Durability in the Life Cycle of Polymer Composites

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Received 25 November 1997; accepted 24 November 1998

ABSTRACT: The effect of an interface structure and stress state on the long-term strength of polymer composites is investigated and related to the adhesion between the polymer and the second phase. The approach specifically accounts for the previous life-cycle steps of the material through the evolution of the size of the reinforcement phase and of the interfacial internal stress state. PET/SiO_x multilayer films are used and found appropriate to tailor the interface interactions and introduce controlled compressive stresses in the interface region. Adhesion is characterized by means of micromechanical and thermodynamic complementary approaches. The long-term strength of PET multilayer composites aged below the glass transition temperature of the polymer is predicted from the failure mechanism of the interface. It is shown that reliable predictions require the knowledge of the evolution of the interface shear strength, interface internal stress, and particle size through the whole life-cycle of the composite. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1427–1434, 1999

Key words: durability; life cycle; PET/SiO_x films; multilayer composites; internal stress; structural recovery

INTRODUCTION

Durability prediction of polymer composites becomes a central activity in structural design, as reflected by the increasing body of literature on the topic.^{1,2} It is also a considerable challenge because these materials exhibit a strong life-cycle memory. Each life-cycle step, including initial manufacture, recycling, and related service lives, changes both material structure and stress state, and therefore, influences the subsequent steps, which ultimately impacts the durability of the material.^{3,4}

It is well established that the reliability of composite materials depends directly upon the adhesion between the different constituents. The longterm evolution of the interface characteristics determines, to a large extent, the durability of the composite. The mechanisms of adhesion between a polymer and another material have been extensively studied, although only partially elucidated. Among the reasons for this lies in the variety of polymer structures and material combinations, and of bonding procedures, resulting in a multiplicity of interface structures and stress states. As a consequence, a large amount of adhesion theories and adhesion measurement methods have emerged since the early 30s, and reviewed by several authors (cf. ref. 5). According to Mittal,⁵ the most appropriate adhesion measurement method is the one that simulates stress conditions achieved during service. This principle is at the base of the development of several quantitative methods developed together with a mechanical description of the interface stress transfer, to model the test results.^{6,7}

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Contract grant sponsors: The Swiss Priority Program for Materials Research, and the Swiss National Science Foundation.

Journal of Applied Polymer Science, Vol. 73, 1427-1434 (1999)

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However, the practical dimensions and geometry of the manufactured product together with the often very complex arrangement of the various material phases, like in fiber-reinforced composite parts, prohibit a direct and comprehensive characterization of interfacial adhesion. Nevertheless, most of the recent techniques have proven to be useful to determine the effect of specific treatments on adhesion performance, although the manufacture of the specimens inevitably generates inhomogeneous interfacial structures and internal stresses, resulting from polymer flow and thermal and pressure gradients.

The influence of such factors on adhesion, and thereafter on the durability of the composite, is *a priori* unknown, although it is recognized that it can be considerable,^{7,8} following, for instance, analyses of Huang and Young.⁹

Another challenging problem is to predict the structural evolution of polymers below their glass transition temperature, in the presence of a second phase, as discussed by Brinson and Gates.¹⁰ In particular, it is of central importance to clarify the role of stresses on this evolution.¹¹

To overcome these issues, the first objective of the study was to tailor the interface structure and independently control the interface stress state to elucidate their specific role on adhesion, with attention paid on long-term evolution. To this end, polyethylene terephthalate films coated with silicon oxide coatings of the thickness of the order of 100 nm (PET/SiO_x) were used. These materials are of considerable interest as an oxygen barrier for food and pharmaceutical packaging applications.¹² The films were processed and aged according to several procedures yielding precise, unique, and homogeneous interface structures or stress states. The second objective was to scale the above understanding to simulate recycling and predict the long-term strength of multilayer PET/SiO_x composites, with attention paid to the effect of the size of the reinforcement phase. Because the recovery of multiphase polymer-based materials has become a central issue, the conclusions drawn from this work thus should be of a broad significance.

THEORETICAL APPROACHES TO ADHESION

The deposition processes of thin films on polymer substrates promote intimate contact between the two substances, resulting in a high density of short-distance intermolecular interactions. The energy of the polymer surface, expressed in terms of dispersive and polar components, relates to the interface formation and, ultimately, to the adhesion between the polymer and its coating.^{13,14} Moreover, when limited delamination occurs at the interface, even at high applied strains, stress transfer models are likely to be best applied to derive a basic adhesion.¹⁵ These two independent approaches—thermodynamics and micromechanics—are briefly described in the following.

Thermodynamic Approach to Adhesion

In the case of SiO_x on PET, the deposition processes lead to the formation of chemical bonds at the interface, typically Si-O-C and Si-C.¹³ Numerous works based on the wetting theory developed by Sharpe and Shornhorn¹⁶ investigate the role of such interactions on interfacial adhesion, particularly when modeling "practical" adhesion measurements such as those derived from mechanical tests.¹⁷ The present work focuses on the dispersive and polar components of the polymer surface subjected to several treatments, prior to the deposition of the oxide. The surface energy of the polymer is the sum of a dispersive component (London interactions), and a nondispersive component (polar interactions, including acidbase interactions such as hydrogen bonds).^{18,19} The various components were derived from contact angles measurements carried out at room temperature with demineralized water and apolar α -bromonaphtalene of known surface energy characteristics.^{20,21}

Micromechanical Approach to the Adhesion

The interface shear strength, τ , was derived from the classical Kelly-Tyson²² model of stress transfer, accounting for the internal stress σ_i^{23} :

$$\tau = 1.337 \cdot h \frac{(\sigma_{\max}(l_c) - 2/3 \ \sigma_i)}{l_{\text{sat}}} \tag{1}$$

where h is the coating thickness, $\sigma_{\rm max}$ is the coating strength at critical length l_c and $l_{\rm sat}$ is the average fragment length at saturation, directly measured from micrographs of fragmented coatings on substrates strained above the saturation onset strain.^{15} The critical length l_c was calculated to be very close to $\frac{3}{2} \cdot l_{\rm sat}$. The dependence of the oxide strength $\sigma_{\rm max}$ with fragment length was



Figure 1 Effect of PET surface treatment on experimental (bars) and theoretical (lines) SiO_x fragment length distributions at saturation; critical fragment lengths are also indicated.

calculated from a linear extrapolation of the initial part of the curve $\ln(CD)$ vs. $\ln(\varepsilon)$, where CD is the crack density, inverse of the average fragment length, and ε is the nominal strain, assuming a two-parameter Weibull distribution.^{24,25} The coating strength was found to be equal to 1500 MPa at a critical length, and to be independent of the various treatments described later, within experimental uncertainty.

THE ROLE OF INTERFACE STRUCTURE AND STRESS STATE ON ADHESION

Effect of Hydrolysis and Silylation on Interfacial Interactions

Different interface structures were prepared by means of hydrolysis or silylation of the PET surface prior to the deposition of 120-nm thick coatings.²¹ The polymer substrates were injectionmolded plaques of the thickness of 1 mm. Their Young modulus equal to 2500 MPa was found to be unaffected by the surface treatments. Hydrolysis was done in a concentrated sodium hydroxide solution for 20 min at 60°C. Silylation was performed in γ -aminopropyltriethoxysilane (γ -APS, OSi Specialties A1100) for 10 min at 60°C.

The experimental and theoretical distributions of fragment lengths at saturation resulting from straining the substrate are shown in Figure 1 for the untreated and treated PET/SiO_x materials. The critical lengths of untreated and hydrolyzed materials, reported in the histograms, can be considered to be equal, the difference being less than 1%, which is well below the typical uncertainty of the order of 10% related to such measurement.²⁵

Conversely, the fragment length distribution of the silylated material is shifted to smaller lengths, its theoretical fit is better, and the corresponding critical length is much lower than that of the two other materials.

The surface energy of the untreated material was found equal to 46.7 mJ/m^2 , with a polar component equal to 7.9 mJ/m^2 . Its interface strength with the oxide coating was found equal to 87 MPa. These values were almost identical in the case of the hydrolyzed material, with a surface energy of 46.6 mJ/m^2 , a polar contribution of 3.9 mJ/m^2 , and an interface strength of 86 MPa.

By contrast, the interface strength of the silylated material was found equal to 112 MPa. This 30% increase compared to the untreated material indicates an increased interface interaction density, which is confirmed by the wetting measurements of the modified polymer surface. The surface energy of the sylilated PET was found equal to 48.9 mJ/m², with a polar component equal to 11.0 mJ/m². The role of the various components of the surface energy of the PET on the PET/SiO_x interface strength is detailed elsewhere,²¹ and confirms that, further to the covalent interactions mentioned previously, acid-base interactions such as hydrogen bonds control to a large extent the interface structure.

Tailoring of Interface Stress and Effect on Long-Term Adhesion

Axial compressive strains up to 1.3% were introduced by bonding with an elastomeric glue biaxially stretched PET films of a thickness of 12 μ m, coated by physical vapor deposition with a 100-nm thin oxide layer, to a 90- μ m thick polypropylene (PP) substrate. The PP was subsequently shrunk by means of an appropriate thermal treatment, resulting in the introduction of the desired compression in the coated PET.⁴

The fragmentation process of the coating during straining the polymer is shown in Figure 2 at different levels of interface compression, by plotting the crack density increase vs. the applied tensile stress.²⁶ It is evident that compressive internal stresses increases the crack onset stress, while it does not significantly affect the crack density at fragmentation saturation. Coated PET films were also aged at several temperatures below the glass transition temperature of the polymer up to 250 days. It was observed that the structural recovery process of the polymer that takes place during aging could be described in



Figure 2 Increase of the crack density CD of the oxide vs. applied stress at different levels of interface compression.

terms of the progressive development of interface internal stress. $^{\rm 23}$

The experimental findings were compared to the prediction [equation (1)], which was found to remarkably reproduce the linear increase shown in Figure 3. This agreement provides clues of the relation between interface stress transfer and internal stress.

SCALING INTERFACE STRUCTURE AND STRESS STATE FROM FILMS TO MULTILAYER COMPOSITES

Scaling to three-dimensional composite structures was performed with multilayer PET/SiO_x composites, in which the oxide particles have the shape of platelets of different aspect ratios. Platelets offer a cost-effective alternative to fibers for reinforced composites with a moderate drop in strength and toughness. The structures depicted in Figure 4 were compression molded from stacks



Figure 3 Experimental (dots) and theoretical (line) interface shear strength vs. internal stress.



Figure 4 Multilayer composite structures compression molded from stacks of 100 films.

of 100 films. One multilayer type was plain PET for a reference, a second type was characterized by oxide platelets all larger than several 100 μ m ("nonfragmented PET/SiOx"), and a third type was characterized by oxide platelets all smaller than the stress transfer critical length, close to 4 μm ("fragmented PET/SiO_x"). Similar to the films, the composites were thermally aged at various temperatures below the glass transition T_g of the polymer to study specifically physical aging effects.²⁷ To prevent the occurrence of other timedependent mechanisms during the aging process, the multilayer materials were initially annealed above the T_g of the polymer to attain the maximum crystallinity, and the aging temperatures were low enough so it was verified that recrystallization and oxidative degradation did not took place within the duration of the experiment.

Analysis of the Structural Recovery Process in Multilayer Composites

The enthalpy recovery peaks of the aged materials resulting from the aging process were analyzed by means of differential scanning calorimetry in the vicinity of the glass transition temperature. Although the plain and fragmented materials were found to exhibit almost identical recovery processes, a clear shift of the enthalpy recovery peak to higher temperatures was systematically observed at all times and temperatures for the nonfragmented material. A linear relationship was further observed between the peak temperature and the logarithm of the aging time, as reported by Hutchinson.²⁷ The slope of this linear relationship, which measures the structural recovery rate of the material, was found to be independent of the aging temperature, in agreement with the work of Hodge.²⁸ It was observed that the aging rates for the plain and fragmented materials were equal within the experimental error. Conversely, the aging rate of the nonfragmented material was significantly higher by almost 40%.

Moreover, the activation energies of the enthalpy recovery process were found to be equal for



Figure 5 Enthalpy relaxation peaks of PET multilayer composites and PET aged under tensile strain.

all material types, indicating that it is not a change in the recovery mechanism that affects the enthalpy recovery peak position, but indeed a change in the enthalpy relaxation kinetics. It is, therefore, clear that a factor, other than the presence of the SiO_x phase and the crystallinity of the PET (which is equal for all specimens and remains constant during the whole aging procedure), affects the aging kinetics of the PET. To elucidate this, plain specimens were aged 1 month at 55°C under constant tensile strains of 0.4 or 0.6%, to simulate internal stresses. A clear shift of the enthalpy recovery peak towards higher temperatures is evident in Figure 5, indicating that it is indeed the internal stresses induced by the presence of the SiO_x phase that increase the aging rate. Tool²⁹ has introduced the concept of a fictive temperature, which controls the aging kinetics, defined as the temperature at which the polymer would be at equilibrium, considering its volume. A tensile strain, whether applied or induced by the presence of a second phase, increases the volume of the polymer affected by this strain, which in turn, increases the fictive temperature and, therefore, the aging rate. This is confirmed by the fact that, as already observed by McKenna et al.,¹¹ the application of stresses during the aging procedure does not affect the time taken by a glass to reach equilibrium. Starting from a higher volume, a strained (or stressed) polymer, has therefore to age faster to reach equilibrium in the same time.

Prediction of the Long-Term Interfacial Failure

The scaling from the film to the composite structure, i.e., from one life-cycle step to another, which simulates recycling, considers two factors.

First is the interfacial adhesion and stress state, characterized on individual PET/SiO, films, where the latter could be precisely related to the aging process. Second is the particle size, accurately controlled from the fragmentation process described previously. A model was developed to predict interfacial crack propagation in multilayer composites, from the long-term evolution of interface stress.²³ The model is based on the stress transfer equations developed by Hsueh³⁰ for the platelet geometry. A criteria for interface failure vs. particle failure was written, where the stress field at the interface vicinity resulting from an applied stress on the composite is balanced with the interface shear strength and oxide tensile strength. A critical toughening particle size ξ is derived from the criteria. Particles smaller than ξ toughen the composite as these induce interface delamination. By contrast, particles larger than ξ fail before the interface, and therefore, the strength of composites containing such particles is expected to mimic that of the plain polymer throughout the aging process. It was observed that ξ decreases from ca 20 μ m to below 6 μ m during aging as the internal interface stress increases. This evolution clearly defines a ductileto-brittle transition: particles initially smaller than ξ may well become larger than ξ upon aging, which, therefore, embrittles the composite, as ξ decreases with aging time.

Predictions of long-term mechanical endurance are compared in Figure 6(a) to 6(c) with experimental data for plain, nonfragmented, and fragmented multilaver composites tested in three-point bending. The nonfragmented material was found to behave similarly to the plain PET reference within experimental scatter, as predicted by the analysis reported above. The strength of both plain and nonfragmented materials is found to gradually decrease during aging, as a result from embrittlement due to structural recovery processes. By contrast, it is evident that the small $\mathrm{SiO}_{\mathrm{x}}$ flakes toughen the polymer. Despite the relatively high experimental scatter, the strength of the fragmented composite is always higher than that of the nonfragmented, and the difference is as high as 100%after 1 year of aging. Such a difference in behavior between composite materials with strictly the same composition but different particle size and stress state is worthwhile to point out. The present agreement obtained in the case of model composite structures indicates that ac-



Figure 6 Effect of aging on the strength of plain, fragmented, and nonfragmented multilayer composites aged at different temperatures below the glass transition temperature of the polymer [(a) 40° C; (b) 55° C; (c) 70° C]. Dots are experimental data, and lines are predictions for the composites.

counting for previous life-cycle steps enables reliable long-term predictions.

The effect of aging and platelet size on the strain at failure of the multilayer materials is shown in Figure 7(a) to 7(c). Interestingly, it is evident that the fragmented multilayer composite fails at a larger strain than both unreinforced and nonfragmented materials, without any decrease during the whole aging duration. Combined with the above finding of higher strength, the present observation clearly confirms the remarkable toughening effect of the small platelets, further improved during aging time by the structural recovery of the matrix.

The implications of this approach should be of a broad importance as life extension of polymerbased materials, including recycling, are central concerns in technological developments.

CONCLUSIONS

Polymer composites are known to present a strong life-cycle memory. To specifically study this issue on the durability of the material, the effect of interface structure and stress state on the long-term strength of PET multilayer composites was investigated. It was related to the adhesion between the polymer and the second phase, and to the previous life-cycle steps of the material.

PET films coated with thin oxide coatings developed for packaging applications were used and subjected to several treatments to tailor the interface structure and introduce controlled levels of internal stress. The films were also aged below the glass transition temperature of the polymer. Wetting measurements were carried out to derive



Figure 7 Effect of aging on the strain at failure of plain, fragmented, and nonfragmented multilayer composites aged at different temperatures below the glass transition temperature of the polymer [(a) 40°C; (b) 55°C; (c) 70°C].

the surface energy components of the polymer prior to the deposition of the coating, and fragmentation tests were performed to obtain the interface shear strength and gain insight into the interfacial interactions. The films were further processed into multilayer composites whose mechanical strength was measured after long-term aging, during which any crystallization and chemical degradation processes was avoided. The analysis of the experimental results leads to several conclusions.

- 1. SiO_x -coated PET films are appropriate to tailor the interfacial structure and independently control the stress state, and explore their specific role on adhesion by combining micromechanical and thermodynamic approaches.
- 2. Besides covalent bonds, polar interactions

such as hydrogen bonding control, to a large extent, the adhesion between PET and SiO_x .

- 3. The interface shear strength between PET and SiO_x increases linearly with the interface internal compression.
- 4. The strength of multilayer PET/SiO_x composites is controlled by a critical toughening SiO_x platelet size. (a) Platelets smaller than the critical size toughen the PET, whereas larger platelets embrittle the polymer. (b) The critical size decreases with aging time as a result of increased internal stresses.

This article was presented at DURACOSYS'97, Third International Conference on the Progress in Durability Analysis of Composite Systems, Blacksburg, VA, Sept. 14–17, 1997. The authors are gratefully indebted to the Swiss Priority Program for Materials Research and to the Swiss National Science Foundation for funding this work.

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