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The strength of the tailored polymer/inclusion interface in polymer composites evaluated *in situ* by acoustic emission

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Summary

A correlation between interface strength and data of acoustic emission measurements in particle filled polymer composites was found. The method allows the evaluation of the interface strength *in situ* in polymer composite specimens at uniaxial loading. The measurements have shown that the tailored interface with the monomolecular tethered polymer layers of various grafting density change the mechanism of microdefect formation.

Introduction

Adhesion between polymer matrix and an inclusion (particle and fibre filled polymers, polymer blends) has an important practical application. The strength of the polymer/inclusion interface can be improved by constructing interface layers of various architecture. Block, random and tethered (grafted) polymers were used to strengthen the model polymer/polymer and polymer/nonpolymer interfaces [1-6]. The limiting factor for the experimental investigation of the polymer/inclusion adhesion is the lack of a method for the direct measurement of the interface strength in composites. It is of a great importance to compare the fracture criteria obtained in the model systems of well defined crack-tip processes at the interface with the strength of the interface with the same chemical nature *in situ* in the polymer composite. Different tests were suggested to measure the interfacial strength *in situ* in composites: fiber fragmentation test [7], single fibre pull-out test [8], tensile dilatometry method [9, 10], acoustic emission (AE) method [11-13] and failure investigation in a single-particle composite [14,19]. It was shown [12,13] that the advantage of AE is a good statistical analysis of failure processes that is often required to get reliable data.

In this paper we report (1) about the possibility found to evaluate the interface strength in a particle filled composite on the basis of acoustic emission data presented by two parameters: a) a microscopic parameter - stress of debonding of a polymer matrix from an inclusion and b) a local (with respect to a local deformation process at the locus of failure) parameter, characterising the energy released due to the debonding process - acoustic emission amplitude. We report also (2) about data, that show the possibility to improve essentially the strength of the solid inclusion/polymer matrix interaction with a monomolecular layer of block copolymer at the interface, so that the failure mechanism is not predetermined by the debonding process at the interface.

Experimental

As a model composite we used polystyrene ($M_w = 2.8 \cdot 10^5$, $M_w/M_n = 2.3$) filled with glass beads with an size of 89 ± 2 μm. The surface of glass beads was covered by a different amount of poly(2-vinylpyridine-block-styrene) (PVP-b-PS) with molecular weight 6000 and 22000 of poly(2-vinylpyridine) (PVP) and polystyrene (PS) blocks respectively, synthesised by ionic polymerisation. All experiments and measurements were performed at a temperature of 20° *C*. The glass beads were dipped together with glass plates and Si-wafers in the toluene solution of PVP-b-PS of different concentrations to ensure the wide range of adsorbed layer regimes from single chain to densely packed brush. After 72 hours adsorption the beads, plates and wafers were separately taken out and rinsed several times with toluene. The plates were dried by dust clean nitrogen, and the beads on a ceramic filter in an air flow. Glass plates were used for asymmetric double cantilever beam (ADCB) test [2, 6], in which the interface fracture toughness between glass plate (covered by the copolymer) and PS film is measured in terms of the energy released when the crack tip is driven along the interface. A Si-wafer was used as a model substrate to evaluate the PVP-b-PS adsorption layer thickness by ellipsometry and the glass beads were used for the preparation of the filled PS composite (2% by volume) by melting under pressure. Dog-bone shaped specimens were cut out from the composite plates and annealed for two hours at 106° *C*.

The test specimens were uniaxial deformed with a Zwick 1445 tensile testing machine. The deformation speed was $1.2 \cdot 10^{-5}$ 1/*s* and constant for all tests. During each test the acoustic emission of the composites was monitored simultaneously on an AET Model 5500 system using a transducer with a resonance frequency of 325 *kHz* and a peak sensitivity of -65 *dB* (1*V*/μ*bar*). The detected signals were preamplified with a total gain of 60 *dB*. Before passing the signals to the signal processing unit of the AET 5500 they were finally amplified with 29.6 *dB*. An AE event was detected if the voltage signal passed a predefined threshold level. The end of the event is defined by the last threshold crossing. From this event the duration, the maximum amplitude ($A = 20 \cdot log\ (U/U_{ref})$, U is the signal voltage and U_{ref} is the reference voltage) and other parameters are recorded. Then the data were post-processed with custom made software.

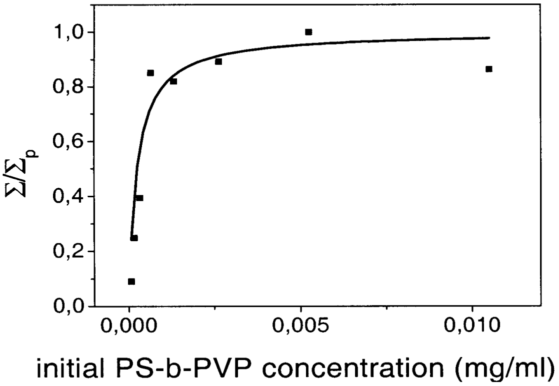

Figure 1: Normalised (by plateau chain density) adsorption isotherm of 5PVP-b-PS on the SI-wafer from toluene

Results and Discussion

The PVP-b-PS block copolymer adsorbs on the substrate by attaching of the PVP anchor blocks and the buoy PS blocks are exposed into the solution. The adsorption isotherm is depicted in Fig. 1 in terms of the chain density (Σ) normalised by the plateau value (Σ_p) vs. initial polymer concentration in the solution. For the used PVP-b-PS block copolymer with very short PVP blocks no association in toluene solution was detected by light scattering experiments [15]. We obtained (from the layer thickness measurement) the adsorbed chain density at the plateau of adsorption $\Sigma_p = 0.062\ nm^{-2}$, that is close to the value 0.04 nm^{-2} calculated from experimental correlation [16]. The surface density Σ_0 above which the PS blocks are overlapping and form a semidiluted solution on the surface can be evaluated as $\Sigma_0 = 1/\pi\ R^2_{PS} = 0.016\ nm$-2, where $R_{PS} = 0.186 \cdot N_{PS}^{0.595} = 4.5\ nm$ is the radius of gyration of the PS block in toluene. Therefore, at plateau adsorption the grafting density is 4 times higher than $\Sigma_{???}$ and from the presented isotherm it is clear that we investigated the adsorbed layer from a single adsorbed chain to a true brush regime, when the nonadsorbing PS blocks are stretched away from the adsorbing substrate.

It was well documented that grafted polymer interface layers improve polymer/polymer and polymer/nonpolymer adhesion [1-3], particularly PVP-b-PS was found to improve glass-polystyrene interface toughness [5,6]. The strengthening effect increases with the grafting density of the copolymer. In our investigation we supposed to detect this strengthening effect with the AE method directly in particle filled polymer composite.

It was shown elsewhere [11-13] that the measured AE signals from uniaxial loaded specimens of the polymer composite, filled with glass beads, correspond to debonding of the matrix from the glass bead surface. The experimental distribution function of the number of AE events per stress interval vs. stress and number of AE events vs. AE amplitude may be fitted with a Weibull distribution function. The cavitation process is characterised by two parameters: average debonding stress (σ_d) and maximum of the amplitude distribution (A_{max}) [12,13]. The meaning of these parameters is clear from Fig.2(a) and Fig.2(b), which are typical for all series of experiments. As can be seen from Fig.2(b) the cavitation process in the composites shows two A_{max}, the first peak at $A_{max1} = 32\ dB$, present in

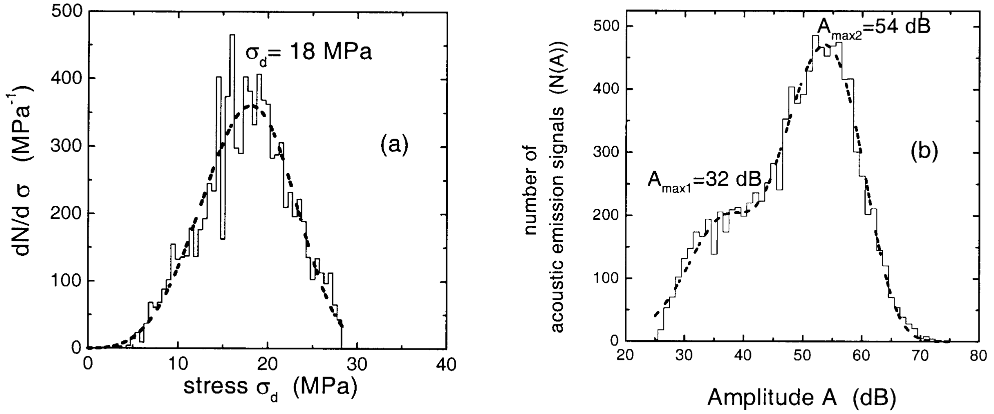

Figure 2: Data of AE experiments for the PS composites filled with glass beads and fit curves (dashed lines): (a) number of Ae events per stress intervall vs. stress ($\Sigma/\Sigma_p = 0.95$); (b) amplitude distribution ($\Sigma/\Sigma_p = 0.57$)

data obtained for all specimens. The second peak with A_{max2} values, depending on surface coverage (Fig.3b), corresponds to AE signals from the debonding process. This was proved by analysis of AE data (the dependence of amplitude distribution function from the stress) and registration of debonding by optical microscopy. No AE signals were detected in the unfilled PS before the fracture of the specimen. At the moment of the brake of the specimen the amplitude of AE signals was 32 *dB*. For the specimens with grafting density of PVP-b-PS higher than 0.060 nm^{-2} we also did not measure AE signals before the fracture of the specimen, and signals with $A_{max} = 32$ *dB* occur at the moment of the specimen brake. These data are the evidence that the filler with a poor adhesion to the PS matrix causes two types of microdefects: the cavities (debonding) at the interface and microdefects relevant to matrix crazing at the interface. When the adhesion is improved no microdefects were formed before the moment of fracture. In this paper we omit the explanation of the first A_{max1} and concentrate on the second A_{max2} which directly correlates with the interface strength.

The dependence between debonding stress and A_{max2} vs. normalised grafting density (Σ/Σ_p) is shown in Fig.3(a) and (b). The data of the control ADCB test are depicted in the Fig.3(c) as a dependence of interface fracture toughness vs. Σ/Σ_p. The control ADCB test was performed using the glass plate with adsorbed copolymer, as described elsewhere [5,6]. From comparison of the data it is clear that both parameters σ_d and A_{max2} are sensitive to interface strength and correlate with the fracture toughness of the interface, measured in the model experiment. From our point of view, the most interesting parameter is A_{max2}, which reflects a local micromechanics behaviour *in situ*. It is interesting to note that inverse behaviour is observed between debonding stress and A_{max2}. Taking into account the Griffith criterion of rupture [17]: $\Delta F = F_s - F_e \leq 0$ (ΔF is the change of free energy, F_s and F_e is the surface and mechanical elastic energy respectively) and comparatively

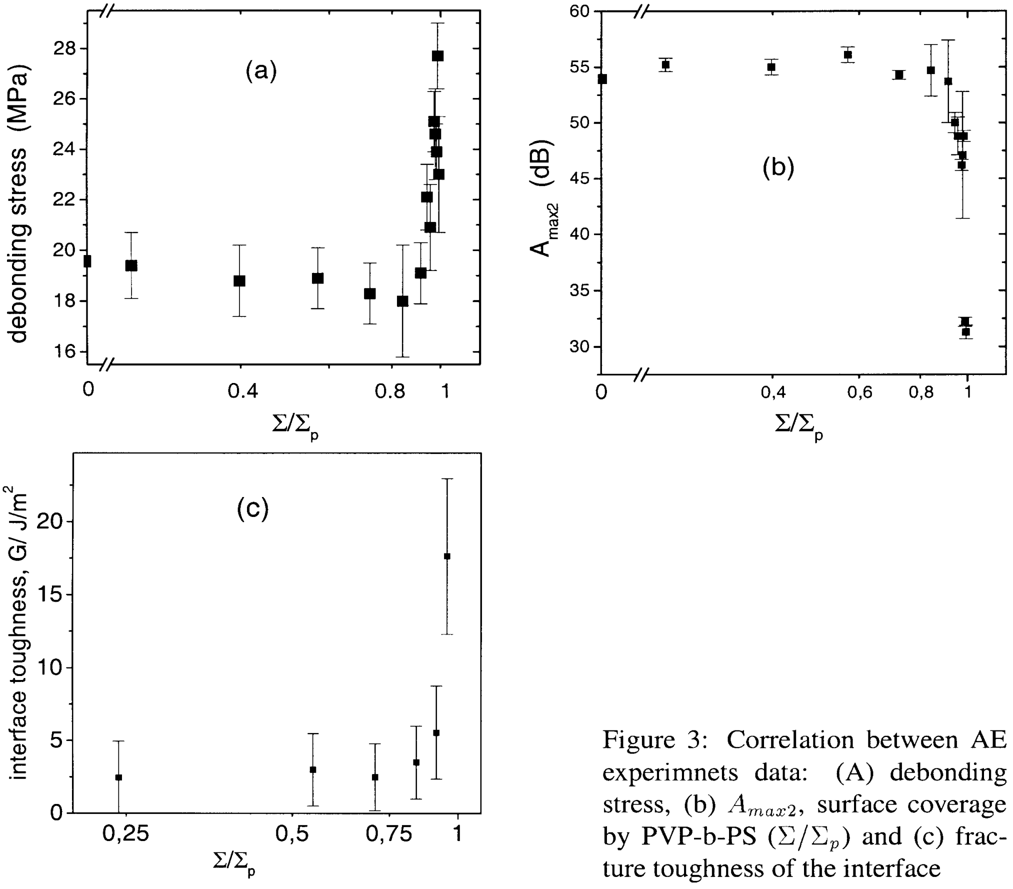

Figure 3: Correlation between AE experimnets data: (A) debonding stress, (b) A_{max2}, surface coverage by PVP-b-PS (Σ/Σ_p) and (c) fracture toughness of the interface

very small F_e value, the AE energy released should be proportional to the elastic energy released after debonding. This was experimentally proved for the composites with glass beads of various size with the same interface strength [13]. From this point of view the inverse proportion between debonding stress and AE amplitude is unexpected. We may speculate, that different degree of covering causes different size of cavities (debonding angle), that was predicted theoretically [18], and elastic energy released is proportional to the local microvolume involved in the relaxation process after the debonding, which depends on the debonding surface. A more detailed discussion we plan in a forthcoming publication.

The second interesting fact obtained from the data is that the strengthening of the interface occurs only near and at the saturated brush regime of the copolymer adsorption. The maximum strengthening effect at the polymer/nonpolymer interface at the saturated brush regime was also observed experimentally [2]. It is interesting to note, that all strengthening effects take place at a very small change of the adsorbed amount with a sharp decrease of the interface strength when Σ increases. It was documented that for the PVP-b-PS copolymer with the same size of buoy PS blocks the failure mechanism is chain pull out of PS blocks [5]. It is likely that strengthening is caused only by very good organised dense polymer brush and is an a co-operative phenomenon. When the concentration of PVP-b-PS in solution increases to more than 0.01 *mg/ml*, we obtained a composite which showed no debonding signals before the fracture of the specimen. Consequently, the improvement of the interface toughness causes a change of the fracture mechanism, when the debonding process does not predetermine the fracture.

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