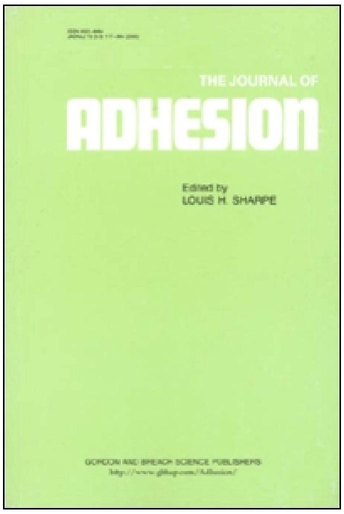

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Adhesion of Polymer Blends
I. Phenomenological Model

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A phenomenological model based on the Takayanagi approach is proposed to describe the adhesion of polymer blends to a solid support. The model consists of three elements corresponding to two components of the blend and a solid surface. The conditions for failure of the adhesion joints at the interface between the solid surface and the polymer blend are found to depend on the blend composition and the moduli and adhesion joint strength of each component to the solid.

KEY WORDS: Polymer blend adhesion; Takayanagi model; adhesive failure; phenomenological model; viscoelasticity; failure.

INTRODUCTION

In spite of the great importance of polymer blends as adhesives, coatings and matrices for composite materials there are no data available to date addressing the theoretical description of adhesion at a polymer blend-solid interface. A first attempt has been made to estimate the thermodynamic work of adhesion, $W_{(AB)C}$ of polymer blends AB to solid C using the values for thermodynamic work of adhesion of each component A and B, W_{AC} and W_{BC}:

$$W_{(AB)C} = \varphi_A W_{CA} + \varphi_B W_{CB} \tag{1}$$

where the φ are volume fractions of components A and B in the blend.

In eq. (1), W_{CA} and W_{CB} are not necessarily equal to the work of adhesion of the pure component, but are the work of adhesion of the phases A and B evolved due to the phase separation in the system under the influence of a solid surface. In this case, both phases A and B are composed of both components.[1] The compositions of phases evolved during phase separation depend on the conditions of the adhesion joint formation, which generally proceeds as a non-equilibrium process.

However, there is a great distinction between the thermodynamic work of adhesion and adhesion joint strength. The aim of this paper is to estimate in a qualitative form the behaviour of the adhesion joint formed by a polymer blend. For this purpose we have used a simplified mechanical model of Takayanagi type.[2]

THE MODEL

To analyze the adhesion of blends and alloys we have used a traditional Takayanagi model modified to account for the presence of a solid surface (filler). It is known that Takayanagi model is used to describe mechanical behavior of two-component mixtures of polymers with different distributions of one component in a matrix of the other. The real structure of a mixture is substituted by a model (see upper part, Fig. 1) where there are two regions of component A and B. The values λ and ϕ are parameters of a model chosen in such a way that $\lambda\phi = \varphi_B$, the volume fraction of component B. These values may be changed arbitrarily at the same amount of phase B to present different distributions of component B in matrix A. For this case, according to Takayanagi,[2] the modulus of elasticity of the model is expressed as

$$1/E_T = \frac{\Phi}{\lambda E_B + (1-\lambda)E_A} + \frac{(1-\Phi)}{E_A} \tag{2}$$

or

$$E_T = (1-\lambda)E_A + \frac{\lambda E_A E_B}{E_A \Phi + E_B(1-\Phi)} \tag{3}$$

The choice of equation depends on the ratio of the moduli, $E_A:E_B$, and on the values of the parameters Φ and λ. To determine the values of the parameters λ and Φ we assume that component B is inserted into the matrix of component A as a cube with the edge length "b", whereas component A is also cube-shaped with the edges of length "a". In

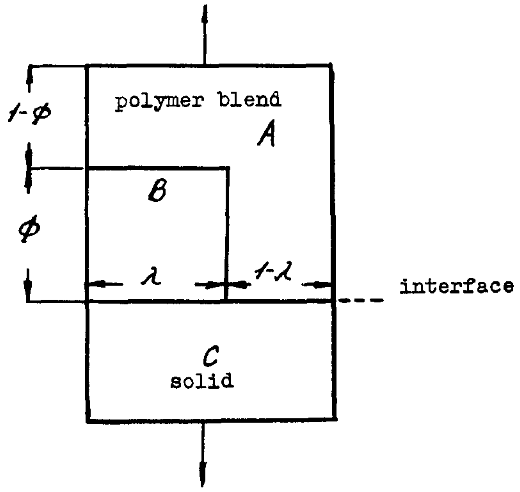

FIGURE 1 Modified Takayanagi model for adhesion of polymer blend AB to solid. Upper part is traditional model for AB blend. This part is adhered to solid C.

such a model the volume of the b component is $V_B = b^3$, and of the A component is $V_A = a^3 - b^3$. The volume concentration of component B is $\varphi_B = V_A/(V_A + V_B) = b^3/a^3$. For the plane Takayanagi model, which is equivalent to the three-dimensional one, the parameter $\Phi = b/a$ and, therefore, $\Phi = \varphi^{1/3}$. Correspondingly, $\lambda = b^2/a^2 = \varphi_B^{2/3}$. To describe the adhesion joint strength we introduce into the traditional model a third element, a modelling solid, C, (Fig. 1) and corresponding parameters characterizing the interfacial interaction. Component A possesses a modulus of elasticity, E_A, and adhesion strength wth solid C equal to σ_{AC}. The adhesion strength and modulus of component B are σ_{BC} and E_B, respectively. It is also assumed that there exists adhesion interaction with streangth, σ_{AB}, between components A and B. The adhesion strength between solid and blend is equal to σ_{TC}.

For this modified model we define the adhesion joint strength between the blend AB and solid C as an average stress at which the solid C and blend AB are fully separated. Deformation of the model in the direction of the arrows (Fig. 1) may result in sequential separation of the blend components. Separation of one of the components proceeds when the local stress in one of the components is equal to the stress corresponding to the adhesion strength. After separation of one of the components, the stresses are redistributed and the load is concentrated on the adhesion contacts of the second component. If this new stress exceeds the strength of the adhesion of the second component, full separation proceeds. In this case, the adhesion strength σ_{TC} is equal to the stress at which the first component is debonded.

If after debonding of the first component the redistributed stress is not sufficient to destroy the adhesion contacts of the second component, the adhesion strength is determined by the stress at which the second component debonds.

The model for failure of the adhesion joint assumes that the process proceeds at the stresses when the viscoelastic behavior of the polymer alloy may be approximately described by the Takayanagi model. This supposition is valid only if we assume that the adhesion joint strength is much less than cohesive strength of the alloy. For the cases of nonlinear behavior of one or both components of the alloy the calculation become more complicated and requires more sophisticated equations. However, the principle of the calculations remains the same. Various combinations of component characteristics may be considered, each resulting in a different σ_{TC}.

RESULTS OF CALCULATIONS

Calculations of adhesion strength for the model have been performed for three cases.

Case 1. $E_A > E_B$ and $\sigma_{BC} > \sigma_{AC}$. In this case, the stress in the parts of the model which are deformed in parallel will increase the fastest at the interface between A and C. Debonding begins at this interface at the deformation $\varepsilon_A = \sigma_{AC}/E_A$ (Hooke's law). The stress in the model is $\sigma_T = \varepsilon_T E_T$. As $\varepsilon_T = \varepsilon_A$ the modulus may be calculated according to Equation (3), so that the value σ_T corresponding to the debonding of component A may be expressed as

$$\sigma_T = (\sigma_{Ac}/E_A)\left[(1-\lambda)E_A + \frac{\lambda E_A E_B}{\Phi E_A + (1-\Phi)E_B}\right] \tag{4}$$

Substituting values of λ and Φ expressed in terms of a model φ_B in Equation (4) yields:

$$\sigma_T = (1 - \varphi_B^{2/3})\sigma_{AC} + \frac{\varphi_B^{2/3} E_B}{\varphi_B^{1/3} E_A + (1 - \varphi_B^{2/3}) E_B} \tag{5}$$

If, after component A is debonded, the stress at the B-C interface is higher than σ_{BC}, full debonding of the blend from solid C will occur. In this case $\sigma_{TC} = \sigma_T$ according to Equation (5). The descending parts of curves 1 and 2 in Figure 2 correspond to this equation. It is seen that at given values of E_A, E_B, σ_{AC} and σ_{BC}, the increase in concentration of component B, having higher adhesion strength as compared with component A, leads to a decrease in σ_{TC}. This behavior seems to be paradoxical, but may be explained by the fact that the predominant contribution to adhesion strength belongs to component A. As φ_B increases, the magnitude of σ_{TC} diminishes with φ_A. The reduction in adhesion accompanies the increase in φ_B up to full debonding of the blend from the solid C. At high φ_B, component B becomes capable of taking the increased load after component A debonds. In this case, further debonding of component B requires an increase in load up to the stress at the B/C interface equal to the value of σ_{BC}. The stress may be calculated as an additive sum of stresses in both parts of the model:

$$\sigma_T = \sigma_B \lambda + \sigma_A (1 - \lambda) \tag{6}$$

When debonding of component B begins, component A is already debonded and does not contribute any resistance to further debonding ($\sigma_A = 0$), in which case

$$\sigma_{TC} = \sigma_{BC} \lambda = \sigma_{BC} \varphi_B^{2/3} \tag{7}$$

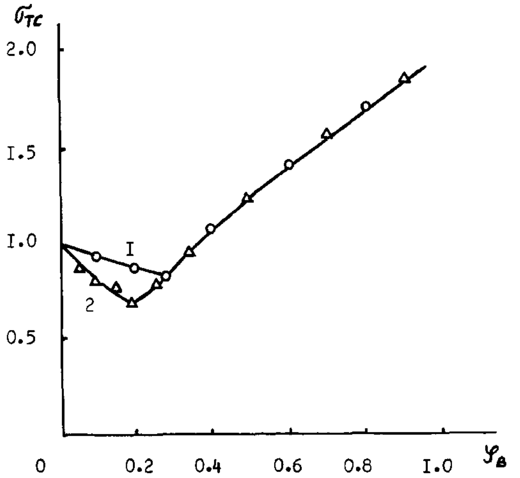

FIGURE 2 Calculated dependencies of the strength of adhesion joints on the concentration of component B at $E_A > E_B$ and $\sigma_{AC} < \sigma_{BC}$. Curve 1: $E_A = 2$, $E_B = 1$, $\sigma_{AC} = 1$, $\sigma_{BC} = 2$; curve 2; $E_A = 10$, $E_B = 1$, $\sigma_{AC} = 1$, $\sigma_{BC} = 2$ (here, and in other figures, values moduli and stresses are given in conventional units)

Thus, at high φ_B, σ_{TC} is determined solely by the properties of component B (Fig. 2, ascending parts of curves 1 and 2).

Case 2. Consider the case when $E_A > E_B$ and $\sigma_{AC} > \sigma_{BC}$. The growth of stresses induced by deformation of the model proceeds faster in component A. However, as $\sigma_{AC} > \sigma_{BC}$, the sequence of component debonding depends on the ratio of elastic moduli and the adhesion strength of the components with the solid. Using the same consideration as in Case 1, the functional dependence of $\sigma_{TC}(\varphi_B)$ has been calculated for various modulus ratios. Some results are provided in Figure 3. If the moduli and adhesion strength of components are comparable, this dependence is almost additive (curve 1). If $E_A \gg E_B$ and $\sigma_A \approx \sigma_B$, σ_{TC} decreases rapidly with φ_B to some minimum (which may be lower than σ_{BC}) and then increases again up to σ_{BC}. The principal reason for the predicted minimum seems to reflect the nonuniformity of the stress of the system state: the greater the difference in component moduli, the more pronounced the nonuniformity. One of the components appears to become overstressed, whereas the other remains understressed. After the failure of the overstressed component, the understressed component is not capable of resisting concentrated stress. With increasing φ_B, the fraction of component A diminishes along with its contribution to σ_{TC}. This decrease proceeds until the concentration of B increases sufficiently so that component B becomes capable of bearing the concentrated stress. After this point, the growth of σ_{TC} proceeds due to increasing contribution of component B to the adhesion strength.

Case 3. Consider now the variations of the model in which the component with higher modulus is distributed in the medium of lower modulus, *i.e.* $E_A < E_B$. Deformation of the system is described by Equation (2) because the rigid B component plays a role of

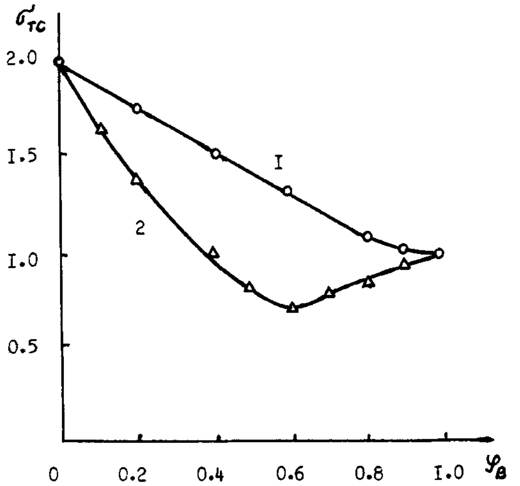

FIGURE 3 Calculated dependencies $\sigma_{TC} = f(\varphi_B)$ at $E_A > E_B$ and $\sigma_{AC} > \sigma_{BC}$: $1 - E_A = 2$, $E_B = 1$, $\sigma_{AC} = 2$, $\sigma_{BC} = 1$; $2 - E_A = 10$, $E_B = 1$, $\sigma_{AC} = 2$, $\sigma_{BC} = 1$.

"would-be-shunt" for the parallel part of component A. Parallel deformation of both parts leads to faster stress growth in component B. If $\sigma_{BC} < \sigma_{AC}$ debonding begins in part B after reaching the stress σ_{BC}. The corresponding deformation of part B will be $\varepsilon_B = \sigma_{BC}/E_B$ and the same deformation will be also observed in the parallel part A. The stress on part A will be $\sigma_A = \varepsilon_A E_A = \sigma_{BC} E_A/E_B$. Taking into account the parameters of the model, we can find the additive stress at the failure of the joint:

$$\sigma_{TC} = \lambda\sigma_{BC} + (1-\lambda)\sigma_{BC}\frac{E_A}{E_B} = \sigma_{BC}\left[\varphi_B^{2/3} + (1-\varphi_B^{2/3})\frac{E_A}{E_B}\right] \tag{8}$$

As in the preceding cases, debonding of one of the components leads to a stress concentration on the other. In the case under consideration, the component A will determine the strength σ_{TC} at small φ_B. Full debonding will take place only when the stress in part A reaches σ_{AC}. As component B is already debonded at the B/C interface, $\sigma_{BC} = 0$ and consequently

$$\sigma_{TC} = \sigma_{BC}\lambda + \sigma_{AC}(1-\lambda) = (1-\varphi_B^{2/3})\sigma_{AC} \tag{9}$$

Equation (9) describes the function $\sigma_{TC}(\varphi)$ at small φ_B. Only after decreasing φ_A up to some limit, depending on the ratios E_A/E_B and σ_{AC}/σ_{BC}, the AC part of the model will be broken simultaneously with the BC part. Then $\sigma_{TC}(\varphi)$ is again described by Equation (8). This combined behavior is illustrated in Figure 4. The increase in φ_B of the high-modulus component distributed in medium A and poorly bonded with solid leads to the sharp decrease of σ_{TC} up to the level below σ_{BC}, followed by an increase in σ_{BC} with increasing φ_B.

If $E_B > E_A$ and $\sigma_{BC} > \sigma_{AC}$, the minimum of $\sigma_{TC}(\varphi_B)$ may not appear as is seen from Figure 5, where calculated data are presented for a given set of component parameters.

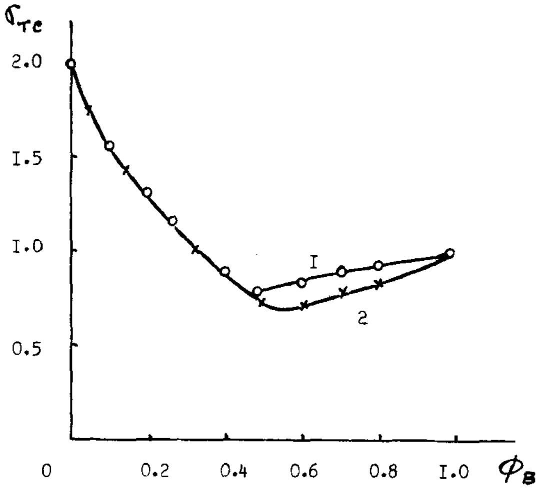

FIGURE 4 Calculated dependencies $\sigma_{TC} = f(\varphi_B)$ at $E_A < E_B$ and $\sigma_{AC} > \sigma_{BC}$. 1: $E_A = 1$, $E_B = 2$, $\sigma_{AC} = 2$, $\sigma_{BC} = 1$; 2: $E_A = 1$, $E_B = 10$, $\sigma_{AC} = 2$, $\sigma_{BC} = 1$.

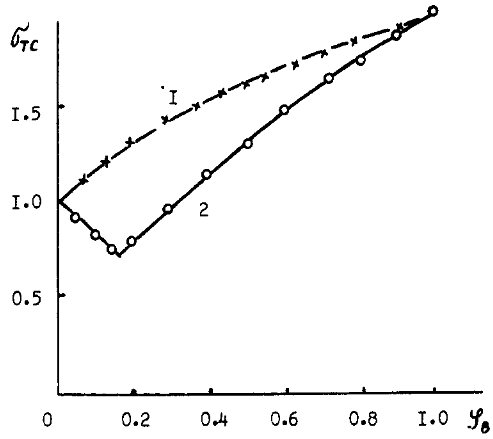

FIGURE 5 Calculated dependencies $\sigma_{TC} = f(\varphi_B)$ at $E_A < E_B$ and $\sigma_{AC} < \sigma_{BC}$. 1: $E_A = 1$, $E_B = 2$, $\sigma_{AC} = 1$, $\sigma_{BC} = 2$; 2: $E_A = 1$, $E_B = 10$, $\sigma_{AC} = 1$, $\sigma_{BC} = 2$.

In particular, when $E_A/E_B = \sigma_{AC}/\sigma_{BC}$ (curve 1, Fig. 5), σ_{TC} monotonically increases as φ_B is increased.

CONCLUSION

The results of several calculations using the Takayanagi model for a two-component polymer blend at the blend-solid interface demonstrate that the adhesion joint strength depends on the modulus of each blend component, their ratio and their adhesion strength to the surface. Calculations have been performed assuming the elasticity of the model. Since the processes leading to failure of adhesion joints generally proceed in the region of nonlinear viscoelasticity, deviations from the trends established here are expected. The results of some experimental studies which facilitate a comparison with theoretical will be presented in a subsequent communication.

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