSTERESIS

A similar dependence of $\Delta_w = f(\gamma_1)$ for polar and non-polar polymers allows one to suppose the existence of some regularity in the wetting hysteresis which is connected with the orienting effect of the surface force field on the molecules of the wetting liquid.

We believe that the most realistic approach to the understanding of interfacial interaction was proposed by Hansen and Miotto.[23] They ascribed the dynamic hysteresis of wetting to the change in orientation of the molecules of wetting liquid, along the ternary contact border, that proceeds by the movement of the liquid boundary. However, they supposed that the movement of the liquid led to the disordering of its molecules.

Meanwhile, the study of the birefringence in the flowing liquid testifies to the orientation of molecules of any liquid.[28,29] Theoretical and experimental investigations of birefringence have shown that in slow flow the axis of the molecular anisotropy is at an angle of less than 45° to the flow direction, whereas in strong flow the direction of the preferential orientation coincides with the flow direction, perfect orientation being reached. It is important that changing the flow direction changes the direction of orientation as well.[28]

The existing data on the hysteresis of wetting and the data on the orientation of the molecules in the flow of liquids give us the possibility to propose the following concept of the hysteresis phenomenon. The hysteresis is supposed to be the result of the orientation of molecules of wetting liquids which is preserved due to the action of the surface forces even after flow ceases (as distinct from birefringence in the flow which disappears after stopping the movement[28]).

In this case, in accordance with the Le Chatelier-Brown principle, for the advancing boundary such orientation appears which prevents wetting, whereas for the receding frontier it enhances wetting, this being supposed to be the main reason for hysteresis.

Let us now consider how the two hysteresis concepts agree with the experimental data. We denote the surface characteristics of the surface with high energy in the heterogeneous concept[16-19] as γ'_2 and $\cos\theta'$, and for low energy surface as γ''_2 and $\cos\theta''$, *i.e.* $\gamma'_2 > \gamma''_2$. The hysteresis, Δ_w, may be calculated using the Young equation.

$$\cos\theta = (\gamma_2 - \gamma_{12})/\gamma_1 \tag{2}$$

and the rule of interfacial interaction[30]

$$\gamma_{12} = \gamma_1 - \gamma_2 \tag{3}$$

In this case

$$\Delta_w = 2(\gamma'_2 - \gamma''_2)/\gamma_1 \tag{4}$$

As for a given polymer the difference $\gamma'_2 - \gamma''_2 = const.$ (according to the heterogeneity concept) from Eq. 4 it follows that the hysteresis should decrease with increase in the surface tension of the wetting liquid. Meanwhile the experimental data show (see Figs. 1 and 2) that the hysteresis increases linearly with growth in γ_1. This fact meets our concept, because according to Eq. 3 the interfacial tension, being the source of molecular orientation at the solid-liquid interface, increases linearly with γ_1.

No contradictions appear in the critical region where $\theta_a \to \theta_r \to 0$. Calculation of critical values for the wetting liquid according to Eq. 1 gives the values 13.2 mN/m for fluoroplast, 33.3 for polystyrene and 37.2 for epoxy resin. This enables one to rewrite Eq. 1 in the following form:

$$\Delta_w = a(\gamma_1 - \gamma_{crit}) \tag{5}$$

where $\gamma_{crit} = -b/a$ (see Eq. 1).

The concept proposed foresees the more strong dependence of Δ_w on γ_1 by transition from dispersion interactions to polar and acid-base interactions.

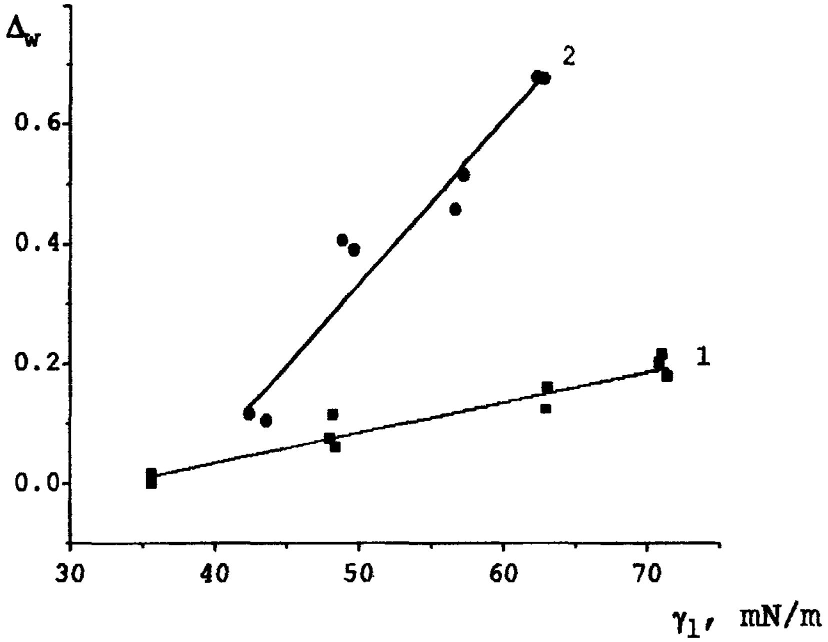

FIGURE 2 Dependence of hysteresis on the surface of wetting liquids: 1-polystyrene, 2-epoxy polymer.

Figure 2 shows that the slope of the dependence is much greater for epoxy polymer as compared with fluoroplast and polystyrene. From the same standpoint one can explain the greater hysteresis for galena due to acid-base interaction with water.

Equation 4 enables one also to calculate the difference between the surface tension of solid polymer calculated from advancing contact angle, γ_2^a, and receding angle, γ_2^r:

$$\gamma_2^r - \gamma_2^a = 0.5a\gamma_1(\gamma_1 - \gamma_{crit}) \tag{6}$$

This equation shows the principal difference of the two approaches to the hysteresis phenomenon. Equations 5 and 6 show also that the coefficient a is connected with the value of polarization, π, of a solid surface. Really, the hysteresis is the higher the higher are the surface froce. Polarization is known to be a function of the dielectric permeability, ε^{33}, therefore the higher is ε, the greater is π.

We have already mentioned that for two liquids (Fig. 1) there are strong deviations from the linear dependence of hysteresis on the surface tension of the liquid when the support is fluoroplast (positive deviation for MEG and negative for 2-acetophenone). These deviations cannot be explained on the basis of the heterogeneous model of the surface. On the contrary, from our point of view these deviations are explained by different polarizability at the interface. MEG has a high polarizability due to a high ε despite low surface tension, whereas 2-acetophenone, due to its structural anisotropy, is capable of high orientation of molecules in flow, which gives no possibility for reorientation in flow and leads to decreasing hysteresis.

Finally, the data on dynamic hysteresis can also be explained.

The growth with increasing flow rate and then leveling off of the hysteresis are connected with increasing degree of molecular orientation which finally reaches its limit. The independence of the hysteresis on the flow rate at low rates (up to 1 mm/min) is connected with resistance of the surface forces to orienting action of a flow.

Thus, the data on the hysteresis for static and dynamic conditions confirm, as we believe, the validity of the proposed concept of wetting hysteresis as a phenomenon based on the preservation of molecular orientation arising during flow at advancing and receding boundaries. This preservation is the result of the action of the surface forces. This orientation should be preserved up to the critical point at which phase transitions proceed either in wetting liquid or in polymer. The effect seems not to be dependent on temperature and duration of experiment for the same reasons that determine the surface tension of a liquid. It disappears at critical conditions where the liquid-vapor phase boundary disappears. Really, the data available show that hysteresis and contact angles depend very weakly on temperature (at least in that temperature region where such measurements were possible).

CONCLUSIONS

Two main conclusions follows from the proposed hypothesis. In our concept we consider only two static orientations at the interface (by advancing and receding boundaries), which are not connected with the energetic heterogeneity of the surface. Then minimum free energy of two-phase system with an interphase layer[1] corresponds to the advancing contact, angle, the angle usually taken in thermodynamic studies of interfacial interactions. Hysteresis determined by the energetic nonuniformity of the surface is probably a second order effect and is revealed only at a very specific structure of the solid surface.[34]

Further, as follows from Figures 1 and 2, the regularities of interfacial interaction are of a statistical character. The interaction of each polymer-liquid pair is individual and to establish general rules it is necessary to exclude from consideration the liquids with high specificity of interaction. To substantiate such exclusion we can use the existence of the interconnection between the surface tension of the wetting liquid and its polarization established in Reference 31:

$$\gamma_1 = C + D\Pi \tag{7}$$

where according to Reference 33

$$\Pi = (\varepsilon - 1)/(\varepsilon + 2) \tag{8}$$

We have used the literature data for 72 liquids[31] to confirm this dependency and have found the correlation coefficient, r, calculated as in Reference 32 to be $r = 0.56$ with an accuracy ± 17%. The coefficients in Eq. 7 are: $C = 18.4$ and $D = 23.6$. Although the value of r is rather low, the accuracy allows one to select nonspecific liquids.

Using the same literature data from Eqs. 7 and 8 we have calculated the theoretical dependence of ε on γ_1 (Fig. 3). As in seen from Figure 3, the experimental points are scattered above and below the theoretical curve. This theoretical curve, being the result of calculations according Eqs. 7 and 8 has, however, the same correlation coefficients. We suppose that wetting liquids may be divided into two great groups: one below and

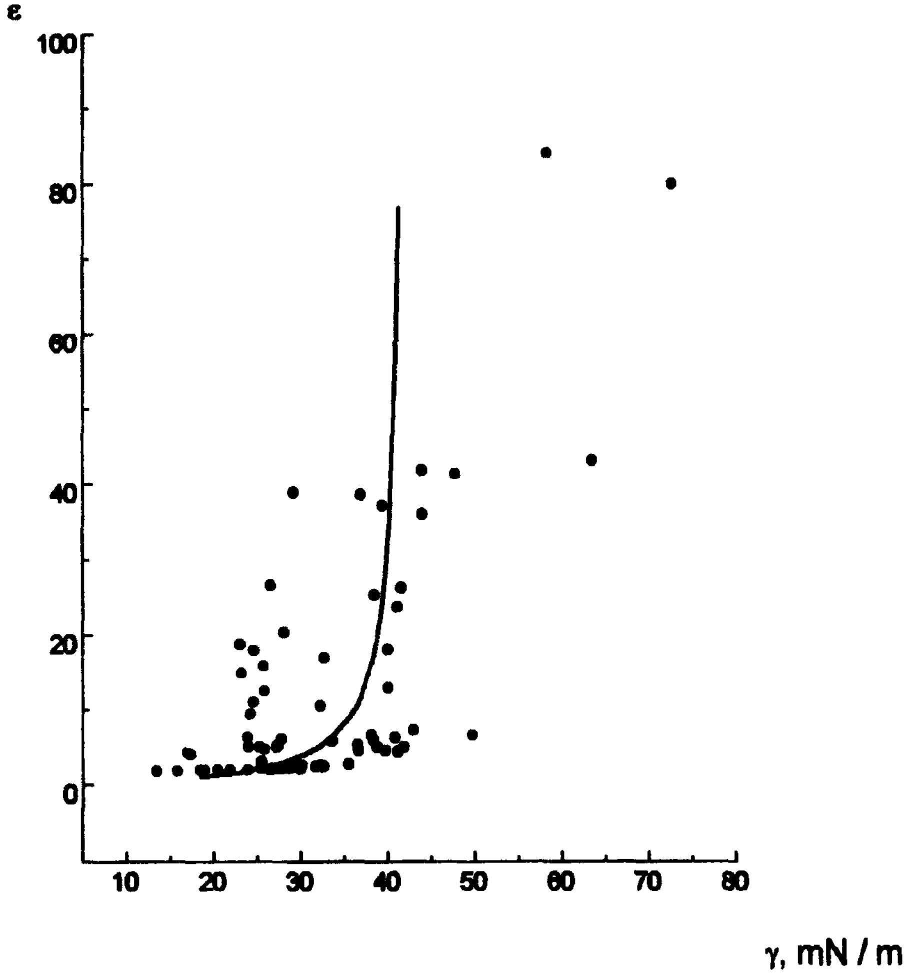

FIGURE 3 Interrelation between the dielectric permeability and surface tension for liquids (points on the curve were calculated).

on the theoretical curve and another above it. The liquids which on this plot are situated on and below the curve may be called normal (nonspecific). We recommend that these liquids be used first of all in searches of regularities of interfacial interactions at the liquid-solid interface.

Our main result is that hysteresis increases with the surface tension of the wetting liquid for one and the same surface. This effect has been demonstrated using three polymers with different surface characteristics and is substantiated by many literature data. These data allow the prelimianry conclusion to be drawn that one of the possible, and most probable, reasons for the appearance of the hysteresis of wetting is orientation of molecules of wetting liquids on the surface, orientation which is preserved under the action of surface forces.

Hysteresis determined by the energetic nonuniformity of the surface is probably a second order effect and is revealed only at a very specific structure of the solid surface.[34]

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APPENDIX

The polystyrene and fluoroplast films, 20 and 40μm in thickness are commercial products for capacitor manufacturing and were cut from the middle part of rolls using a special 6 × 10 mm punch. Films of the epoxy polymer were formed from the reaction mixture (epoxydiane resin with 20% of epoxy groups + polyethylene polyamine as a hardener). Thses films were cast on 100μm-thick aluminium foil in such a way that the total thickness of bilateral film and foil was 180μm. All of the films before measurements were washed with ethanol of high purity and dried in air. All of the films were used for only one measurement.

The suspension of the film on the balance beam was done using a special clamp. The surface tension of the wetting liquid was checked before and after measurements, using a platinum plate, for the absence of impurities on the surface of the investigated polymer film. Constancy with time of the weight of the film immersed in the liquid allowed one to judge the lack of dissolution or swelling of the film in the wetting liquid. In the opposite case the liquids were not used.

The roughness of the films was estimated by the mean height of the microuneverness, $\bar{h}$, determined from the dependence of this height on the reflection coefficient, r, of light incident at an angle, α, using the equation[35,36]:

$$r/r' = \exp\{-(k\bar{h}\cos\alpha/\lambda)\}^2 \tag{9}$$

where r' is the Fresnel reflection coefficient, k is the constant and λ is the wavelength of the incident light. The reflection coefficients were measured using a Lustremeter FB-2 (Analytical Apparatus, Armenia) with incident light at an angle of 45° and the receiver at the same angle. The device was calibrated using a standard sample for which $r/r' = 0.65$.

The solution of Eq. 9 accroding to $\bar{h}$ gives:

$$\bar{h} = a\sqrt{\ln(r/r')} \tag{10}$$

where $a = \lambda/(k \cos\alpha)$. At $\lambda = \lambda_D = 0.5876\ \mu\text{m}$, $k = \pi^{36}$ and $\alpha = 45^\circ$, $a = 0.2645\ \mu\text{m}$. For calculations we have used also the known relation for r' nonpolarized light:

$$r' = 0.5[\sin^2(\alpha - \beta)/\sin^2(\alpha + \beta) + tg^2(\alpha - \beta)/tg^2(\alpha + \beta)] \tag{11}$$

and the determination of the refractive index

$$n = \sin\alpha/\sin\beta \tag{12}$$

where β is the refraction angle. The results of the calculations of the values of $\bar{h}$ for the investigated films are given in Table I.

The correctness of the calculation of $\bar{h}$, according for the errors of the device and the coefficient k (20 and 10%, respectively) is about 30%. It is seen from Table I that for polystyrene and epoxy polymer films $\bar{h} << 0.5\ \mu\text{m}$. It is evident that at such roughness the question about its influence on the wetting hysteresis may not even be discussed. For fluoroplast, the value of $\bar{h}$ is in the critical region. However, for this film there is direct evidence for the lack of a roughness effect on the wetting hysteresis (see Fig. 1 and its description).

TABLE I
Calculation of values of $\bar{h}$ by Eqs. 10–12 for films under test

i	Film material	n_D^*	r_i/r^F%	SQR($\lvert\ln(r/r^F)_i\rvert$)	$\bar{h}$ mkm
1	PTFE	1.375	13	1.092	0.29
2	PS	1.5901	80	0.205	0.05
3	epoxy polym.	1.59	76	0.305	0.08

*from Ref. 37.