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Evaluation of the extent of interfacial debonding in polymer blends

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A proposed evaluation of the extent of interfacial debonding in binary blends is based on the comparison of tensile (or yield) strength with model predictions. The predictive scheme employs a two-parameter mechanically equivalent model and data on the phase continuity of constituents acquired from percolation theory. The upper and lower bounds of strength are related, respectively, to interfacial adhesion sufficient ($A = 1$) and insufficient ($A = 0$) for stress transmission between constituents. The values of A in the interval $0 < A < 1$ are interpreted in terms of partial debonding of the fractions of constituents formally coupled in series.

(Keywords: polymer blends; interfacial debonding; interfacial adhesion)

INTRODUCTION

Adhesion between components is of basic importance for the mechanical properties of heterogeneous polymeric materials, e.g. particulate composites, fibre composites, blends, etc. At small strains, say below 1%, where a linear stress–strain relationship is usually observed, virtually all polymer systems show good interfacial adhesion sufficient for complete stress transmission without any debonding (dewetting). Thus, measurements of elastic properties can hardly give any direct evidence about the strength of interfacial adhesion S_a in such systems. However, elastic properties of particulate composites may reflect a decline in molecular mobility in part of the polymer matrix due to partial immobilization of chain segments adsorbed on the surface of filler particles[1–7]. The immobilized layer can then give rise to some peculiarities on the temperature dependence of reinforcement (relative modulus)[8,9]. As 'perfect' adhesion is tacitly presumed[10–12], no adhesion terms occur in the models for the elastic properties of particulate systems. It can only be presumed[1,2,6,9] that the thicker the immobilized layer the stronger the matrix–filler interaction, but quantitative information on S_a cannot be acquired.

In polymer blends the components are intermixed in a thin interphase layer along the interface[13–15]. The interphase volume fraction v_{ip} is proportional to the intermixed layer thickness and to the interface area in unit volume of a blend. If v_{ip} is high enough (which is quite exceptional) the presence of the interphase can be detected[16,17], e.g. as an 'intermediate' glass transition in the middle of the interval between the glass transitions of the constituents. In ordinary blends, the interphase does not perceptibly affect elastic properties, so that no relevant information on interfacial interaction can be obtained.

The shape of the stress–strain dependence of many polymer blends changes[10,18] in a conspicuous manner at higher strains, usually between 4 and 6%, when acting (tensile) stress exceeds the linearity limit and attains a value corresponding to the yield strength of the blend S_{yb}. No matter whether or not the material shows yielding, the stress–strain dependence finally achieves the stress at break for the blend S_{ub}. Both S_{yb} and S_{ub} are co-determined by interfacial adhesion of constituents[10,19,20]. Most of the models predicting yield or tensile strength of particulate systems assume either 'zero' or 'perfect' interfacial adhesion (corresponding to complete or negligible debonding), which is then related to the lower or upper bound of the considered strength. S_{yb} or S_{ub} of blends with poor interfacial adhesion are habitually estimated by means of simple formulae[10,21–24] (originally derived for particulate composites) reflecting the reduction of the effective cross-section of the load-transmitting matrix by the non-adhering particles of dispersed phase(s). The upper bound of S_{yb} or S_{ub} is sometimes approximated[25–27] by the rule of mixing. However, this rule generally holds for systems with components coupled in parallel and cannot be valid for isotropic heterogeneous systems.

There are probably only two models for the tensile strength S_{uc} of particulate systems encompassing S_a or a related term:

(i) Leidner and Woodhams[28] modified the shear lag analysis[29] of short-fibre composites to derive the following formula:

$$S_{uc} = (S_a + 0.83\tau_{um})v_d + S_a(1 - v_d)SCF \qquad (1)$$

where S_a is the strength of matrix–filler adhesion, τ_{um} is the shear strength of the matrix, v_d is the volume fraction of the dispersed phase (filler) and SCF is the stress concentration factor. We have found[30] that this equation

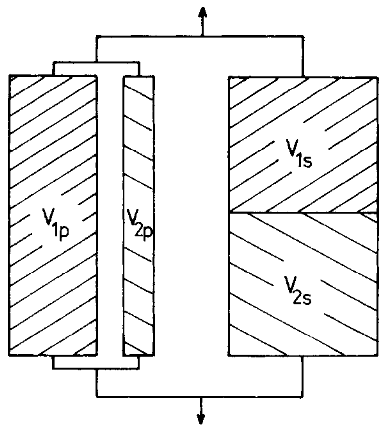

Figure 1 Equivalent box model (EBM) for a binary blend 60/40

fits (assuming $SCF = 1$) also the experimental data for the yield strength S_{yc} of functionalized polypropylene filled with calcium carbonate.

(ii) Pukanszky[31,32] combined a term expressing the matrix cross-section reduction (caused by a dispersed component) with an empirical exponential term encompassing a parameter B ($0 < B < 1$), which reflects the effects of the interfacial interaction, of the size and shape of dispersed particles, of their aggregation, etc.:

$$S_{\mathrm{uct}} = S_{\mathrm{umt}}(L/L_0)^n[(1 - v_{\mathrm{d}})/(1 + 2.5v_{\mathrm{d}})]\exp(Bv_{\mathrm{d}}) \quad (2)$$

where S_{uct} and S_{umt} are respectively the 'true' tensile strengths of the composite and of the matrix (related to the 'true' cross-section of the deformed specimen), L/L_0 is the relative elongation and n is a parameter characterizing the strain hardening of the matrix. Also, some attempts have been made to correlate the constants of empirical equations for yield (or tensile) strength with interfacial adhesion in particulate systems[33,34].

Equations (1) and (2) were derived and found adequate for systems with one component continuous (matrix) and another component dispersed, i.e. primarily for particulate composites. They are not convenient for polymer blends for at least two reasons: (i) they cannot allow for co-continuity of constituents (phase duality and phase inversion); (ii) they do not consider S_{u} (or S_{y}) of the second component, either dispersed or co-continuous.

In our previous papers[35,36] we have presented a predictive scheme for yield (or tensile) strength of binary blends based on a two-parameter mechanically equivalent box model (EBM) and data on the continuity of phases acquired from a formula for modulus rendered by percolation theory[37,38]. The objective of this communication is to utilize the proposed scheme for the evaluation of the extent of interfacial debonding at breaking (or yielding) of binary blends by comparing theoretical and experimental values of S_{ub} (or S_{yb}).

MODEL CONSIDERATIONS

In general, the elastic properties of isotropic heterogeneous materials cannot be accurately represented by means of a parallel or series model, but more complex models are needed (*Figure 1*) that combine the parallel and series couplings of components[11,39–42]. The blocks are presumed to have the mechanical properties of the corresponding components[40–44]; the dimensions of the blocks indicate which volume fractions of each constituent can be regarded as coupled in parallel or in series in relation to the acting force so that the EBM response to loading may be equivalent to that of the modelled system. EBMs are usually viewed as a convenient framework for a systematic phenomenological description of elastic behaviour of various systems; in such cases, their adjustable volume fractions are determined by fitting experimental data[44]. If EBM is to be used as a predictive model, its parameters (volume fractions of components formally coupled in parallel and in series) have to be determined beforehand with the aid of another model or theory.

We have shown in our previous papers[35,36] that a two-parameter EBM (*Figure 1*), which was previously used only for the discussion of elastic properties of blends[42], can be used for the prediction of S_{yb} or S_{ub}. However, EBM can be attempted only under a simplifying condition that the properties of the constituents are identical with those of the parent polymers. Obviously, EBM is not applicable for the prediction of mechanical properties of blends if the process of mixing accounts for a significant change in structure, e.g. in the degree of crystallinity, of a constituent. Similarly, EBM cannot encompass 'synergistic' effects or newly introduced mechanisms, e.g. enhancement of toughness due to multiple crazing induced in a matrix by elastomeric inclusions.

The following formula was derived[35,36] for yield and/or tensile strength of binary blends on the basis of the EBM given in *Figure 1* (in this paper we will use notation for tensile strength with regard to the following comparison with experimental data):

$$S_{\mathrm{ub}} = (S_{\mathrm{u1}}v_{\mathrm{1p}} + S_{\mathrm{u2}}v_{\mathrm{2p}}) + AS_{\mathrm{u1}}v_{\mathrm{s}} \quad (3)$$

where S_{u1} and S_{u2} stand for the tensile strength of the components 1 and 2, respectively; volume fraction v_{s} equals the sum ($v_{\mathrm{1s}} + v_{\mathrm{2s}}$). Two limiting cases of the tensile (or yield) strength of blends, which we will identify with the lower or upper bound, can be distinguished[35] by means of EBM:

(i) $A = 0$. In this case, the interfacial adhesion is so weak that complete debonding occurs (before rupture) between the fractions of constituents coupled in series (*Figure 1*); thus the series branch does not contribute to the resulting S_{ub}, which is therefore determined only by the parallel elements.

(ii) $A = 1$. In this case, the interfacial adhesion is strong enough to transmit acting stress between constituents so that no debonding precedes rupture; thus, the contribution of the series branch of EBM is added to that of the parallel elements. However, when two components differing in strength are coupled in series, it may be expected that the branch will fail at S_{u1} or S_{u2}, whichever is lower; thus, $S_{\mathrm{u1}} < S_{\mathrm{u2}}$ is assumed in equation (3).

The meaning of $0 < A < 1$ can easily be understood: A denotes that part of v_{s} which does not undergo interfacial debonding under acting break (or yield) stress and contributes to stress transmission between the constituents. This situation may occur because at a constant adhesion S_{a} (given, for example, by partial miscibility of components[19,20,45]) the stress necessary for the debonding of a spherical particle embedded in a matrix is inversely proportional to the particle radius[46,47]. As there is always a distribution of particle sizes in polymer blends[48], it may happen that the stress approaching the strength (tensile or yield) of a blend will cause debonding of larger particles, while smaller particles (more generally, interfaces of smaller diameter) will remain bound to the matrix. In reality, the rise of particle diameter can be brought about by raising the volume fraction of dispersed component[48–51], increasing interfacial energy[51–53], phase structure coarsening at elevated temperatures[54–56], etc. Thus observed changes in S_{ub} (or S_{yb}) may be more affected[35] by the changes in the phase structure than by the changes in S_a.

CALCULATION OF THE DEGREE OF PHASE CONTINUITY

The volume fractions encountered in EBM (*Figure 1*) can be calculated by means of the following formula[37] proposed by the percolation theory for the E modulus of a two-component system with a negligible contribution of the second component:

$$E = E_0(v - v_{cr})^T \tag{4}$$

where E_0 is a constant, v_{cr} is the critical volume fraction (the percolation threshold) and T is the critical universal exponent. It has been shown[38] for several binary blends that equation (4) is valid (from $v = v_{cr}$) up to $v = 1$, for which:

$$E_{01} = E_1/(1 - v_{1cr})^{T_1}$$

and

$$E_{02} = E_2/(1 - v_{2cr})^{T_2}$$

Assuming $E_1 >> E_2$ (or alternatively $E_2 >> E_1$), it holds for the EBM modulus (*Figure 1*) that $E_{1b} = E_1 v_{1p}$ (or $E_{2b} = E_2 v_{2p}$). Combining the latter expressions with equation (4), we obtain formulae for the volume fractions in *Figure 1*:

$$v_{1p} = [(v_1 - v_{1cr})/(1 - v_{1cr})]^{T_1}; \quad v_{1s} = v_1 - v_{1p} \tag{5a}$$

$$v_{2p} = [(v_2 - v_{2cr})/(1 - v_{2cr})]^{T_2}; \quad v_{2s} = v_2 - v_{2p} \tag{5b}$$

In the marginal region $0 < v_1 < v_{1cr}$ (or $0 < v_2 < v_{2cr}$), it holds that $v_{1p} = 0$ and $v_{1s} = v_1$ (or $v_{2p} = 0$ and $v_{2s} = v_2$). The theory[37,38] predicts $v_{cr} = 0.156$ for discrete spherical domains and $T = 11/6$ for the three-dimensional lattice. Experimental values[57] are in reasonable accord with predicted ones: $0.10 < v_{cr} < 0.22$, $1.7 < T < 1.9$. To perform the indicated calculations, v_{1cr}, v_{2cr}, T_1 and T_2 are to be adjusted.

RESULTS AND DISCUSSION

To utilize the outlined procedure for the evaluation of the A parameter we will employ experimental data[58] on the tensile strength of blends consisting of low-density polyethylene (LDPE) and poly(vinyl chloride) (PVC). This pair of polymers is known to be immiscible (incompatible) so that their interfacial adhesion is very low. *Figure 2* shows that S_{ub} actually coincides with the lower bound calculated from equation (3) for $A = 0$, i.e. complete interfacial debonding. The minimum value of S_{ub} is slightly shifted on the composition scale towards the component with lower S_u; we have shown[35,36] that such a shift is the larger the higher and difference between S_{u1} and S_{u2}.

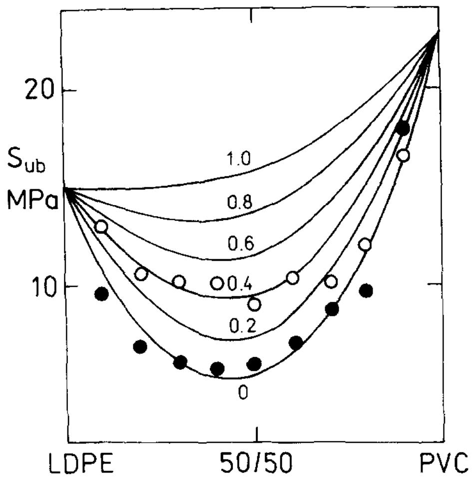

Figure 2 Comparison of tensile strength calculated from equation (3) with experimental data for LDPE/PVC blends[58]: (●) blends without DCP; (○) blends with 2% of DCP; values of A are given for each theoretical curve. Parameters used[38,57] in equations (5a) and (5b): $v_{1cr} = v_{2cr} = 0.2$, $T_1 = T_2 = 1.9$

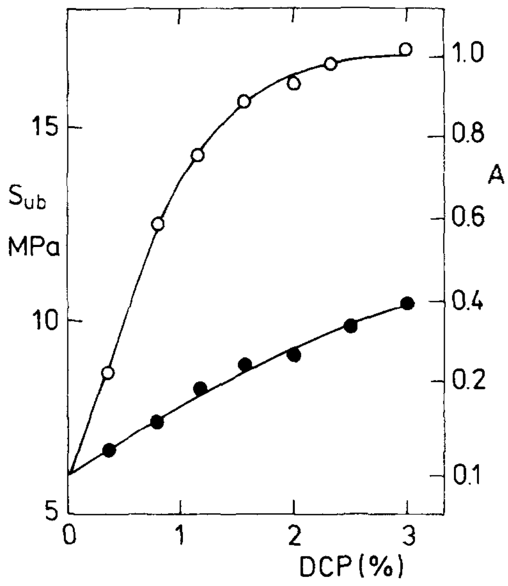

Figure 3 Effect of DCP concentration on tensile strength of LDPE/PVC = 40/60 blends. Experimental data[58]: (●) blends without NBR; (○) blends with 9% of NBR

In order to enhance the interfacial adhesion, Xu *et al.*[58] blended LDPE and PVC in the presence of dicumyl peroxide as a crosslinking agent. Their experimental data (*Figure 2*) approximately follow the curve calculated for $A = 0.4$, but only up to the volume fraction of PVC equal to 0.6; at a higher PVC content, the data approach the curve for $A = 0$. It is obvious that the interfacial adhesion has been somewhat strengthened in the co-crosslinked product, probably due to formation of crosslinks across the interface. However, as PVC is rather resistant to crosslinking, the effectiveness of the latter drops with rising content of PVC in the blends.

Figure 2 also reveals that all dependences for $A < 1$ pass through a minimum. Thus we can say that a minimum on the strength vs. composition plot is a symptom of partial debonding before the break (or yield) point is achieved. Only if experimental data fit the theoretical dependence calculated for $A = 1$ can it be assumed that no interfacial debonding has taken place.

To augment the effectiveness of the co-crosslinking process, Xu *et al.*[58] added a small percentage of acrylonitrile–butadiene rubber (NBR), which is compatible with PVC and increases the propensity of the PVC-rich phase for crosslinking. The data plotted in *Figure 3* indicate that S_{ub} and related A rise with the DCP content much faster for the blends containing NBR than for the original LDPE/PVC blend (without NBR). It is essential to note that S_{ub} of the former system attains the values corresponding to $A = 1$ (at 2% of DCP) while the latter blends achieve only $A = 0.4$ (for 3% of DCP). Thus it is evident that sufficient interfacial adhesion can be achieved owing to the NBR addition, which prevents interfacial debonding during the stress–strain experiments before the break point. The model prediction is also useful in that it allows us to assess whether or not the capacity of the system has been exploited. In *Figure 3* we can see that the theoretical upper bound ($A = 1$) is achieved at 2% of DCP; consequently, further increase in DCP concentration cannot bring any additional improvement.

CONCLUSIONS

The extent of interfacial debonding in binary blends can be evaluated by comparing the data on tensile (or yield) strength with model predictions. Parameter A introduced in the model expresses that part of the components formally coupled in series which does not undergo interfacial debonding at the break (or yield) stress. If some debonding occurs ($A < 1$), the strength vs. composition dependence passes through a minimum. Thus, the predictive scheme allows us to judge whether or not the interfacial adhesion is sufficient for achieving the theoretical upper bound at which the potential strength of a blend is fully utilized. In a system with controlled interfacial adhesion it is possible to decide which adhesion is sufficient for exploiting the strength of the constituents.

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