Composition-Dependent Properties of Polyethylene/Kaolin Composites. III. Thermoelastic Behavior of Injection-Molded Samples

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ABSTRACT: Injection-molded samples of high-density polyethylene (HDPE) differing in the orientation pattern (with respect to the melt flow direction) and in filler content (untreated and surface-treated kaolin, respectively) were characterized by wide-angle X-ray scattering, microhardness, and stretching calorimetry techniques. The crystallinity of the polymer matrix in filled samples shows the same value as that found for the neat polymer regardless, filler content, and/or filler surface treatment. The thermoelastic behavior of all samples in the strain interval below the apparent yield point ε^* is quantitatively discussed in terms of classical equations for elastic solids. Analysis of thermoelastic parameters of the boundary interphase (BI) reveal an unusually stiff, highly oriented structure of the matrix polymer within BI. Discrepancies of experimental values for the internal energy increment in the inelastic strain interval above ε^* between unfilled and filled samples is explained in terms of the filler debonding process. The latter process is discussed in light of the formation of a polymer-free filler surface and of the concomitant inelastic deformation (plastic flow) of a polymer matrix in the interstitial space between filler particles. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1041–1048, 1999

Key words: injection molding; polyethylene/Kaolin composites; X-ray scattering; mechanical properties

INTRODUCTION

The apparently straightforward approach to improve the mechanical performance of low-modulus polymer materials (as well as to reduce their production costs) is the incorporation of highmodulus, disperse fillers. In technological practice, however, the expected benefits of this approach are sometimes severely underscored by the formation of polymer-free voids inside loosely packed aggregates of filler particles and/or at the filler/matrix interface. As demonstrated in our preliminary report¹ and in the Part I of the present series² on structure-property relationships for high-density polyethylene (HDPE) filled with Kaolin, void formation could be minimized by treatment of the filler surface with an appro-

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priately chosen coupling (or sizing) agent. In addition, better wetting of the surface-treated filler by polymer matrix presumably resulted in an improved balance of mechanical properties of filled composites (e.g., stiffness/toughness ratio).

Formation of microvoids at a polymer/filler interface (debonding) is currently assumed to be a major structural event preceding the mechanical failure of a filled polymer; in fact, a polymer-free filler surface is a common feature of electron microphotographs of the fracture surface of a filled polymer.^{1,3,4} The potential of the stretching calorimetry technique to characterize the energetics of a debonding process was demonstrated in preceding studies on blow-molded HDPE filled with surface-treated Kaolin (Part II⁵). In this article (Part III), this technique is applied to study the thermodynamics of uniaxial deformation of injection-molded HDPE filled with both untreated and surface-treated Kaolin, respectively.

EXPERIMENTAL

Materials

Injection molding grade (melt flow index MFI = 4.00 g/10 min) of high-density polyethylene (hereafter referred to as HDPE 1) was used as a matrix material. Filled composites prepared on a twin-screw extruder by compounding a polymer matrix with Kaolin particulates (mean equivalent diameters of 0.8 μ m and 1.4 μ m for short and long particles, respectively) with and without the custom coupling agent were supplied by the manufacturer (ENICHEM, Italy). Kaolin with the formula Al₂O₃ × SiO₂ × 2H₂O was calcinated by heating above 600 K. This treatment is assumed¹ to improve the catalytic activity of Kaolin surface and to destroy its crystalline structure.

Composite samples of lateral dimensions 5 \times 50 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, longitudinal orientation.

Techniques

Wide-angle X-ray scattering (WAXS) patterns were taken with a DRON-2,0 diffractometer (cop-

per K_{α} radiation with nickel filter was used in the 5–40° (2 Θ) range). The WAXS patterns were recorded in the step-scanning mode using a scintillation counter and digital conversion. The scattering curves for all samples were normalized by thickness and X-ray absorption.^{6,7}

A Leitz Tester equipped with a square-based diamond indenter was used for the room-temperature microhardness (*H*) measurements. The *H* values were calculated from the standard equation,^{8,9} *H* (MPa) = kS, where *S* is the slope of the straight-line plot of the residual projected indentation area A (m²) = d^2 versus the contact load applied *P* (N), *d* (m) is the diagonal length of the impression, and k = 1.854 is the geometrical factor. In a loading cycle of 0.1 min, the loads of 0.5, 1, and 1.5 N were used. For each point, at least three to five measurements were averaged. The correlation coefficients and the standard deviations for the linear *A* versus *P* fits obtained were 0.998 and 1.16, respectively.

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.^{10–13} 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 relaxations, and thereafter allowed to contract at the same velocity q^{-} to zero force. The typical difference between fixed strains in two successive steps, ε_{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

Degree of Crystallinity and Microhardness

The WAXS pattern as well as the angular positions of crystalline reflections of the polymer matrix (Fig. 1) are nearly identical to those for a blow-molding HDPE 2.5 The same conclusion also applies to the filled samples (see the representative patterns in Fig. 2); the absence of extra re-



Figure 1 Wide-angle X-ray scattering patterns for HDPE 1-L (solid line) and HDPE 1-T (broken line).

flections on the WAXS patterns of the samples containing Kaolin confirms its assumed¹ noncrystalline structure. As is the case with blow-molded samples,⁵ with increasing filler volume content φ , we observe a decrease in the intensities of WAXS patterns (Fig. 2). However, the degree of crystallinity of the matrix estimated by the standard procedure^{6,7} compares well with those estimated by calorimetry² and remains essentially constant at $X_c = 0.60 \pm 0.05$, irrespective of sample composition and/or orientation.

The microhardness values H of HDPE 1-L and HDPE 1-T (Table I) are close to those for their blow-molding counterparts⁵ and are typical for a semicrystalline HDPE with small crystallite size.¹⁴ The observed increase of H with φ for all studied samples (Table I) fits reasonably well to a straight line that extrapolates for $\varphi = 1.0$ at H_2 = 110 ± 7 MPa. This should be regarded as the microhardness of bulk Kaolin, because the experimental value of H_2 for bulk Kaolin is unavailable. However, the tabulated value of its Mohs' hardness $(M = 2.3)^{15}$ can be converted into the Vicker's hardness $H'_2 = 575$ MPa using the empirical relationship H [MPa] = 192.7 exp(0.476M).⁵ As suggested in Part II,⁵ the fivefold lower value found for H_2 may be attributable to the real effect of amorphization of the virgin, polycrystalline (hence, presumably, much harder) bulk Kaolin.

Thermoelasticity

Elastic Strain Range

In the interval of small strains ($\varepsilon \leq 0.025$), the specific (per sample mass *m*) mechanical work (*W/m*) and heat effects (*Q/m*) data for both HDPE 1-L and HDPE 1-T can be quantitatively fitted (Fig. 3) to the classical equations of the thermoelasticity of solids.¹⁶

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



Figure 2 Wide-angle X-ray scattering patterns for samples of series INS-L (a): HDPE 1-L (broken line); 10 INS-L (solid line); and 30 INS-L (dotted line) and samples of series INS-T (b): HDPE 1-T (broken line); 10 INS-T (solid line); and 30 INS-T (dotted line).

Sample	H (MPa)	E (GPa)	$10^5 \ \alpha_L \ ({ m K}^{-1})$	ε^*	ε_b	C	$\Delta U \; (\mathrm{m^{-1}\!/\!J} \; \mathrm{kg^{-1}})$	arphi
HDPE 1-L	45.4	0 74	7.2	0.024	1.02	23	1290	
HDPE 1-T	46.8	0.73	9.9	0.022	0.94	2.9	1150	
10 INS-L	46.9	0.80	11.1	0.018	0.20	3.3	810	0.064
30 INS-L	50.2	1.20	7.8	0.014	0.15	3.0	500	0.110
10 IYS-L	47.4	0.78	9.3	0.017	0.27	3.6	995	0.040
30 IYS-L	61.2	1.11	6.4	0.019	0.23	2.9	720	0.079
10 IYL-L	56.3	1.05	7.4	0.017	0.79	3.1	890	0.032
30 IYL-L	56.3	1.20	5.8	0.019	0.50	2.5	700	0.050
10 INS-T	51.1	0.90	8.0	0.018	0.36	3.1	930	0.030
30 INS-T	53.4	1.12		0.019	0.12	2.5		
10 IYS-T	53.1	0.90	14.3	0.016	0.60	3.7	1040	0.015
30 IYS-T	67.2	1.30	8.5	0.018	0.64	2.9	750	0.055
10 IYL-T	56.3	0.91	8.0	0.017	0.42	3.6	910	0.020
30 IYL-T	61.2	1.20	6.9	0.017	0.63	3.0	720	0.036

Table IMicrohardness, Young's Modulus, Thermal Expansion Coefficient, Apparent Yield Strain,Strain at Break, Proportional Coefficient and Specific Thermal Energy of Studied Samples as aFunction of Kaolin Volume Content

$$Q/m = E\alpha_L T\varepsilon/\rho \tag{1b}$$

where E is the Young's modulus, α_L is the linear thermal expansion coefficient, and ρ is the density. As can be seen from Table I, the values of Eand α_L , respectively, for HDPE 1-L are slightly higher and smaller than those for HDPE 1-T. Because the crystallinity for both these samples is nearly the same, the observed differences can be attributed¹⁶ to the somewhat more extended conformation of tie-chains in the interlamellar space of HDPE 1-L.

Eqs. (1) also proved applicable to describe the experimental data for all filled samples at low strains (see the representative plots in Fig. 3); the best-fit values of Young's moduli E and of linear thermal expansion coefficients α_L are collected in Table I. Qualitatively, the observed trend for the E increase and for the α_L decrease with filler content φ can be considered as a natural consequence of much higher Young's modulus and of much lower linear thermal expansion coefficient of bulk polycrystalline Kaolin ($E_2 \approx 20$ GPa and $\alpha_{L,2} \approx 1 \times 10^{-6}$ K⁻¹, respectively)¹⁷ compared to those for the neat matrix polymer. The essentials of the step-by-step averaging (SSA) approach¹⁸ used for a quantitative treatment of these data are outlined below.

A unique feature of the structural model adopted in the SSA model¹⁸ is the possibility to account explicitly for the smearing out of a sharp (i.e., of zero thickness) interface between a filler and a matrix polymer into a "physical" boundary interphase (BI) structurally different from the neat polymer. It is assumed that even at relatively low nominal filler contents φ , the isolated filler particles of size 2r coated with a BI of thickness Δr can coalesce into isolated clusters (IsC) containing a constant limiting volume fraction of a filler $\varphi^* \gg \varphi$. The effective concentration φ' of such IsC with $\varphi^* = \text{const}$ will increase with the nominal filler content φ until an infinite cluster (InC) spanning the entire system is formed at the percolation threshold $\varphi' = \varphi_c$. The bulk representative elements (BRE) of the InC are Voronoi polyhedra constructed by the intersection of planes drawn normal to the vectors connecting the centers of particles at their midpoints. In this fashion, the InC is sectioned into a system of different Voronoi polyhedra with the number of faces dependent on the coordination number N_c $= f(\varphi^*)$ of corresponding particles. The effective properties of a disordered system of such BRE are calculated assuming its identity to the appropriately chosen, "mutually adequate" (as concerns isotropicity, mechanical stability, geometrical equivalence, etc.) one with an ordered structure (e.g., a spherical particle embedded into a cube).

The calculations were carried out for variable values of the effective Young's modulus and linear thermal expansion coefficient of the BI ($E_{\rm BI}$ and $\alpha_{L,\rm BI}$, respectively) at fixed values of $\varphi_c = 0.15$, $\varphi^* = 0.60$, $\nu_1 = 0.4$ and $\nu_2 = 0.2$ (the latter two parameters are Poisson's ratios of the polymer matrix and of the Kaolin, respectively). The quality of theoretical fits to the experimental Young's



moduli and linear expansivities for samples of series IYL-L (at the best-fit values $E_{\rm BI} = 10.74$ GPa, $\nu_{\rm BI} = 0.4$ and $\alpha_{L,\rm BI} < 1 \times 10^{-7} \, {\rm K}^{-1}$) can be assessed from the representative plots in Figure 4; similar plots for all other series are essentially identical and are not reproduced here. As would be expected,¹⁸ the change of the effective BI thickness $\Delta r/r$ by an order of magnitude produced only a relatively minor effect on the quality of fit to the experimental *E* data (Fig. 4a) and did not affect at all the theoretical curves of α_L (Fig. 4b).

The effective values of $E_{\rm BI}$ and $\alpha_{L,\rm BI}$ (if real) would imply unusually stiff, highly oriented state of HDPE 1 in the BI of filled samples (the representative values of E = 8.0 GPa and $\alpha_L = -3.65$ $\times 10^{-5}$ K⁻¹ were reported¹⁶ for a sample of HDPE stretched 20-fold). This is an obvious price for fitting the experimental values of thermoelastic parameters of filled samples to predictions of the SSA model over the entire concentration interval from neat HDPE to a polycrystalline Kaolin (Figs. 4). Unfortunately, lacking thermoelastic parameters of an amorphized Kaolin, it is impossible at the moment to arrive at more realistic values of $E_{\rm BI}$ and $\alpha_{L,\rm BI}$ from our model calculations.

Inelastic Strain Range

As can be seen from Figure 3, the fit of experimental data to theoretical Eqs. (1) for elastic solids is limited to a relatively narrow strain interval below the apparent yield strain ε^* . The increasing deviations of experimental data from theoretical curves at higher strains are the evidence for the onset and subsequent development of irreversible (inelastic) structural changes within the samples (commonly referred to as a "plastic flow" phenomenon).

It is worth mentioning at this point that the data available (Table I) are consistent with the expected⁸ correlation between the microhardness, H, and the apparent yield stress, $\sigma^* = E\varepsilon^*$. As can be seen from Table I, the proportionality coefficients C in the relationship $H = C\sigma^*$ for all studied samples randomly fluctuate around the theoretical value (C = 3) for compression loading of solids.⁶ As suggested elsewhere,¹⁹ the discrepancy between experimental and theoretical val-

Figure 3 Specific mechanical work (open squares) and specific heat effects (filled circles) for HDPE 1-L (a), 10 INS-L (b), and 30 INS-L (c).

ues of C most probably is related to the different loading regimes assumed (stretching and compression, respectively).

We discuss next the structural implications of thermoelastic behavior of the studied samples in the plastic flow strain interval above ε^* with reference to the specific internal energy change, $\Delta U/m = (W + Q)/m$. As can be seen from the representative plots in Figure 5, the initial steep rise of $\Delta U/m$ with ε for both HDPE 1-L and



Figure 4 Concentration dependence of Young's modulus (a) and linear expansivity (b) for samples of series IYL-L. Theoretical curves were calculated assuming $\Delta r/r = 0.01$ (solid lines) and 0.001 (broken lines).



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

HDPE 1-T in the interval of elastic strains ($\varepsilon < \varepsilon^*$) is followed by a gradual decrease of the slope of corresponding dependencies in the strain interval above ε^* . This behavior can be explained¹⁶ in terms of the elastic (endothermic) response of tiechains 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.

The overlap of experimental data for unfilled and filled samples of both series in the interval ε $< \varepsilon^*$ (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 in Part II,⁵ 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 because of the formation of a free (debonded) filler surface; that is,

$$\delta(\Delta U/m) \approx f \varphi \gamma_{12} S_{12} \tag{2}$$

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; $S_{12} \approx 3 \times 10^5$ cm²/g is the tabulated value of the specific surface area of Kaolin particles²⁰; consequently, there are only two unknowns in the r.h.s. of eq. (2); namely, f and γ_{12} . In a previous paper, ${}^5\gamma_{12}^0 \approx 100 \times 10^{-7}$ J/cm² was assumed as a representative value for the heat of wetting of the surface-treated Kaolin by HDPE. A higher value ($\gamma_{12}^0 \approx 200 \times 10^{-7}$ J/cm²) would be reasonable for systems without a coupling agent. The contribution of $\gamma_{12}^{\rm in}$ can be estimated as $\gamma_{12}^{\rm in} \approx \Delta H^{\rm in} L$, where $\Delta H^{\rm in} = 3.8$ J/g = 3.5 J/cm³ is the latent heat of HDPE plastic flow, ${}^{16}L = 2r [(\varphi^*/\varphi)^{1/3} - 1]$ is the mean surface-to-surface interparticle distance¹⁸ (i.e., the matrix ligament thickness), 20 and $\varphi^* = 0.60$ (see above).

As can be deduced from Table I, despite 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 values of f for samples with a coupling agent (at equal filler loadings) can be regarded as a natural consequence of a 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)⁵ 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 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 (Table I).

Strain at Break

A final remark is reserved for the strains at break ε_b (Table I). In line with the above arguments, the observed dramatic decrease of ε_b with filler content for nearly all filled series can be regarded as a natural consequence of debonding (i.e., the increase of the over-all population of microvoids). Thus, coalescence of the latter into a major crack spanning the entire sample cross section becomes significantly more probable. Judging by the observed values of E, ε_b , and f (Table I), the stiffness/toughness balance of filled samples can be improved by use of longer filler particles and/or by filler surface treatment.

CONCLUSIONS

The results obtained in the present study confirm the conclusions reached in Part II of this series. First, the degree of crystallinity of the polymer matrix in the filled samples is equal to that in the neat polymer, regardless of the filler content and/or filler surface treatment. Second, the thermoelastic behavior below the apparent yield point ε^* is quantitatively described by classical equations for elastic solids. Thermoelastic parameters of the boundary interphase (BI) that give the best fit to predictions of the step-by-step averaging approach imply a stiff, highly oriented structure of the matrix polymer at the interface. Third, the difference of experimental data for the internal energy increment in the inelastic strain interval above ε^* between unfilled and filled samples, is explained by the onset and further progress of the filler debonding process. The latter process involves contributions of the formation of a polymer-free filler surface and of the concomitant inelastic deformation (plastic flow) of a polymer matrix in the interstitial space between filler particles. Fourth, the fraction of a debonded interface is smaller in samples containing a coupling agent and larger filler particles.

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