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(Journal of the Korean Chemical Society)
Vol. 23, No. 4, 1979
Printed in the Republic of Korea

용융 고분자간의 계면장력에 대한 이론적 예측

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한국과학원 화학과

(1979. 5. 1 접수)

Theoretical Estimation of Interfacial Tension between Molten Polymers

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(Received May 1, 1979)

요 약. 특성구조액체이론(significant structure theory of liquids)에 입각하여, 섞이지 않는 두 용융 고분자중에서의 계면장력을 예측하는 간단한 계산방법을 연구하였다. 접착에너지는 응집에너지들의 기하평균과 보정항의 곱으로 표시되며, 응집에너지는 고분자 사슬의 격자상을 가정하므로써 계산된다. 계면장력을 계산함에 있어서 고분자사슬의 구성요소간 분산력(dispersion force) 외에 극성력(polar force)를 포함시켜야 함이 확인되었다.

ABSTNACT. A simple method to calculate the interfacial tension between two immiscible molten polymers has been developed. The theory is based on the significant structure theory of liquids. The energy of adhesion is expressed as a geometric mean of the cohesion energies multiplied by correction factor (Φ_{12}), $\Delta E_{12}=\Phi_{12}\sqrt{\Delta E_{11}\Delta E_{22}}$. In the calculation of ΔE_{11} and ΔE_{22}, a quasilattice of polymer chains has been assumed. It is assured that, besides the dispersion force, the polar force interactions between polymer constituent groups should be considered in the calculation of the interfacial tensions.

INTRODUCTION

Knowledge of surface and interfacial tension can provide informations on the intermolecular forces and structural characterestics of condensed matters. The surface tension of molten polymers against air has been a subject of both experimental and theoretical studies[1~8], and the interfacial tension between two immiscible molten polymers has been measured for various polymeric materials[8~10]. We have, recently, examined the surface tension of amorphous polymers based on the significant structure theory of liquids[11]. Using the same framework, we now evaluate the interfacial tension between two molten polymers.

Since the interfacial tension is the difference between the free energy of the interfacial layer and that of the bulk, both the energy and entropy terms must be considered if one is to obtain a complete picture of the interfacial region. The energy term is attributed to the

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fact that a molecule (or chain constituent group) experiences a modified configurational energy due to the replacement of some fraction of its near neighbors by different molecular species at the interface. And also, a molecule (or the chain constituent group) at the interface occupies a modified free volume due to the replaced constraining neighbors, thus the entropy term may arise.

In the calculation of the interfacial tension for molten polymers, the two main assumptions are employed:

(i) the boundary between two phases is sharp, and the two different flat monomolecular layers at the boundary only contribute to the interfacial tension;

(ii) the free volume of a chain constituent group in the boundary layer is equal to the one in the interior.

Assumption (i) is based on the analogy of the monolayer approximation in calculation of surface tension for simple liquids[22]. For the liquid-air interfacial system (*i. e.*, the liquid surface), surface molecules (or chain constituent groups) experience enhanced freedom of movements due to the loss of some fraction of constraining nearest neighbors.[11] For the molecules at the liquid-liquid interface, the freedom of movements is not enhanced so much as the surface molecules due to the new constraining neighbors in one direction, thus the assumption (ii) is introduced.

Ignoring the entropy effect according to the assumption (ii), the interfacial tension γ_{12} is expressed in terms of the energy of adhesion per unit area for the interface between the phases 1 and 2, ΔE_{12}, and the energy of cohesion per unit area for each phases, ΔE_{11} and ΔE_{22},

$$\gamma_{12}=\frac{\Delta E_{11}}{2}+\frac{\Delta E_{22}}{2}-\Delta E_{12} \qquad (1)$$

A diagram of the process for thermodynamic definition of ΔE_{11}, ΔE_{22}, and ΔE_{12} are illustrated in *Fig.* 1. It has been recognized by Girifalco and Good[12] that the energy of adhesion is given by the geometric mean of the energy of cohesion multiplied by a correction factor Φ_{12},

$$\Delta E_{12}=\Phi_{12}(\Delta E_{11}\Delta E_{22})^{1/2} \qquad (2)$$

And they derived the expression for Φ_{12} using a quasi-continuum model of condensed phase,

$$\Phi_{12}=\frac{A_{12}}{(A_{11}A_{22})^{1/2}}\ \frac{d_{11}d_{22}}{d_{12}^{2}} \qquad (3)$$

Here, A_{11} and A_{22} are the inverse sixth power dispersion coefficients for molecular species 1 and 2 respectively, A_{12} is the dispersion coefficient for the interaction of molecular species 1 and 2; d_{11}, d_{22}, and d_{12} are the equilibrium separation distances between the two semi-infinite bodies of individual phases respectively. The problem is, then, reduced to the calculation of ΔE_{11} and ΔE_{22} for the molten polymeric systems through an appropriate model.

THEORY

The significant structure theory of liquids[13,14] has been widely applied. In this theory, the liquid is regarded as having a quasi-lattice structure in which the sites are occupied by

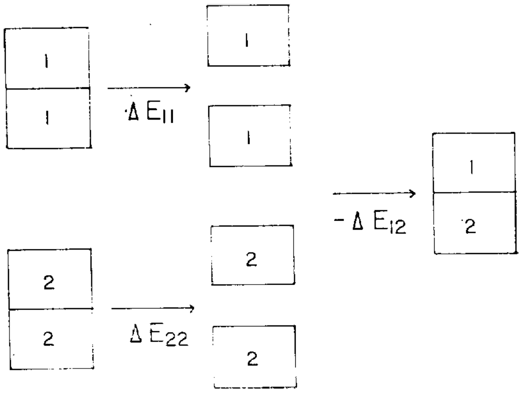

Fig. 1. A diagrammatic definition of energy of cohesion and adhesion.

molecules or by fluidized vacancies. Because these fluidized vacancies are moved about cooperatively by neighboring molecules jumping into them, a vacancy confers gas-like degrees of freedom on three vibrational degrees of freedom. If V is the molar volume of the fluid system and V_s measures molar volume occupied by molecules, then a vibrating molecule moves into a vacancy on $\frac{V-V_s}{V}$ of its excursions, conferring gas-like properties on this fraction of the degrees of freedom. Thus, a mole of liquid behaves as though it were made up of $N\frac{V-V_s}{V}$ gas molecules and $N\frac{V_s}{V}$ solid-like. Let us consider a surface of the liquid, whose area is Ω. If the surface is composed of M lattice sites, $M\frac{V_s}{V}$ sites are occupied by molecules and the remaining sites are occupied by fluidized vacancies. Since the fluidized vacancies confer gas-like properties on the neighboring moles, $M\frac{V_s}{V}$ molecules in the surface behave as though they were made up of $M\frac{V_s}{V}\ \frac{V-V_s}{V}$ gas molecules and $M\frac{V_s}{V}\ \frac{V_s}{V}$ solid-like. Per unit area of the surface, there are $\frac{1}{w}\ \frac{V_s}{V}\ \frac{V-V_s}{V}$ molecules of gas-like, and $\frac{1}{w}\left(\frac{V_s}{V}\right)^2$ molecules of solid-like, where $w\left(=\frac{\Omega}{M}\right)$ is the area occupied by a molecule.

In order to apply the model of significant liquid structures to the polymeric systems, we regard a chain molecule as being built up of identical repeating constituent groups neglecting end group effect. The size of a repeating constituent group is taken as a principal structural unit (*i.e.*, monomer unit), and assumed to be a mass point. Each repeating constituent group contributes to the lattice modes with its one-dimensional degree of freedom independently and contributes to the internal vibrations (*i.e.*, stretching and bending modes of the chain skeleton) with its remaining two dimensional degrees of freedom[15]. Therefore, the fluidized vacancies confer one dimensional gas-like degree of freedom on the neighboring chain constituent group.

Assuming that the gas-like properties of chain constituent group in the surface (or the interface) are not different from that in the bulk, the number of repeating constituent group in the surface, which are practically important to the interfacial tension, is then $\frac{1}{w}\left(\frac{V_s}{V}\right)^2$ where w is the area occupied by one monomer unit at the surface. Thus, the energy of cohesion can be expressed as

$$\varDelta E_{11}=\frac{1}{w_1}\left(\frac{V_{s1}}{V_1}\right)^2[\phi_1'-\phi_1] \tag{4a}$$

$$\varDelta E_{22}=\frac{1}{w_2}\left(\frac{V_{s2}}{V_2}\right)^2[\phi_2'-\phi_2] \tag{4b}$$

Here, ϕ_i' and ϕ_i represents the configurational energy of a constituent group in the surface and in the bulk respectively, the subscripts 1 and 2 denotes the different polymer species.

CALCULATION

The experiments of neutron scattering[16] and light scattering[17] from amorphous polymers have shown the persistence length (10~15Å) of chain segments and the existence of short range correlations due to packing of chain molecules, although no evidence of long range orientational order has been found. But the equilibrium properties of a condensed amorphous system depend inherently on the interaction energy between the objects which constitute the system. Since the interaction diminishes rapidly as the objects are distant apart from each other, one should consider a short range structure of the objects to evaluate to interaction energy. Thus, a lattice arrangement of solid-like chain constituent group, which follow a parallel alignment in the bulk and surface state, can be assumed (see *Fig.* 2.). From the assumed lattice model, and assuming the Lennard-Jones (6~12) potential, we have obtained the followings[11],

$$V_{si}=N\sigma_{0i}a_i^2 \tag{5a}$$

$$w_i=\sigma_{0i}a_i \tag{5b}$$

$$\phi_i=4\varepsilon_i\left(\frac{a_i}{\sigma_{0i}}\right)\left[3.1633\left(\frac{\sigma_i}{a_i}\right)^{12}-5.8869\left(\frac{\sigma_i}{a_i}\right)^{6}\right] \tag{5c}$$

$$\phi_i'=4\varepsilon_i\left(\frac{a_i}{\sigma_{0i}}\right)\left[2.3552\left(\frac{\sigma_i}{a_i}\right)^{12}-4.2201\left(\frac{\sigma_i}{a_i}\right)^{6}\right] \tag{5d}$$

where a_1 : the nearest neighboring distance between the polymer chain, σ_{0i} : distance between the neighboring monomer units in the same chain, ε_1 and σ_1 : Lennard-Jones(6~12) potential parameters.

Hence, by substituting the Eqs. (5a), (5b), (5c), and (5d) into the Eqs. (4a) and (4b) the energy of cohesion is written immediately as

$$\Delta E_{11}=\beta_1^{-3/2}\frac{\sigma_1^4}{(V_1/N)^2}\varepsilon_1[7.1072\beta_1^{5/2}-3.2324\beta_1^{11/2}] \tag{6a}$$

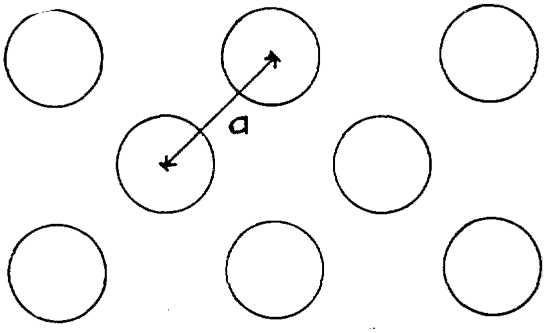

Fig. 2. A lattice arrangement of solid-like polymer chains.

$$\Delta E_{22}=\beta_2^{-3/2}\frac{\sigma_2^4}{(V_2/N)^2}\varepsilon_2[7.1072\beta_2^{5/2}-3.2324\beta_2^{11/2}] \tag{6b}$$

where

$$\beta_i=\frac{N\sigma_{0i}\sigma_i^2}{V_{si}}$$

The dimensionless parameter, β_i, has the same meaning of the Askadskii's packing coefficient[18] of the solid-like. The value $\beta_i=0.98$ best fits the experimental surface tensions of various molten polymers over a wide range of temperature[11].

An approximate method of estimating the (6~12) potential parameters, $\frac{\varepsilon}{k}$ and σ, for polymer constituent groups has been proposed by Davis[5]. His empirical formulas correlate the $\frac{\varepsilon}{k}$ and σ with the polarizability α and dia magnetic susceptbility χ as follows:

$$\ln(\sigma^2-5.4)=1.456+0.797\ln(\alpha\times10^{24}) \tag{7a}$$

$$\ln\left(\frac{\varepsilon}{k}\frac{\sigma^6}{10^4}\right)=-0.1445+1.1148\ln(-\alpha\chi\times10^{30}) \tag{7b}$$

The polarizabilities and diamagnetic susceptibilites are obtainable by adding atomic or partial group contributions from tables given by Van Krevelen[19]. In *Table* 1, the group values of α, χ, $\frac{\varepsilon}{k}$, and σ are summarized.

On the basis of the functional dependence of Eq. (7b) and the Kirkwood-Müller eqation, the expression for Φ_{12}, also, is proposed by Davis[5], *i.e.*,

$$\Phi_{12}=\frac{d_{11}d_{22}}{d_{12}^2}\left\{\frac{2(\alpha_1\chi_1\alpha_2\chi_2)^{1/2}}{(\alpha_1\chi_2+\alpha_2\chi_1)}\right\} \tag{8}$$

For the equilibrium d_{11}, d_{22}, and d_{12}, we assume the followings;

$$d_{12}=C\frac{d_{11}+d_{22}}{2} \tag{9a}$$

$$\frac{d_{11}}{d_{22}}=\frac{\sigma_1}{\sigma_2} \tag{9b}$$

where C is a proportional constant. At first sight, one might expect the value of C to be unity, however, the incompatibility of the two chemically dissimilar polymers suggests that the proportional constant must be somewhat larger than unity. The Eq. (8) is, rereduced to

$$\Phi_{12}=\left(\frac{1}{C}\right)^2\frac{4\sigma_1\sigma_2}{(\sigma_1+\sigma_2)^2}\left[\frac{2(\alpha_1\chi_1\alpha_2\chi_2)^{1/2}}{(\alpha_1\chi_1+\alpha_2\chi_1)}\right]^{1.1148} \tag{10}$$

With the aids of Eqs. (1), (2), (6a), (6b), (10), aad the value $\beta_i=0.98$, the equation for interfacial tension is rewritten as

$$\gamma_{12}=1.995\left\{\frac{\sigma_1^4}{2V_1^2}\left(\frac{\varepsilon_1}{k}\right)+\frac{\sigma_2^4}{2V_2^2}\left(\frac{\varepsilon_2}{k}\right)-\left(\frac{1}{C}\right)^2\right.$$
$$\frac{4\sigma_1\sigma_2}{(\sigma_1+\sigma_2)^2}\left[\frac{2(\alpha_1\chi_1\alpha_2\chi_2)^{1/2}}{\alpha_1\chi_2+\alpha_2\chi_1}\right]^{1.1148}$$
$$\left.\times\frac{\sigma_1^2\sigma_2^2}{V_1V_2}\left(\frac{\varepsilon_1}{k}\right)^{1/2}(\varepsilon_2/k)^{1/2}\right\} \tag{11}$$

Here, σ_i's in Angstroms, and V_i's are in cm^2/mole. Calculations are carried out for 19-pairs of molten polymers in order to get the optimum value of the parameter C. When the value $\left(\frac{1}{C}\right)^2=0.96$ is taken, the Eq. (11) predicts the interfacial tensions at 150 °C within ±2.9 dyne/cm. In the calculations the observed molar volumes of molten polymers, which are shown in *Table* 1, are used. The results are given in *Table* 2.

Obviously, we have considered only dispersion interactions for the polymers whose constituent groups have permanent dipole moments. A rigorous treatment of the polar interaction in the polymeric system is quite difficult due to the complexity of the restricting force on the dipolar rotations. Neverthless, one can consider the simplified treatment of the polar force contributions to the interfacial tension assuming a free rotation of dipoles. In the case of freely rotating dipoles, any fixed orientation of the dipole persists for a very short period of time,

Table 1. Constituent group values for polarizabilities, molar diamagnetic susceptibilities, (6~12) potential parameters, dipole moments, and molar volumes at 150 °C.

Polymer constituents segments	$\alpha\cdot 10^{24}$ (cc)	$-\chi\cdot 10^5$ (cgs)	σ (Å)	ε/k (°K)	μ^a (Debyes)	V^b (cm^3/mole)
$-\mathrm{CH_2}-\mathrm{CH_2}-$	3.68	22.8	4.19	225	0	36.1
$-\mathrm{CH(CH_3)}-\mathrm{CH_2}-$	5.49	34.1	4.70	275	0	54.0
$-\mathrm{C(CH_3)_2}-\mathrm{CH_2}-$	7.32	45.4	5.13	306	0	66.3
$-\mathrm{CH(C_6H_5)}-\mathrm{CH_2}-$	13.4	75.9	6.27	321	0.59	104.9
$-\mathrm{CH(O}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH_3)}-\mathrm{CH_2}-$	8.01	48.5	5.29	308	1.78	79.4
$-\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{C}}}(\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{OCH_3})-\mathrm{CH_2}-$	9.81	58.5	5.65	317	1.60	88.5
$-\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{C}}}(\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{OC_4H_7})-\mathrm{CH_2}-$	15.3	92.6	6.57	351	1.57	145.9
$-\mathrm{CH_3}-\mathrm{CH_2}-\mathrm{O}-$	4.34	27.3	4.38	251	1.30	42.8
$-\mathrm{Si(CH_3)_2}-\mathrm{O}-$	7.39	47.0	5.15	316	0.24	85.4

[a] Referencce (21); [b] References (6), (8) and (9).

Table 2. Comparison of calculated interfacial tension with experimental values.

Polymer pairs	γ_{12}(dyne/cm) at 150 °C		
	Calc. (I)	Calc. (II)^b	Exp.^{c}
Poly(ethylene) *vs.*			
Poly(propylene)	4.5	3.5	1.1
Poly(styrene)	8.1	7.1	5.7
Poly(vinyl acetate)	6.0	7.2	9.8
Poly(methyl methacrylate)	6.5	6.5	9.5
Poly(*n*-butyl methacrylate)	10.1	9.6	5.2
Poly(ethylene oxide)	4.2	6.1	5.4
Poly(dimethyl siloxane)	7.2	6.7	5.4
Poly(propylene) *vs.*			
Poly(styrene)	5.5	4.6	5.1
Poly(dimethyl siloxane)	4.7	4.3	3.0
Poly(isobutylene) *vs.*			
Poly(vinyl acetate)	4.0	5.2	7.4
Poly(dimethyl siloxane)	5.1	4.7	4.3
Poly(styrene) *vs.*			
Poly(vinyl acetate)	4.2	5.2	3.7
Poly(methyl methacrylate)	3.8	3.7	1.6
Poly(dimethyl siloxane)	5.2	4.7	6.0
Poly(vinyl acetate) *vs.*			
Poly(*n*-butyl methacrylate)	3.9	4.2	2.8
Poly(dimethyl siloxane)	3.2	3.3	7.4
Poly(methyl methacrylate) *vs.*			
Poly(*n*-butyl methacrylate)	4.0	3.6	1.8
Poly(ethylene oxide) *vs.*			
Poly(dimethyl siloxane)	6.1	6.6	9.8
Poly(dimethyl siloxane) *vs.*			
Poly(*n*-butyl methacrylate)	3.3	2.8	3.8

^{a}Calculated from Eq. (11); ^{b}Calculated from Eq. (13); ^{c}References (8), (9) and (10).

and the average interaction energy between two dipoles is[20]

$$\varphi_{12}{}^{(p)}=-\frac{2\mu_1{}^2\mu_2{}^2}{3kTr_{12}{}^6} \tag{12}$$

with conventional notations. Inclusion of this term of dipolar interaction to the Lennard-Jones (6~12) potential energy expression results the following interfacial tension equation with the same procedure described in the ref. (11) and preceding section.

$$\begin{aligned}\gamma_{12}=1.995\Big\{&\frac{\sigma_1{}^4}{2V_1{}^2}\Big(\frac{\varepsilon_1}{k}+1.53\times10^7\frac{\mu_1{}^4}{\sigma_1{}^6T}\Big)\\&+\frac{\sigma_2{}^4}{2V_2{}^2}\Big(\frac{\varepsilon_2}{k}+1.53\times10^7\frac{\mu_2{}^4}{\sigma_2{}^6T}\Big)\\&-\Big(\frac{1}{C}\Big)^2\frac{4\sigma_1\sigma_2}{(\sigma_1+\sigma_2)^2}\,\frac{\sigma_1{}^2\sigma_2{}^2}{V_1V_2}\Big[\Big(\frac{\varepsilon_1}{k}\Big)^{1/2}\Big(\frac{\varepsilon_2}{k}\Big)^{1/2}\\&\Big(\frac{2(\alpha_1\chi_1\alpha_2\chi_2)^{1/2}}{\alpha_1\chi_2+\alpha_2\chi_1}\Big)^{1.1148}+1.53\times10^7\frac{\mu_1{}^2\mu_2{}^2}{\sigma_1{}^3\sigma_2{}^3T}\Big]\Big\}\end{aligned} \tag{13}$$

Here, σ_i's are in Angstoms, μ_i's are in Debyes, V_i's are in cm^3/mole, and T is the absolute temperature. The paramete C is readjusted, and the value $\left(\frac{1}{C}\right)^2=0.97$ predicts the interfacial tension at 150 °C within ±2.3 dyne/cm. The dipole moments of chain constituent groups are taken as the values of gaseous monomer molecules, and are shown in *Table* 1. The results are given in *Table* 2, and are compared with the experimental values.

DISCUSSION

The present work provides a semi-qualitative method for predicting the interfacial tension between two different polymer liquids. The model of significant liquid structures is employed to formulate the interfacial tension-equation. If the additional polar force interactions besides the dispersion-force interactions are included, better agreements between the calculated and observed values are achieved as shown in *Table* 2. This fact implies that the polar force interactions should be considered in the calculations of interfacial tensions for the polymers having permanent dipole moments in their constituent group, as well as the dispersion force interaction.

It may seems surprising that the values of ε/k and σ evaluated by a very crude method, and the assumption of freely rotating dipoles predict the interfacial tensions so well. In the case where the hydrogen bonding occurs, the term which represents the hydrogen bonding effect is to be added.

ACKNOWLEDGEMENT

One of the authors (M. S. Jhon) express appreciation to Korea Science and Engineering Foundation for the financial support to continue U. S-Korea Cooperative Research.

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