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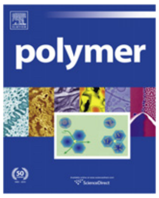

Polymer Communication

Particle size dependence of the elastic modulus of particulate filled PMMA near its T_g

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Models for composition dependence of elastic modulus of particulate filled polymers inherently assume modulus of the matrix independent of particle content and size. In this letter, experimental evidence is presented for existence of a critical particle size below which elastic modulus of the matrix becomes strongly dependent on the particle content due to the extensive chain stiffening. It is also suggested that below the critical particle size, specific interface area should replace volume fraction as the structural variable.

1. Introduction

The reinforcement of the filled amorphous polymers consists of a contribution related to the volume of the rigid filler and a contribution due to the molecular stiffening caused by the interaction between particle surface and matrix chains [1]. The first one is dominating for coarse particles, while the second one prevails for submicron particles. Commonly used models inherently assume modulus of the matrix independent of particle content and size, i.e. [2]:

$$\frac{M_c}{M_m^0} = M_r = f\left(v_f\right). \tag{1}$$

The steep increase of the elastic modulus of polymers filled with relatively small amount of submicron particles is generally ascribed to the molecular stiffening [3] with its extent proportional to the specific filler–matrix interface area, S_f, thus, should be particle size dependent [4]. In this case, the composite modulus can be expressed phenomenologically as

$$M_c = M_m^* f\left(v_f\right), \tag{2}$$

where

$$M_m^* = M_m^0 \Phi\left(S_f\right) \tag{3}$$

is the modulus of the matrix in the presence of particles which differs from that for the neat polymer, M_m^0. The $\Phi(S_f)$ is an unknown dependence of the extent of molecular stiffening on the specific interface area, spatial arrangement of particles and the strength of the filler–matrix interactions. For large particles, i.e., $r \gg R_g$, and large v_f, the $\Phi \to 1$ and $M_m^* \approx M_m^0$. For small v_f and $r \approx R_g$, the $f(v_f) \to 1$ and the reinforcement is predominantly due to the matrix stiffening, i.e., $M_c \approx M_m^*$. Since the molecular stiffening is pronounced the most for highly mobile chains, the effect of particle size on the elastic modulus has been investigated near the neat matrix T_g.

2. Experimental

PMMA Plexiglas (Rohm, Germany) with the $M_w = 1.15 \times 10^5$ g mol^{-1}$M_w/M_n = 1.7$ and $T_g = 100$ °C has been filled with either fumed silica (Sigma Aldrich, 390 m^2/g), fused silica microbeads (Mizusawa, 3.9 m^2/g) or E-glass beads (Owens–Corning, 0.3 m^2/g) (Fig. 1). Particles were dispersed in acetone and sonicated (Kraintek K-5 LM, CZ). PMMA was dissolved in acetone under stirring at 1000 rpm. Particle dispersion was mixed into polymer solution and sonicated for 1 h. Then, solvent was removed using a vacuum oven at 80 °C for 4 h and dry nanocomposite was milled. Milled powder was dried at 140 °C for 1 h and then compression molded at 190 °C at 2 × 10^4 pounds into sheets. Rectangular bars $40 \times 10 \times 0.5$ mm^3 and dog-bone ISO 293 specimens were cut from the sheets for DMTA and tensile testing. Tensile elastic modulus, E_c, was measured using Zwick Z010 Universal Tensile Testing Machine (Zwick Roel, Germany) below T_g at +80 °C and using the ARG2 rheometer (TA, USA) at 1 Hz and strain aplitude of 1% above T_g at

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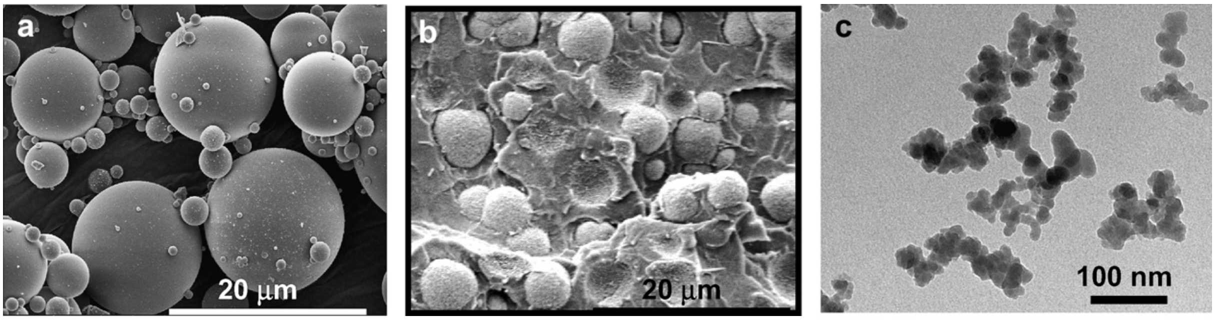

Fig. 1. SEM micrographs of glass beads (a), fused silica beads (b) and TEM of fumed silica nanoparticles (c).

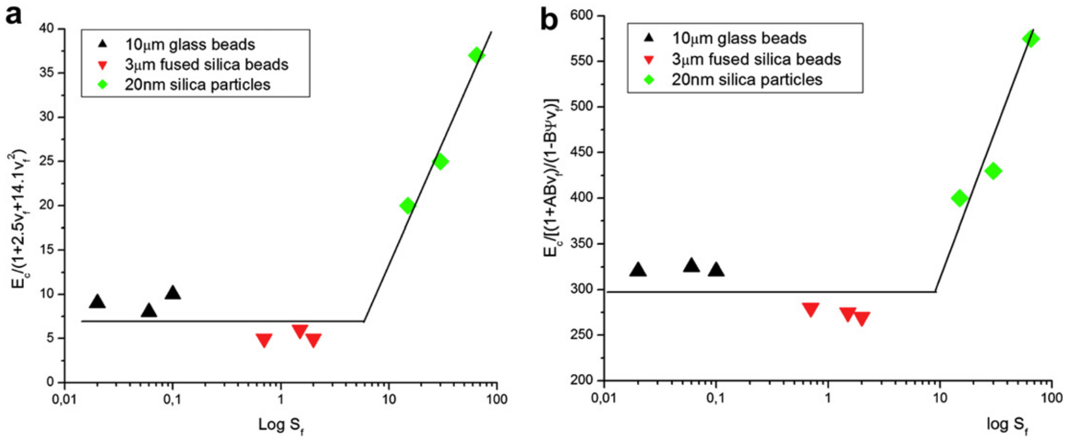

Fig. 2. Dependence of the matrix modulus, $M_{\mathrm{m}}^{*} = E_{\mathrm{c}}/f(\nu_{\mathrm{f}})$, on the logarithm of the logarithm of the specific interface area, S_{f}, above T_{g} using the Guth model (a) and below T_{g} using the Kerner–Nielsen model (b).

+130 °C for the v_{f} ranging from 0 to 0.3. Constant true strain rate was $10^{-3}\ \mathrm{s}^{-1}$ and laser extensometer was used in the tensile measurements. Standard deviation of less than 5% has been obtained for all the measurements (SD is represented by the size of symbols).

3. Results and discussion

It was assumed that the amount of stiffened chains was scaling with the specific filler–matrix interface area, S_{f} [5]:

$$M_{\mathrm{m}}^{*} = M_{\mathrm{m}}^{0}\cdot K\cdot\log\left(S_{\mathrm{f}}\right), \tag{4}$$

where K is a constant dependent on the extent of interfacial interactions. The S_{f}, can be expressed considering the filler specific surface area, S_{A} and the filler weight fraction, w_{f}:

$$S_{\mathrm{f}} = S_{\mathrm{A}}w_{\mathrm{f}}. \tag{5}$$

Under grossly simplified assumptions of monodisperse spherical filler with the radius, r, and monodisperse coiled chains with radius of gyration, R_{g}, the ratio of filler to matrix density is

$$\frac{\rho_{\mathrm{f}}}{\rho_{\mathrm{m}}} = \frac{m_{\mathrm{f}}N_{\mathrm{g}}R_{\mathrm{g}}^{3}}{m_{\mathrm{m}}N_{\mathrm{f}}r^{3}}, \tag{6}$$

where m_{f} is the weight of N_{f} monodisperse filler spheres, m_{g} and N_{g}, respectively, is the weight and number of monodispersed coiled chains in a unit volume of the composite. The monodisperse filler specific surface area equals to

$$S_{\mathrm{A}} = \frac{3}{r\rho_{\mathrm{f}}}. \tag{7}$$

Eqs. (6) and (7) can be substituted in Eq. (5) which then can be substituted in Eq. (4). For $r \gg R_{\mathrm{g}}$ and $r < R_{\mathrm{g}}$, respectively, Eq. (4) becomes:

$$M_{\mathrm{m}}^{*} = M_{\mathrm{m}}^{0}\cdot K \quad \text{and} \quad M_{\mathrm{m}}^{*} = M_{\mathrm{m}}^{0}\cdot K\cdot\log\left(\frac{3}{\rho_{\mathrm{f}}r}\right) \tag{8}$$

In order to test this hypothesis, experimental data were reduced using the Guth–Gold model for $T > T_{\mathrm{g}}$ (Fig. 2a) and the Kerner–Nielsen model for $T < T_{\mathrm{g}}$ (Fig. 2b). Young's modulus used was 2 GPa for PMMA and 70 GPa for silica; the shear modulus of 0.5 GPa for PMMA and 30 GPa for silica was used. The maximum achievable filler volume fraction of 0.637 was considered. Poisson's ratio of 0.33 and 0.25 for PMMA and silica, respectively, was used to calculate Kerner–Nielsen constants. In agreement with the proposed hypothesis, $E_{\mathrm{m}}^{*} \approx E_{\mathrm{m}}^{0}$ for particles larger than 1 μm and became strongly dependent on particle content for nanometer sized particles, increasing approximately linearly with $\log(S_{\mathrm{f}})$ at both temperatures investigated (Fig. 2). Needless to point out that the scale of matrix stiffening below T_{g} is only about 1/8 of that above the T_{g}.

4. Conclusions

Effect of particle size on the elastic modulus of the particulate filled PMMA was investigated for $T < T_{\mathrm{g}}$ and $T > T_{\mathrm{g}}$. It was found that for particles larger than 1 μm, the extent of molecular stiffening was negligible and, thus, matrix modulus was independent of v_{f}. For nanometer sized particles, the extent of chain stiffening was large resulting in a strong dependence of the matrix modulus on the filler content for both temperatures investigated. Even though the proposed simple model does not describe the actual molecular mechanism of chain stiffening, it can provide a simple framework for analyzing the experimental data.

Acknowledgements

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