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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

COMPOSITION-DEPENDENT PROPERTIES OF POLYETHYLENE/KAOLIN COMPOSITES
VI. Thermoelastic behavior in the melt state

V. P. Privalko[1*], *V. V. Korskanov*[1], *E. G. Privalko*[1], *R. Walter*[2]
and K. Friedrich[2]

[1]Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 253160 Kyiv
Ukraine
[2]Institute of Composite Materials Ltd., University of Kaiserslautern, D-67663, Kaiserslautern
Germany

Abstract

The equilibrium pressure-volume-temperature properties and thermoelastic behavior of kaolin-filled composites of the injection molding grade of high density polyethylene (HDPE) were studied in the temperature interval 423–473 K and in the pressure range 30–100 MPa. It was established that the HDPE melts in filled composites existed in a somewhat expanded, more compressible state. This effect was quantitatively accounted for by the increased number of external degrees of freedom derived from the Simha-Somcynsky equation of state. The effect of the coupling agent on thermal diffusivities and specific heat capacities of filled samples turned out negligibly small.

Keywords: filled polyethylene, *P-V-T* properties, specific heat capacity, thermal diffusivity

Introduction

In our previous publications [1–5], the solid state of kaolin-filled high-density polyethylene (HDPE) composites was characterized by electron microscopy, wide-angle X-ray diffraction, microhardness and thermoelasticity measurements. 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 results of calorimetric studies of the crystal nucleation and the overall crystallization kinetics from the melt state [6] also implied significant changes in the local structure of the polymer melt in the immediate vicinity to the surface of untreated ka-

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[*] Author to whom all correspondence should be addressed.
Present address: (c/o Prof. M. Narkis), Department of Chemical Engineering, Technion, 32000 Haifa, Israel

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olin particles for the injection molding HDPE-1 grade. However, these changes seemed much less severe for filled composites containing the coupling agent (presumably, due to weaker interactions at the polymer melt/kaolin interface).

In this paper, thermodynamic properties and heat transfer parameters of these composites in the melt state were characterized by thermoelastic measurements in the intervals of temperatures and pressures close to those commonly used in the melt processing technology.

Experimental

Materials

The injection molding grade (melt flow index MFI=4.00 g10 min^{-1}) high-density polyethylene (hereafter referred to as HDPE) was used as a matrix material. Filled composites prepared on a twin-screw extruder by compounding a polymer matrix with kaolin particulates (mean equivalent diameter about 0.8 μm) with and without the custom coupling agent (coded as 'Y' and 'N', respectively), were supplied by the manufacturer (ENICHEM, Italy). Before compounding, kaolin with the formula $Al_2O_3.SiO_2 2H_2O$ was treated by calcination above 600 K to destroy its crystalline structure.

Method

The detailed description of the experimental set-up (commonly referred to as the 'thermoelastometer') was published elsewhere [7–11]. A polymer sample is placed at room temperature into the pressure chamber which is equipped with the shielded micro-thermocouple located at the geometrical center of the latter. The differential signal between this inner thermocouple and the identical reference one fixed in the body of the pressure chamber, is converted into corresponding temperature difference ΔT (the estimated mean error $1.12 \cdot 10^{-2}$ deg [7–11]).

The experiments were carried out in two alternative regimes. In the regime of isobaric cooling, the sample was heated to T_0=473 K at the nominal pressure P_0=30 MPa, stored for 15 min to erase the previous structural memory of the polymer, loaded to a predetermined pressure $P_i=P_0+\Delta P_i$ (where ΔP_1=10 MPa, ΔP_2=20 MPa, and so on) and then cooled step-like to T=353 K. After storage during 5 min at each step the isochronal values of the polymer specific volume ν_{isot} were calculated (estimated mean error about 0.15%) from the known mass and geometrical dimensions of the sample (with appropriate corrections for pressure and temperature dependencies of the pressure chamber) [6–8]. As can be seen from Fig. 1, each specific volume isobar is reasonably approximated by two linear segments with different slopes $(\partial\nu_{isot}/\partial T)_P$ separated by a discontinuous ν_{isot} drop in the temperature interval of crystallization.

In the regime of isothermal loading, the sample was heated again to T_0=473 K at the nominal pressure P_0=30 MPa, stored for 15 min to erase the previous structural

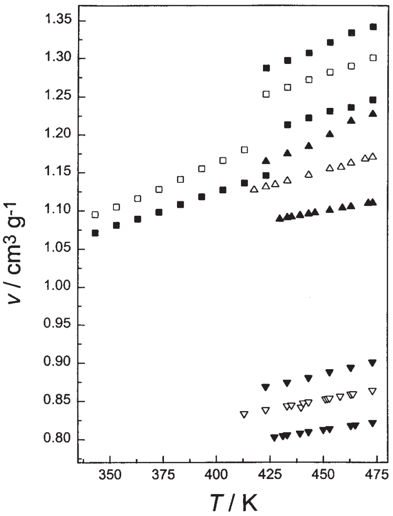

Fig. 1 Specific volumes of the neat HDPE (squares) and kaolin-filled composites INS-10 (up triangles) and INS-30 (down triangles) at pressures=0.1, 50 and 100 MPa (from top to bottom)

memory, cooled to a predetermined temperature T_i, equilibrated during 15 min and then 'instantaneously' loaded by a pressure increment ΔP_i. After completion of the contraction cycle (associated with the levelling-off and subsequent apparent invariance of readings for the sample height, h_∞, and for the ΔT baseline at $P_i=P_0+\Delta P_i$), the sample was instantaneously unloaded by a decrement ΔP_i, and the reverse (expansion) cycle was recorded. During relaxation at each temperature and pressure, the time-dependent values of the polymer specific volume ν_t were calculated as described above.

Thermal diffusivities *a* in both loading/unloading cycles were obtained (the estimated mean error 3.3%) from the best fits of the descending tails of experimental ΔT_t *vs*. time *t* curves to the exponential expression [7, 12],

$$\Delta T_t \sim \exp\left[-(A+BF_{oR})\right], \tag{1}$$

where $F_{oR}=at/R^2$ is the Fourier number, $2R$ is the inner diameter of the pressure chamber, *A* and *B* are the numerical parameters.

Results and discussion

Isobaric cooling regime

As expected, both the absolute values of melt specific volume, ν_l, along each isotherm, and the slopes of isobars, $d\nu_l/dT$, decreased, the higher the pressure *P* (Fig. 1). The observed smooth decrease of ν_l of the neat HDPE-1 with *P* can be adequately accounted for by the Tait equation [13],

$$1-\nu_l/\nu_{l0}=0.0894\ln(1+P/B_T), \qquad (2)$$

where ν_{l0} is the specific volume at normal pressure which is obtained by Eq. (2) as that assuring minimum variation of parameter B_T at each temperature over the entire experimental pressure range [8–10]. As can be seen from Fig. 2, the B_T *vs.* T plot can be represented by two straight-line segments intersecting at T=443 K; alternatively, the temperature dependence of B_T can be also reasonably approximated (dashed line in Fig. 2) as [13]

$$B_T=B_{T0}\exp[-A_T(T-273)] \qquad (3)$$

It can be easily checked that the numerical values of the fitting coefficients (A_T=4.38.10^{-3} deg^{-1} and B_{T0}=175 MPa), as well as the absolute values of ν_l are very close to those for the HDPE sample studied in [13].

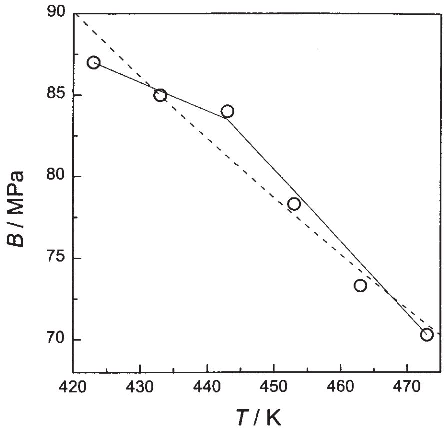

Fig. 2 Temperature dependence of the Tait B parameter for the neat HDPE

Quantitative treatment of the experimental results for filled composites would require P-V-T data for the neat kaolin which are unavailable ; however, reasonable estimates of the latter can be made by appropriate extrapolation procedures. As established in our previous paper [4], the apparent specific volume of kaolin particles in composites (ν'_K=0.380 cm^3 g^{-1}) obtained by linear extrapolation of the room-temperature specific volumes (ν_{298}) *vs.* filler mass fraction (W) plots to W=1.0 (cf. lower part of Fig. 3) coincides with that reported for a bulk kaolin [14]. Therefore, a similar procedure was used to derive the apparent values of ν'_K at different temperatures and pressures from ν_l *vs.* W plots for composites in the melt state of HDPE (cf. upper part of Fig. 3). The apparent coefficients of bulk thermal expansion at normal pressure (α_K=dlnν'_K/dT≈6.0.10^{-4} K^{-1}) and of isothermal compressibility at 473 K (β_K=–dlnν'_K/dP≈3.7.10^{-4} MPa^{-1}) of kaolin particles derived from such plots, are typical for ‘soft’ amorphous solids [14, 15].

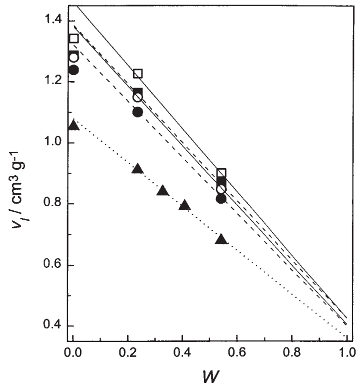

Fig. 3 Dependencies on the filler mass fraction of specific volumes of kaolin-filled composites of series INS at room temperature and normal pressure (filled triangles), at T=473 K (squares) and T=453 (circles) and pressures P=0.1 MPa and P=100 MPa (opened and filled symbols, respectively)

The same data were subsequently used to estimate the apparent melt specific volumes v'_l of the polymer matrix in kaolin-filled composites at each temperature and pressure by linear extrapolation of v_l *vs.* W plots to W=0 (Fig. 3). As can be inferred from higher values of v'_l and smaller values of the Tait parameter B_T, the HDPE melts in filled composites exist in a somewhat expanded, more compressible state. These results are thus qualitatively consistent with our earlier claim [6] about possible structural changes in the HDPE melt near kaolin surface as responsible for changes of crystallization kinetics.

The P-V-T properties of HDPE melts in the neat state and in kaolin-filled composites will be also quantitatively discussed within the framework of the Simha-Somcynsky (SS) reduced equation of state [13, 16]

$$\bar{P}\bar{V}/\bar{T}=[1-2^{-1/6}y(y\bar{V})^{-1/3}]^{-1}+(2y/\bar{T})(y\bar{V})-2[1.011(y\bar{V})^{-2}-1.2045] \tag{4a}$$

which is valid under the additional equilibrium condition,

$$\begin{aligned}(3C/p)^{-1}[1+y^{-1}\ln(1-y)]=(y/6\bar{T})(y\bar{V})^{-2}[2.405-3.033(y\bar{V})^{-2}\\ +[2^{-1/6}y(y\bar{V})^{-1/3}-1/3][1-2^{-1/6}y(y\bar{V})^{-1/3}]^{-1}\end{aligned} \tag{4b}$$

In Eqs (4a) and (4b), $\bar{P}=P/P^*$, $\bar{T}=T/T^*$ and $\bar{V}=V/V^*$ are the reduced pressure, temperature and volume; $P^*=CkT^*/V^*$, $T^*=qz\varepsilon^*/Ck$ and V^* are the corresponding characteristic reducing parameters; qz is the number of external (i.e., volume-dependent) contacts ; z is the coordination number of a liquid quasi-lattice (in practice, z=12 is usually assumed); C is the number of external degrees of freedom per chain, ε^* is the energy parameter of the potential of non-bonded interactions; y is the fraction of occupied sites in the quasi-lattice, and p is the degree of polymerization.

The values of the characteristic SS reducing parameters P^*, V^* and T^* obtained by computer fits of the relevant experimental data to Eq. (4) are collected in Table 1; the quality of fits can be assessed from the representative isothermal compression

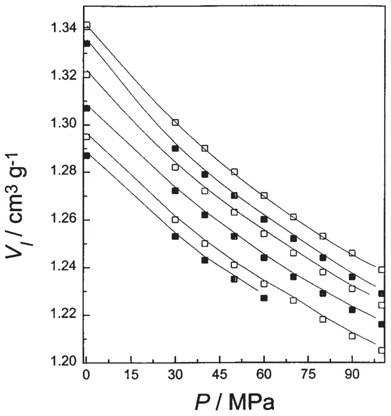

Fig. 4 Fits of experimental specific volumes of the neat HDPE to theoretical SS curves (solid lines) at 473, 463, 453, 443, 433 and 423 K (from top to bottom)

plots for the neat HDPE melt (Fig. 4). The molecular mobility as expressed through the effective number of external degrees of freedom per chain repeating unit, $3C/p=(P^*V^*/T^*)(3mR)$, turned out higher for the HDPE matrix in filled composites of both INS and IYS series (Table 1) compared to the neat HDPE melt (here m=28 is the mass of the chain repeating unit). This is an obvious consequence of the expanded state of the former, as mentioned above.

Table 1 Characteristic parameters of the Simha-Somcynsky equation of state, thermal diffusivities and specific heat capacities in loading/unloading cycles

Sample	P^*/MPa	T^*/K	V^*/cm^3 g^{-1}	$3C/p$	a/10^8 m^2 s^{-1}	C_p/J (g K)$^{-1}$
HDPE	865	18280	1.241	0.60	12.3/12.4	2.25/2.30
HDPE-INS	1300	18285	1.276	0.92	11.8/11.9	2.70/2.22
HDPE-IYS	1355	18285	1.283	0.97	11.4/11.4	2.30/2.10

Isothermal loading regime

As could be expected [11], the instantaneous (solid-like) contributions δ_{inst} made over 90% of the total reduced specific volume changes, $\delta=(\nu_0-\nu_t)/(\nu_0-\nu_\infty)$, recorded in both loading/unloading cycles for all studied samples in the HDPE melt state far above T_m (here ν_t, ν_0 and ν_∞ are the sample specific volumes at times t , t=0 and $t\to\infty$, respectively). The patterns of the ΔT_t *vs*. t curves during the unloading cycle (sample expansion) were also nearly exact mirror images of the corresponding curves in the loading (sample compression) cycle (Fig. 5). These observations are consistent with the equilibrium state of HDPE melts assumed in the previous discussion.

The values of thermal diffusivity a derived from the fits of the descending tails of the ΔT_t *vs*. t curves for both contraction/expansion cycles (Fig. 5) to Eq. (1) did not ex-

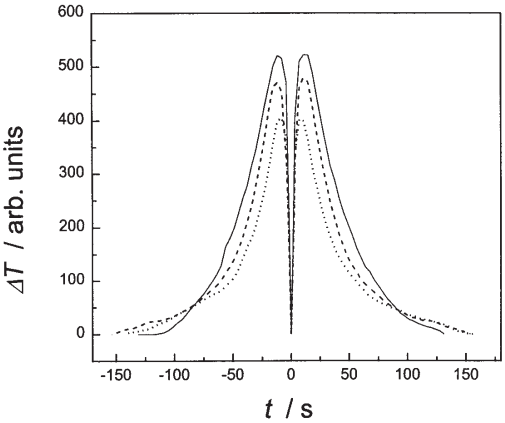

Fig. 5 Time dependencies of temperature jumps ΔT_t in compression (t>0) and in expansion (t<0) cycles at T=453 K for the neat HDPE (solid lines) and for kaolin-filled composites INS-10 (broken lines) and INS-30 (dotted lines)

hibit a clear-cut dependence on ΔP_i but were somewhat smaller in filled composites (Table 1). The specific heat capacities C_p calculated by the Thomson equation [6],

$$(\Delta T_{cor}/\Delta P)_S \approx (\partial v/\partial T)_P T/C_p, \quad (5)$$

were also reasonably close to the tabulated values for HDPE [17] (here ΔT_{cor} is the corrected value of the temperature jump obtained by extrapolation of exponential tails in Fig. 5 to t=0 [6]). Again, no definite differences between thermal diffusivities and specific heat capacities for samples of INS and IYS series could be detected.

Conclusions

1. The HDPE melts in filled composites exist in a somewhat expanded, more compressible state. This effect can be quantitatively accounted for by the increased number of external degrees of freedom derived from the Simha-Somcynsky equation of state.
2. The effect of the coupling agent on thermal diffusivities and specific heat capacities of filled samples is negligibly small.

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