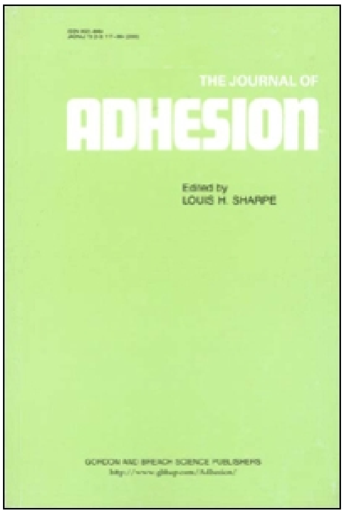

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Effect of Substrate on the Properties of Polymer Alloys and Blends

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The thermodynamic aspects of the influence of the solid surface on the properties and adhesion of polymer blends and alloys are discussed. It is shown that under the influence of the surface the properties and composition of the interphase may be changed. The effects are explained by the influence of the surface on the phase equilibrium in compatible and incompatible blends.

KEY WORDS interphase, polymer alloys and blends, adhesion of compatible and incompatible polymers, thermodynamic work of adhesion.

INTRODUCTION

The interaction between solid surfaces and polymer molecules leads to the essential changes in the properties of surface polymer layers. These changes are connected with conformational restrictions imposed by the surface which influences the packing density in the surface layer, molecular mobility, and relaxation.[1,2] In 1972, Sharpe[3] used the term "interphase" to describe the transition zone between the surface of a substrate and the bulk of a polymer that is cured or solidified against this substrate. The same zone, which plays an important role in determining the properties of composite materials, was called a "mesophase" by Theocaris.[4]

Using these terms one has to keep in mind that this region is not a phase in a true thermodynamic sense but a nonequilibrium state and its properties depend on the distance from the surface. There are many data for properties of the polymer interphase in various systems, including reinforced and filled polymers.[2,4] However, up to now the structure of an interphase which is formed by polymer alloys or blends has not yet been studied thoroughly.

In discussing this problem one should bear in mind the effects of the surface on the properties of the interphase, typical for one-component and one-phase systems, which already have been rather well explained. In addition, phenomena connected with the selectivity of the interaction between various components of the polymer alloy or blend and with the influence of the surface on the phase equilibrium in the surface layer should also be considered.

1 Thermodynamic Approach

Let us consider some simple thermodynamic relations. The free energy of mixing two different polymers ΔG_m may be approximated as

$$\Delta G_m = RT\,\chi_{AB}\,\psi_A\psi_B \tag{1}$$

where χ_{AB} is the thermodynamic interaction parameter and ψ_A and ψ_B are volume fractions of polymers A and B. For a binary mixture, we can express the change in the free energy of the system by adsorption or adhesion as

$$\Delta G_m = \Delta G_{AS} + \Delta G_{BS} - \Delta G_{AB} \tag{2}$$

where ΔG_{AS} and ΔG_{BS} are the changes in free energy of mixing of polymers A and B with active centers of the surface and ΔG_{AB} is the free energy of mixing two polymers. The thermodynamically stable system is formed if $\Delta G_m<0$. Two cases can be distinguished.

Case 1. The interaction of each component with the surface is symmetric, i.e., the energies of pair interactions are approximately equal. In this case

$$\Delta G_{AS} \approx \Delta G_{BS} \tag{3}$$

If ΔG_{AS} and ΔG_{BS} have negative values and the components are incompatible ($\Delta G_{AB}>0$) then ΔG_m is negative. In this case, adsorption of both components at the interface takes place and promotes adhesion. For compatible polymers ΔG_{AB} has a negative value and adsorption will proceed only if

$$| -\Delta G_{AS} - \Delta G_{BS} | > | -\Delta G_{AB} | \tag{4}$$

This means that adsorption and adhesion would be preferential if the polymer mixture is noncompatible. These relations are valid independent of the fraction of polymer A or B interacting with the surface.

For symmetric interaction there is no selective adsorption and the composition of the mixture in the interphase is the same as in the bulk.

Case 2. The interactions are nonsymmetric.

$$\Delta G_{AS} \gtrless \Delta G_{BS} \tag{5}$$

In this case, if the sum ($\Delta G_{AS} + \Delta G_{BS}$) is negative and the components are incompatible, there will be selective adsorption of one of the components. The composition of the interphase will differ from the bulk. Preferential adsorption is equal to increasing the motive power for phase separation of two incompatible polymers. The interphase is enriched in component A if $-\Delta G_{AS} > -\Delta G_{BS}$ and vice versa.[6]

For compatible mixtures with nonsymmetric interactions for adsorption and adhesion the following relation should be valid:

$$| \Delta G_{AS} + \Delta G_{BS} | > | \Delta G_{AB} | \tag{6}$$

Thus, simple thermodynamic analysis allows the conclusion to be drawn that for binary polymer mixtures the promotion of adhesion will be achieved more easily for incompatible mixtures.

These considerations are consistent with experimental data which show the enrichment or depletion of a surface layer in one of the components of the binary mixture. As a result of changing the composition of the system, a component's compatibility in the interphase may increase or decrease. One of the important factors here is also the redistribution of polydispersed components between the surface and the bulk.

The second reason for the changing compatibility is the difference in conditions of interaction between two polymers due to conformational restrictions in the interphase and in the bulk.[5]

2 Influence of the Substrate on the Properties of the Interphase Formed by a Polymer Blend or Alloy

To make the discussion clear we introduce the following thermodynamic definitions.

We classify as polymer alloys, binary polymer mixtures which have an upper critical solution temperature and form a one-phase system in the melt. On solidification of these systems, phase separation takes place according to a spinodal or nucleation mechanism.

We classify as polymer blends, binary polymer mixtures which do not form a one-phase system in the melt as they have a lower critical solution temperature. In the case of polymer alloys applied to the surface as a melt it is important to take into account not only the change in composition but the effect of the substrate on the completeness of phase separation in binary polymer mixtures. It was shown earlier[6] that the addition of fillers to a binary polymer mixture may change the shape and position of the phase diagram. For a filled binary mixture of poly(vinyl acetate) (PVA)-poly(methyl methacrylate) (PMMA) introducing particulate filler results in a considerable shift of the cloud point curves to higher temperatures.

Thus the solid surface influences the phase equilibrium in the system. If so, one should also observe the effect of the surface layer thickness and substrate nature both on the phase separation temperature and on the kinetics of phase separation. We have studied the phase separation temperatures and kinetics for thin films of a PVA-PMMA binary mixture applied to two substrates—silanized and nonsilanized glass. Films of various compositions and thicknesses were used. The phase separation temperature was determined from the intensity of scattered light.

Figure 1 shows the dependence of the phase separation temperature on film thickness for various substrates. There are two phase separation temperatures for film thicknesses >5 μm on the non-silanized glass. Films applied to a silanized glass regardless of their thickness, exhibited only one phase separation temperature. These results can be accounted for as follows. The relaxation processes in the surface or adsorption layers are known[2] to be more impeded than those in the bulk. For the system studied, one also observes the selective adsorption of PVA at the interface[7] which changes the composition in the surface layer as compared with the initial one.

Reich and Cohen[8] ascribed the variation of the phase separation temperature for a polystyrene-poly(vinyl ether) system in a thin layer to both of these factors—relaxation and selective adsorption. It follows that a possible cause for the appear-

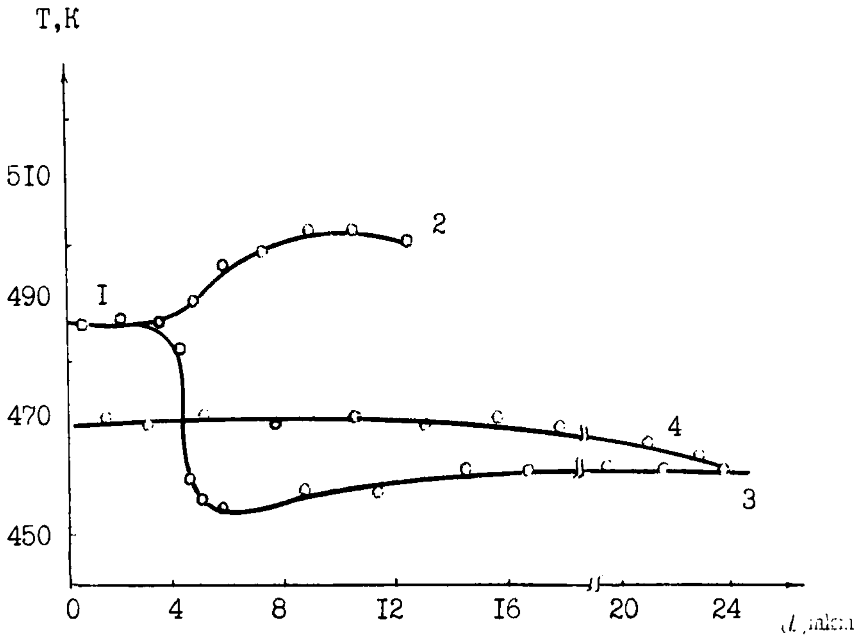

FIGURE 1 Temperature of phase separation of 0.7/0.3 PVA/PBMA mixture on nonsilanized[1,2,3] and silanized[4] glass as a function of the film thickness.

ance of the "second" temperature of phase separation may be due to a changing composition near the interface and to a considerable impediment of relaxation processes in the boundary layer. As the film thickness decreases, the fraction of the boundary layer in the overall film thickness rises, and hence very thin films may be considered to consist of the boundary layer alone having a composition which differs from the average composition of the film. At greater thicknesses, the boundary layer fraction is smaller and the phase separation primarily in the bulk is observed.

On the other hand, on a silanized glass surface, i.e., on a low energy surface, the probability of formation of a boundary layer with properties substantially different from those in the bulk is low, and therefore only one phase separation temperature should be observed.

The slowing down of relaxation processes in the boundary layer also diminishes the phase separation rate. As can be seen from Figure 2, the value of the concentration fluctuation "amplification factor" (2R (β)) drops sharply as the film thickness decreases below 20 μm. The results for silanized glass in Figure 2 are not explained.

Thus, for polymer alloys the structure of the interphase should strongly affect the conditions of phase separation. For a polymer alloy applied to the solid surface we are dealing with a more complicated structure of the interphase as compared with a one-phase system.

When a molten polymer blend is applied to a surface the former has a two-phase structure as the blend has a LCST according to the definitions given above. In this case by solidification there may proceed only the process of transition to a one-phase system. Usually this process is hindered by high viscosity and never is

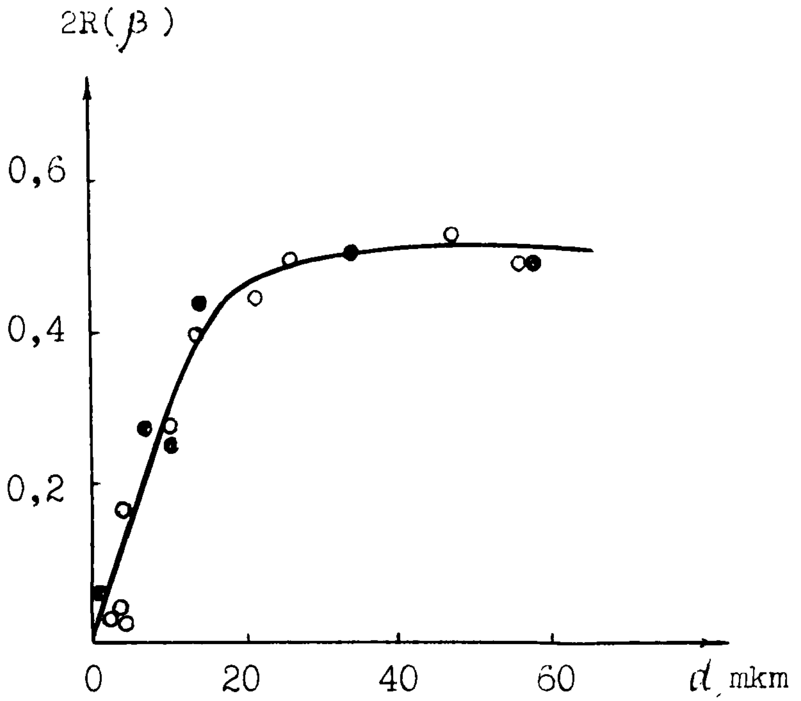

FIGURE 2 Amplification factor 2R (β) as a function of the film thickness for 0.7/0.3 PVVA/PMBA mixture on nonsilanized (○) and silanized (●) glass at 482 K.

completed. The completeness of this transition will be less the stronger the interaction between the surface and blend components.

Pronounced changes in structure by solidification of polymer blends were not observed as compared with polymer alloys.

3 Adhesion of Polymer Blends and Alloys

Earlier using some thermodynamic relations we have established[9] that in the absence of specific interactions between the surface and adhesive, the thermodynamic work of adhesion W_A is given by

$$W_A = W_C = 2\gamma_l \tag{7}$$

where W_c is the thermodynamic work of cohesion of the polymer adhesive and γ_l is its surface tension. Later[10] it was shown that this equation is valid only if W_c is taken to be the cohesion energy of the interphase. For polymer blends and alloys, according to the model of the interphase formed by polymer mixture,[5] we should have

$$W_A = \psi_A W_{CA} + \psi_B W_{CB} \tag{8}$$

where W_{CA} and W_{CB} are the cohesion energies of two phases and ψ_A and ψ_B are their volume fractions. In equation (8) W_{CA} and W_{CB} are not equal to the cohesion energies of pure components, but correspond to the values for the equilibrium composition of the two evolved phases. The composition of phases evolved during phase separation, which as a rule, proceeds under non-equilibrium conditions for the polymer pair, depends on the conditions of phase separation.[5] Thus, the thermodynamic work of adhesion of binary polymer system depends not only on the ratio of components in the system but also on the composition of two phases which may be different depending on the conditions of phase separation. As the substrate surface influences the phase separation process, adhesion at the polymer blend or polymer alloy/substrate interface will depend on the conditions of adhesive joint formation.

CONCLUSION

The substrate surface influences the structure of the interphase for binary polymer systems due to changes in composition of the interphase as compared with the bulk and due to its effect on the phase separation by adhesive joint formation. The thermodynamic work of adhesion in this case depends on the composition and ratio of two evolved phases. Thermodynamic analysis shows that the conditions for better adhesion will be realized if the polymer pair is noncompatible.

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