THERMOPHYSICAL CHARACTERIZATION OF THE DEFORMATION BEHAVIOR OF POLYETHYLENE/KAOLIN COMPOSITES*

*V.P. Privalko¹ **, F.J. Balta Calleja¹, D.I. Sukhorukov², E.G. Privalko², R. Walter³*

and K. Friedrich³

¹ Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain,

² Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 253160 Kyiv, Ukraine,

³ Institute of Composite Materials Ltd., University of Kaiserslautern, D-67663, Kaiserslautern, Germany

ABSTRACT

The deformation behavior at room temperature of injection-molded and blow-molded samples of HDPE differing in orientation (with respect to the melt flow direction) and in filler content (untreated and surface-treated kaolin, respectively) were characterized by the stretching calorimetry technique. Samples with longitudinal and transversal orientations were examined. Strain-softening and strain-hardening phenomena are respectively observed in the range of inelastic strains above the yield point. The depression of yield stresses for the filled composites compared to those for the corresponding neat polymers is associated with the onset of debonding of the matrix polymer from the filler surface. The analysis of the energy balance of debonding process suggests that the fraction of a debonded interface is smaller in samples containing a coupling agent and larger filler particles.

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** Permanent address: Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 253160 Kyiv, Ukraine

INTRODUCTION

Combination of low cost with a reasonably good mechanical performance makes Kaolin-filled high-density polyethylene (HDPE) composites attractive for less demanding technological applications. In our previous publications /1-4/ these composites were characterized by electron microscopy, wide-angle X-ray diffraction, microhardness and thermoelasticity measurements, with the main emphasis on their initial structure and deformation behavior in the elastic strain range. It was established that the crystallinity of the polymer matrix in filled samples showed the same value as that found for the neat polymer regardless of orientation, filler content and/or filler surface treatment. Analysis of thermoelastic parameters of the filled composites in the elastic strain interval suggested the formation of the boundary interphase with an unusually stiff, highly oriented structure of the matrix polymer.

The present paper is devoted to the evaluation of the effect of matrix orientation, Kaolin content and its surface treatment on the thermoelastic behavior of HDPE/Kaolin composites in the strain range through and above the yield point.

EXPERIMENTAL

Materials

Injection molding grade (melt flow index MFI = 4.00 g/10 min) and blow molding grade (MFI = 0.27 g/10 min) high-density polyethylene samples (hereafter referred to as HDPE 1 and HDPE 2) were used as matrix materials. Filled composites of both HDPE grades, prepared on a twin-screw extruder by compounding a polymer matrix with Kaolin particles (mean equivalent diameters of 0.8 μm and 1.4 μm for Short and Long particles, respectively) with and without the custom coupling agent, were supplied by the manufacturer (ENICHEM, Italy). Before application of the coupling agent, Kaolin with the formula $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ was calcined by

heating above 600 K. This treatment is assumed /1/ to improve the catalytic activity of Kaolin surface and to destroy its crystalline structure.

Composite samples of lateral dimensions 5x50 mm with longitudinal (L) and transversal (T) orientation (with respect to the melt flow direction) cut from sheets of thickness 0.3 mm were used for subsequent structural and thermoelastic characterization. As an example, the sample coding 10 INS -L means: **10** vol. % of the Kaolin, Injection molding grade of a matrix, absence of the coupling agent (No), Small kaolin particles, **L**ongitudinal orientation.

Experimental technique

The mechanical work (W) and concomitant heat effects (Q) in the step-wise loading (stretching)/unloading (contraction) cycles were measured (with the estimated mean error below 2 %) at room temperature with the stretching calorimeter described in detail elsewhere (5-7). In a typical experimental run, each specimen was stretched at a constant velocity q^+ to a predetermined strain ε_i , stored at fixed ε_i to the full completion of mechanical and thermal relaxation, and thereafter allowed to contract at the same velocity q^- to zero force. The typical difference between fixed strains in two successive steps, $\varepsilon_{i+1} - \varepsilon_i$, varied from several digits in the fourth place to a few digits in the third place within the strain intervals below and above 0.02, respectively. In the interval of large (above 0.1) strains, the data were taken in the stretching regime only, the successive step-like strains increasing with stretching ratio from about 0.05-0.10 to 0.15-0.20.

RESULTS AND DISCUSSION

Stress-strain relationships

As illustrated by the representative plots of Fig. 1, in the interval of small strains below the apparent yield point ε^* , the specific (per sample mass m) mechanical work (W/m) and heat effects (Q/m) data, can be quantitatively fitted to the classical equations of the thermoelasticity of solids /8/

$$W/m = E\varepsilon^2 / 2\rho ; \quad (1a)$$

$$Q/m = E\alpha_L T\varepsilon / \rho \quad (1b)$$

where E is the Young's modulus, α_L is the linear thermal expansion coefficient, and ρ is the density. The best-fit values of E and α_L are observed to decrease and increase, respectively, with the filler volume content ϕ (Tables 1 and 2). A detailed discussion of this dependence within the framework of the step-by-step-averaging model /9/ is presented elsewhere /3, 4/.

As mentioned above, the apparent yield strain, ε^* , is defined as the upper limit of the elastic strain range where equations (1) apply. The inelastic deformation behavior of polymers in the strain range above ε^* can be also characterized by the "true" yield point with the coordinates σ_y (true yield stress) and ε_y (true yield strain) corresponding to the zero slope ($d\sigma/d\varepsilon = 0$) on the stress-strain diagrams /10/. The latter diagrams can be constructed in the coordinates, $\sigma = d(W/m)/d\varepsilon$ and ε , by a graphical differentiation of W/m vs. ε plots.

As expected, the L- and T-oriented samples of both matrix polymers behave essentially similar below ε^* , whereas strong differences can be seen at higher strains (Fig. 2). In fact, the apparent tensile stresses for L-samples pass through maxima σ_y at the yield points and then tend to decrease (this behavior is usually referred to as the "strain softening" phenomenon /10/); in contrast, the "strain hardening" phenomenon (i.e., an uprise of the σ at higher ε) is observed for T-samples above σ_y . The former process (strain softening), for the L-samples, can be attributed to the breakdown and subsequent plastic flow of the fragments of pre-L-oriented lamellar crystals /8/. On the other hand, the latter process (strain hardening) in the T-samples is assumed to be the result of successive processes of rotation and reorientation of pre-T-oriented lamellar crystals in the direction of the stretching force. In this respect, the final structure of initially T-oriented samples after strain hardening well above ε_y may be regarded as qualitatively similar to the initial structure of L-oriented samples below ε_y .

The stress-strain diagrams for L- and T-oriented filled samples are qualitatively similar to those for corresponding matrix polymers (cf. representative plots in Fig. 3); however, the coordinates of the respective yield points are markedly different (Tables 1 and 2). As can be inferred from experimental data for closely related HDPE/CaCO₃ composites /11/, stretching of filled samples through and above a yield point is accompanied by the onset and subsequent increase of the apparent sample volume (dilatation) caused by the formation of a polymer-free filler surface ("matrix debonding" phenomenon). As a result of the concomitant decrease of the effective cross-sectional area of a matrix, the yield stress σ_y of filled composites is expected to become smaller than that (σ_y^0) for a neat polymer according to the following relationship /12/:

$$\sigma_y = \sigma_y^0 (1 - 1.21 \varphi^{2/3}) . \quad (2)$$

As can be seen from Tables 1 and 2, the predicted depression of the yield stress is in fact observed for the majority of studied filled composites, although the agreement with equation (2) is far from quantitative, especially for samples of the BYS series (Fig. 4). The origin of this discrepancy remains obscure for the moment; it is worth mentioning, however, that the equation (2) proved to be reasonably applicable to the experimental data obtained during a continuous loading of samples /11, 12/, whereas the data discussed in the present work were obtained in a step-wise loading regime. It seems also likely that the non-spherical shape of Kaolin particles can be another source of the observed discrepancy.

Energy balance of the debonding process

Structural implications of thermoelastic behavior of the studied samples in the plastic flow strain interval above ε^* will be discussed now with reference to the specific internal energy change, $\Delta U/m = (W + Q)/m$. The initial steep increase of $\Delta U/m$ with ε for unfilled polymers (cf. the representative plots in Fig. 5) in the interval of elastic strains ($\varepsilon < \varepsilon^*$) is followed by a gradual decrease of the slope of $\Delta U/m$ in the strain interval above ε^* . According to current views /8/, this behavior can be explained by the elastic (endothermic) response of the tie-chains connecting randomly oriented lamellar crystals in the initial isotropic sample in the interval $\varepsilon < \varepsilon^*$, and by the onset of successive (exothermic) processes of lamella reorientation and breakdown at higher strains, respectively. In subsequent discussion, $\Delta H^{in} = 3.8 \text{ J/g} = 3.5 \text{ J/cm}^3$ will be assumed as representative for the latent heat of the HDPE plastic flow /8/.

The overlap of experimental data for unfilled and filled samples of all composite series in the interval $\varepsilon < \varepsilon^*$ (Fig. 5) suggests the occurrence of identical structural mechanisms responsible for their thermoelastic behavior (i.e., the elastic response of tie-chains between crystalline lamellae in the matrix polymer). However, the $\Delta U/m$ values at equal strains in the range $\varepsilon > \varepsilon^*$ for filled samples are significantly smaller than those for the corresponding neat polymer, and tend to decrease with the filler content. This can be regarded as experimental evidence for extra exothermic processes of structural reorganization in filled samples, the contribution of which increases, the higher the filler content.

As suggested elsewhere /3, 4/, the deficit of the specific internal energy change in filled samples compared to the neat matrix polymer, $\delta(\Delta U/m)$, can be equated to the heat released due to the formation of a free (debonded) filler surface, i.e.,

$$\delta(\Delta U/m) \approx f\varphi\gamma_{12}S_{12} \quad , \quad (3)$$

where $\gamma_{12} = \gamma_{12}^0 + \gamma_{12}^{in}$, γ_{12}^0 is the “true” excess interfacial energy (heat of wetting), γ_{12}^{in} is the contribution of a plastic flow preceding the debonding, S_{12} is the total polymer/filler interfacial area, and f is the fraction of a debonded interface.

The $\delta(\Delta U/m)$ and φ values are known from the experiment ; $S_{12} \approx 3 \times 10^5 \text{ cm}^2/\text{g}$ is the tabulated value of the specific surface area of Kaolin particles /13/ ; consequently, there are only two unknowns in the r.h.s. of equation (2), namely, f and γ_{12} . In previous papers /3, 4/, $\gamma_{12}^0 \approx 200 \times 10^{-7} \text{ J/cm}^2$ and $\gamma_{12}^{in} \approx 100 \times 10^{-7} \text{ J/cm}^2$, respectively, were assumed as representative values for the heats of wetting of the untreated and of the surface-treated Kaolin by HDPE. The plastic

flow of a polymer matrix is assumed to occur in the interstitial space between filler particles; hence, the contribution of γ_{12}^{in} can be estimated as $\gamma_{12}^{in} \approx \Delta H^{in} L$, where $L = \frac{2r}{[(\varphi^* / \varphi)^{1/3} - 1]}$ is the mean surface-to-surface inter-particle distance /9/ (i.e., the matrix ligament thickness /14/), and $\varphi^* = 0.60$ is the limiting volume content of a filler.

As can be deduced from Tables 1 and 2, in spite of the approximations involved, the calculated values of f at a fixed strain above ε^* ($\varepsilon = 0.06$) are of a reasonable magnitude and tend to increase with the Kaolin content. Systematically lower f -values for samples with a coupling agent (at equal filler loading) can be regarded as a natural consequence of better coupling at the polymer/filler interface.

It is convenient to comment here on the possible factors responsible for the different f -values obtained for the injection-molded (HDPE 1), and for the blow-molded (HDPE 2) samples. The key factor is likely the higher melt viscosity of HDPE 2. In fact, the time needed for a complete wetting of a solid surface with a polymer melt may be expected to increase, the higher the melt viscosity. Therefore, at equal times of melt processing, the probability of a complete wetting of Kaolin particles by the HDPE 2 melt should be lower than that for HDPE 1. Hence, a smaller fraction of the total filler surface area available is expected to be in a direct contact with the polymer matrix in the filled samples. This argument is consistent with smaller f -values observed during stretching of the filled blow-molded samples. Moreover, the lower melt viscosity of HDPE 1 seems an obvious prerequisite for its easier orientation in the flow direction. As a result, higher orientation of a polymer matrix in samples of L-series should initiate the earlier onset and/or the larger contribution of inelastic effects to the debonding process (i.e., larger f) as compared to their counterparts in the T-series (Tables 1 and 2).

CONCLUSIONS

1. Strain-softening and strain-hardening phenomena for L- and T-oriented samples, respectively, are observed in the range of inelastic strains above the yield point.

2. Depression of yield stresses for the filled composites compared to those of the corresponding neat polymers is associated with the onset of debonding of the matrix polymer from the filler surface.

3. Analysis of the energy balance of debonding process suggests that the fraction of a debonded interface is smaller in samples containing a coupling agent and larger filler particles.

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TABLE 1

Thermoelastic parameters of blow-molded samples

Sample	E / GPa	$10^5 \alpha_L$ / K ⁻¹	ε^*	ε_y	σ_y / J g ⁻¹	ε_b	$\Delta U m^{-1}$ / J kg ⁻¹	f
HDPE 2-L	0.74	9,9	0.019	0.062	8.30	1.10	1070	...
HDPE 2-T	0.45	13.5	0.032	0.032	7.50	0.65	1280	...
10 BYS-L	0.85	9.6	0.023	0.040	7.26	1.02	910	0.025
10 BYS-T	0.72	10.5	0.024	0.053	8.78	0.49	1130	0.020
30 BYS-L	1.30	7.6	0.019	0.032	7.28	0.44	630	0.061
30 BYS-T	1.26	6.6	0.020	0.036	9.44	0.25	880	0.055

TABLE 2

Thermoelastic parameters of injection-molded samples

Sample	E / Gpa	$10^5 \alpha_L / \text{K}^{-1}$	ε^*	ε_y	$\sigma_y / \text{J g}^{-1}$	ε_b	$\Delta U m^{-1} / \text{J kg}^{-1}$	f
HDPE 1-L	0.74	7.2	0.024	0.070	13.35	1.02	1290	...
HDPE 1-T	0.73	9.9	0.022	0.082	10.68	0.94	1150	...
10 INS-L	0.80	11.1	0.018	0.050	6.80	0.20	810	0.064
30 INS-L	1.20	7.8	0.014	0.034	6.49	0.15	500	0.110
10 IYS-L	0.78	9.3	0.017	0.032	7.09	0.27	995	0.040
30 IYS-L	1.11	6.4	0.019	0.051	7.85	0.23	720	0.079
10 IYL-L	1.05	7.4	0.017	0.034	9.10	0.79	890	0.032
30 IYL-L	1.20	5.8	0.019	0.055	7.30	0.50	700	0.050
10 INS-T	0.90	8.0	0.018	0.039	8.26	0.36	930	0.030
30 INS-T	1.12	...	0.019	0.026	7.44	0.12	...	...
10 IYS-T	0.90	14.3	0.016	0.047	8.59	0.60	1040	0.015
30 IYS-T	1.30	8.5	0.018	0.035	8.99	0.64	750	0.055
10 IYL-T	0.91	8.0	0.017	0.036	7.86	0.42	910	0.020
30 IYL-T	1.20	6.9	0.017	0.065	7.69	0.63	720	0.036

FIGURE CAPTIONS

Fig. 1. Specific mechanical work (opened squares) and specific heat effects (filled circles) for HDPE 1-L (a), 10 IYS-L (b) and 30 IYS-L (c).

Fig. 2. Stress-strain diagrams for neat polymers.

Fig. 3. Stress-strain diagrams for samples of series IYS-L (a) and IYS-T (b) containing 0 (opened circles), 10 (filled squares) and 30 (opened triangles) vol. % of Kaolin.

Fig. 4. Yield point depression for samples of the series BYS (a) with L-orientation (opened squares) and T-orientation (filled squares), and for L-oriented (b) and T-oriented © samples of series INS (squares), IYS (circles) and IYL (triangles).

Fig. 5. Specific internal energy changes for samples of series IYS-L: HDPE 1-L (circles), 10 IYS-L (squares) and 30 IYS-L (triangles)

Fig. 1

Fig. 1

Fig. 1

Fig. 2

Fig. 2

Fig. 3

Fig. 3

Fig. 4

Fig. 4

Fig. 4

Fig. 5