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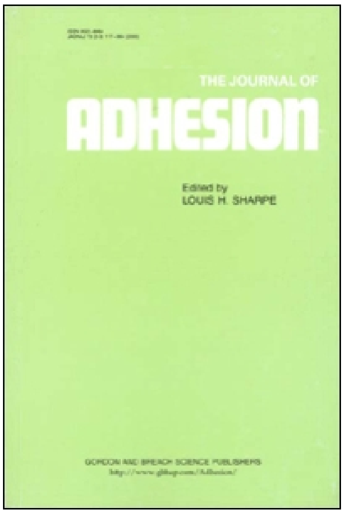

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Temperature Dependence of Wetting: n-Hydrocarbons on Perfluorinated Ethylene-Propylene Copolymer

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ABSTRACT

The contact angles, as a function of temperature, of n-hydrocarbons on a perfluorinated ethylene-propylene copolymer are computed using the Fowkes approach to interfacial phenomena. Provided certain reasonable assumptions are made, the computed contact angles agree quite well with the experimental values of Johnson and Dettre.

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INTRODUCTION

CONSIDERABLE interest has been generated in the recent literature in the temperature dependence of the contact angle (θ) of simple liquids on polymeric solids [1-5]. It has been shown that at moderately low temperatures, the change in contact angle as a function of temperature is small and negative [1-5]. Recently, Johnson and Dettre [6] have found that at elevated temperatures (vicinity of boiling points), both n-octane and n-hexadecane tend to spread on a perfluorinated ethylene-propylene copolymer. Although no detailed explanation for the reduction in contact angles was attempted, it was stated that the Fowkes approach to interfacial phenomena was not suited to explain these data.

The purpose of this paper will be to demonstrate that the Fowkes formulation can explain adequately the observed contact angles of the n-hydrocarbons on the perfluorinated ethylene-propylene copolymer at elevated temperatures, provided certain reasonable assumptions are made.

Assume

1. The n-hydrocarbons and the fluorocarbon polymer are immiscible at all temperatures.
2. Spreading pressures are essentially zero.
3. The surface of the polymer is amorphous (i.e., supercooled liquid).

With the above assumptions and a knowledge of the temperature dependence of the surface tensions of both n-hydrocarbons and fluorocarbon polymer, the contact angles can be computed using the Fowkes-Young equation. The calculated contact angles agree quite well with those reported by Johnson and Dettre [6].

Surface Structure of Fluorocarbon Polymer

To permit a quantitative explanation of the temperature dependence of the contact angle of a liquid on a solid polymer surface, a knowledge of the surface structure of the polymer at all temperatures is mandatory. Without knowledge of the surface structure, analysis is hopeless.

Based on the now extensive data for the melt surface tensions (γ_{LV}) of polymers [7] and the correlation of these data with the critical surface tension of wetting (γ_C), the author proposed [8] that for melt-crystallized polymers

$$\gamma_{SV}{}^{d} = \gamma_C = \gamma_{LV} \tag{1}$$

where the superscript d refers to the dispersion component of the surface free energy. This is true for non-polar polymers where only dispersion forces are operative. Obviously, when $\gamma_{LV}{}^{d} \neq \gamma_{LV}$, Eq. 1 is no longer valid. From the above correlations, the surface layer of melt-crystallized polymers is concluded to be essentially amorphous. Roe [9] and Lee, Muir and Lyman [10] have shown that to obtain reasonable agreement between γ_C and the parachor, the amorphous density of the polymer must be used. A more detailed examination of the surface structure of polymers is presented elsewhere [7]. Based on the above reasoning, we conclude that the surface layer of the perfluorinated ethylene-propylene copolymer is amorphous at both ambient and elevated temperature.

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Surface Tensions of n-hydrocarbons

Surface tension data for the n-hydrocarbons are well known up to 150°C [11]. Beyond 150°C, use is made of the well known Katayama-Guggenheim expression [12] relating γ_{LV} and T. Here

$$\gamma_{LV} = \gamma_{LV}{}^{o}(1\text{-}T/T_C)^{11/9} \tag{2}$$

where T_C is the critical temperature, and $\gamma_{LV}{}^{o}$ is the surface tension at 0°K. Since the T_C values for the n-hydrocarbons up to C_{20} are known, γ_{LV} vs T profiles can be obtained. Figure 1 depicts these data for a variety of n-hydrocarbons.

Surface Tension of Fluorocarbon Polymer

To estimate the surface tension versus temperature profile for the perfluorinated ethylene-propylene copolymer, several approximations are necessary. An estimate of the critical temperature can be made if the surface

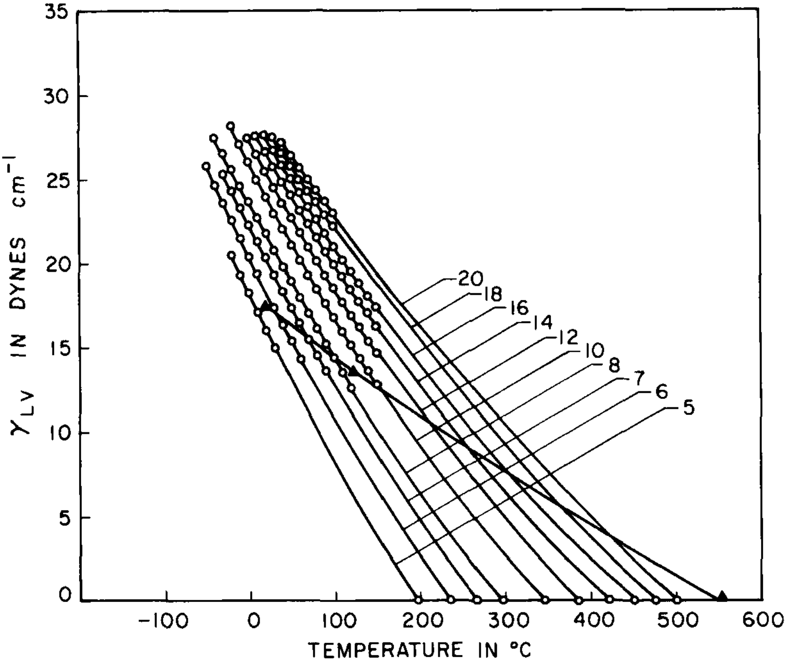

Figure 1. The surface tensions of both n-hydrocarbons and perfluorinated ethylene-propylene copolymer are plotted as a function of temperature.
○—n-hydrocarbons
△—perfluorinated ethylene-propylene copolymer

tension at two temperatures are known, then,

$$\frac{(\gamma_{LV})_1}{(\gamma_{LV})_2}=\frac{(1\text{-}T_1/T_C)^{11/9}}{(1\text{-}T_2/T_C)^{11/9}}$$

or

$$\frac{(\gamma_{LV})_1}{(\gamma_{LV})_2}=\left(\frac{T_C\text{-}T_1}{T_C\text{-}T_2}\right)^{11/9} \tag{3}$$

At 20°C, the value of γ_C or γ_{LV} equals 17.5 dynes/cm. To obtain a value of γ_{LV} at a higher temperature, we use the data of Sutula et al [13], which involves the variation of θ with temperature for n-hexadecane on the fluoropolymer, and the Fowkes-Young Equation.

A combination of the Young's equation

$$\gamma_{SV}=\gamma_{SL}+\gamma_{LV}\cos\theta \tag{4}$$

and the Fowkes equation

$$\gamma_{SL}=\gamma_{SV}+\gamma_{LV}-2\,(\gamma_{SV}{}^{d}\gamma_{LV}{}^{d})^{1/2} \tag{5}$$

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yields, neglecting spreading pressures,

$$\cos\theta = 2\,\frac{[\gamma_{SV}{}^{d}\gamma_{LV}{}^{d}]^{1/2}}{\gamma_{LV}} - 1. \tag{6}$$

For n-hydrocarbon as the wetting liquid, $\gamma_{LV}{}^{d} = \gamma_{LV}$. Equation 6 then reduces to simply

$$\cos\theta = 2\left[\frac{\gamma_{SV}{}^{d}}{\gamma_{LV}}\right]^{1/2} - 1. \tag{7}$$

Further, since $\gamma_{SV}{}^{d}$ equals $(\gamma_{LV})_p$, where p refers to the polymer, we have

$$\cos\theta = 2\left[\frac{(\gamma_{LV})_p}{\gamma_{LV}}\right]^{1/2} - 1. \tag{8}$$

Sutula et al [13]. found $\left(\frac{\partial\theta}{\partial T}\right) \cong -0.05°/°\text{C}$ for temperatures up to 150°C, a value consistent with the results of Whalen and Wade [14] for n-hexadecane on another perfluorinated polymer, polytetrafluoroethylene. Using Eq. 8 and the data of Sutula et al [13]. a value of γ_{LV} is calculated for $T = 120°\text{C}$. When this is incorporated into Eq. 3 a value for the critical temperature of the fluorocarbon polymer is computed. The T_C is computed to be 828°K. This is consistent with the value determined for polyethylene [15]. The estimated surface tension data for the fluorocarbon polymer are plotted in Figure 1.

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Contact Angles of n-hydrocarbons on Fluorocarbon Polymer

Johnson and Dettre [6] have observed (Figure 2) that in a particular temperature region the apparent value of θ approaches zero. As stated earlier, it was suggested that the Fowkes scheme was not applicable. However, if the values of θ are computed as a function of temperature, using the data of Figure 1 incorporated into Eq. 8, excellent agreement is obtained (Figure 2). In fact, the estimated intersections of the γ_{LV} vs T lines correspond closely to those obtained by Johnson and Dettre [6]. When $(\gamma_{LV})p = \gamma_{LV}$, assuming no miscibility, zero spreading pressure, amorphous polymer surface, and only dispersion forces operative between the polymer and the wetting liquid, the contact angle of any n-hydrocarbon on the fluorocarbon polymer may be estimated by using Eq. 8 and the γ_{LV} vs temperature plots. It is interesting to note that n-pentane should form finite contact angles at temperatures well below room temperatures. In light of the extreme difficulty in obtaining contact angle data at elevated temperatures, agreement between the data and the Fowkes-Young approach is quite satisfactory.

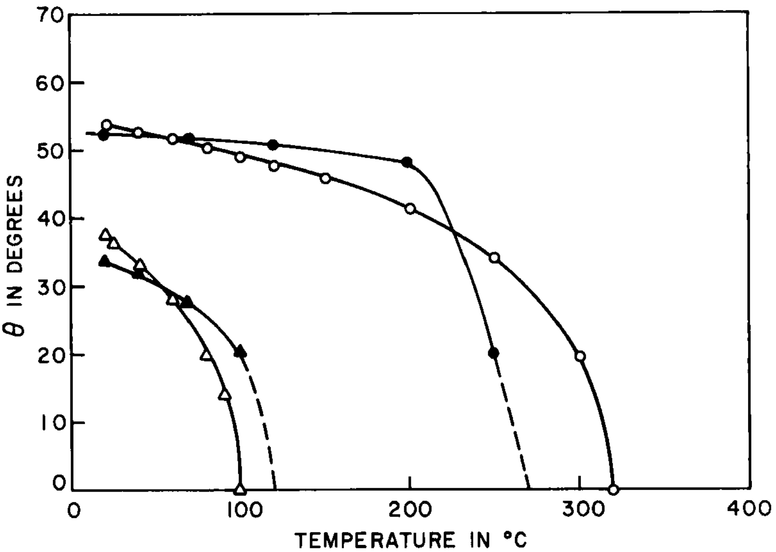

Figure 2. Both the measured and calculated contact angles are plotted as a function of temperature.

●—n-hexadecane-fluoropolymer: experimental
○—n-hexadecane-fluoropolymer: calculated
▲—n-octane-fluoropolymer: experimental
△—n-octane-fluoropolymer: calculated

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