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Immobilization of polyvinylacetate macromolecules on hydroxyapatite nanoparticles

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Abstract

Concentration dependence of the storage modulus, E', was investigated for polyvinylacetate (PVAc) filled with hydroxyapatite (HAP) nanoparticles. The filler volume fraction, v_f, varied from 0 to 0.05 and the E' and loss tangent, tan δ, were measured below neat matrix T_g at −40 °C and above neat matrix T_g at +50 °C at 1 Hz. The T_g determined as the position of the maximum on the temperature dependence of tan δ increased by 14 °C compared to the neat PVAc (39 °C) by adding 5 vol.% of HAP. At −40 °C, the observed small increase of E' with v_f was in agreement with the prediction based on the simple Kerner equation. At +50 °C, the increase of E' with v_f observed was an order of magnitude greater than that predicted using the simple continuum mechanics model. An attempt was made to explain the observed deviation employing the hypothesis of immobilized entanglements.

Keywords: Nanocomposite; Elastic modulus; Immobilized layer

1. Introduction

Conformation entropy, S_c, controls viscoelastic behavior of amorphous polymers above the glass transition temperature, T_g, while the cohesive energy controls mechanical response below T_g [1–4]. Above the T_g, the number of conformations of a polymer chain is related to the number of skeletal bonds in the macromolecule and the conformation entropy, S_c, is proportional to the logarithm of the partition function of the chain, Ω. Similarly to the glass transition, immobilization of macromolecules on a solid surface can result in a substantial reduction of the S_c [5], leading to a significant increase of the elastic modulus of the immobilized polymer layer. The higher the specific surface area of the filler, the larger the polymer volume in contact with its surface and the higher the extent of polymer immobilization.

The steep increase of the elastic modulus of a nanocomposite with addition of very small volume fraction of silica was attributed to the substantial reduction of the S_c near the rigid surface [5–8]. It is generally accepted that the immobilized layer plays a crucial role in the viscoelastic behavior of nanocomposites because of the large filler specific surface area commonly ranging from 100 $m^2 g^{-1}$ to 1000 $m^2 g^{-1}$. Moreover, for particles with diameter less than 20 nm, their size is comparable with the size of polymer coils which, most probably, can disturb the Gaussian chain statistics. Therefore, a simple continuum mechanics approach may not be applicable to predict the concentration dependence of the elastic modulus of polymer nanocomposites. In addition to immobilization effects, filler percolation and formation of a 3D network of immobilized matrix described earlier [7,9] were assumed to affect the deformation response of polymer nanocomposites.

In this paper, experimental evidence is presented supporting the validity of the immobilized entanglement model for the description of the viscoelastic response of model nanocomposites proposed currently by Sternstein and Zhu [10].

2. Experimental

Polyvinylacetate (PVAc), $M_w = 9.2 \times 10^4$ g mol^{-1}, $M_w/M_n = 3.5$, $T_g = 39$ °C (Sigma–Aldrich, Germany), was used

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as the matrix. Hydroxyapatite (HAP) with spherical particles with mean-average diameter, $d_{ave} = 20$ nm, and specific surface area, $S_f = 190$ m^2 g^{-1} (BET Quantachrome, USA), was used as the filler. To prevent particle agglomeration, PVAc/HAP composites were prepared by dissolving PVAc in acetone followed by the addition of HAP slurry. Solution was ultrasonicated for 10 min. Then, the acetone was partially removed under vigorous stirring at 50 °C to form a gel. The gel was deposited on an aluminium sheet and dried at 90 °C for 90 min. Stack of dried sheets (1 mm thick) was heated at 120 °C for 5 min and then compression molded at 120 °C for 2 min and cooled to 15 °C for 2 min. Rectangular specimens were cut from the sheets using a hand press. Slices 20 nm thick were cut from the prepared sheets using an ultramicrotome and observed using a transmission electron microscope (FEI, CZ). TEM showed dispersion of individual HAP particles.

The measurement of the storage modulus, E', and tan δ was carried out using DMA (TA 2986, USA) at the frequency of 1 Hz, over the temperature interval ranging from −60 °C to 80 °C. The storage modulus, E', was determined at −40 °C and at +50 °C. The T_g of the nanocomposite was determined as the position of the maximum on the thermal dependence of tan δ. The overall standard deviation of the measured E' and tan δ was about 10%.

3. Results and discussion

3.1. Glass transition temperature

The dependence of the measured T_g on the v_f is shown in Fig. 1. The observed significant shift of T_g to higher temperatures with increasing v_f suggested significant segmental immobilization of the PVAc chains by the filler surface causing significant decrease of the S_c near filler surface. In addition to surface immobilized chains, it seems reasonable to assume that a transformation from the Gaussian coil to the Langevine coil occurred near the filler surface [9], and mobility of PVAc chains relatively far from the surface can be reduced *via* immobilized entanglements [10]. Because of the large area of the matrix–filler interface, significant portion of the matrix was immobilized resulting in the observed shift of the T_g to higher temperatures.

3.2. Storage modulus

In Fig. 2, the concentration dependence of the relative storage modulus, E_r, on the v_f is shown at −40 °C and at +50 °C. At −40 °C, the increase of E_r with v_f was in agreement with the simple Kerner equation [14]. Below T_g, the presence of the filler can affect only low temperature secondary transitions which is of marginal importance for the composite mechanical response. Hence, the reinforcing mechanism of adding HAP nanofiller was only the replacement of a small portion of the soft PVAc matrix with the rigid filler as assumed by the Kerner model.

At +50 °C, the E_r increased an order of magnitude more than predicted using the Kerner model. Hence, an additional reinforcement mechanism has to exist in addition to that observed below T_g. An extensive segmental immobilization of the polymer matrix at the filler surface was considered to be the dominating reinforcement mechanism above T_g. From a simple estimate of the amount of immobilized polymer to fit the experimental data, it was assumed that the immobilization effect expanded further from the filler surface into the matrix bulk. The proposed hypothesis was further supported by TEM showing dispersion of 3–7 nm particles embedded in an immobilized PVAc layer (Fig. 3). This was in agreement with the model proposed recently by Sternstein and Zhu [10]. It was also speculated that the segmental density distribution function differs most probably from that in the polymer bulk [3]. The distribution is probably less symmetrical in its shape, compared to the Gaussian distribution function for an undisturbed single chain in the bulk [13].

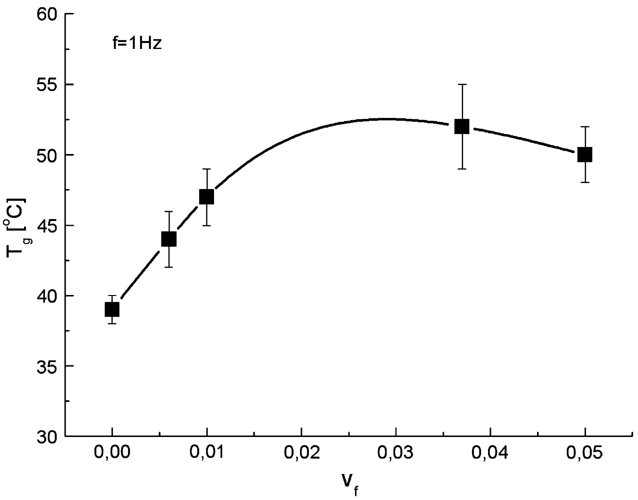

Fig. 1. Glass transition temperature dependence on filler content for PVAc/HAP composites.

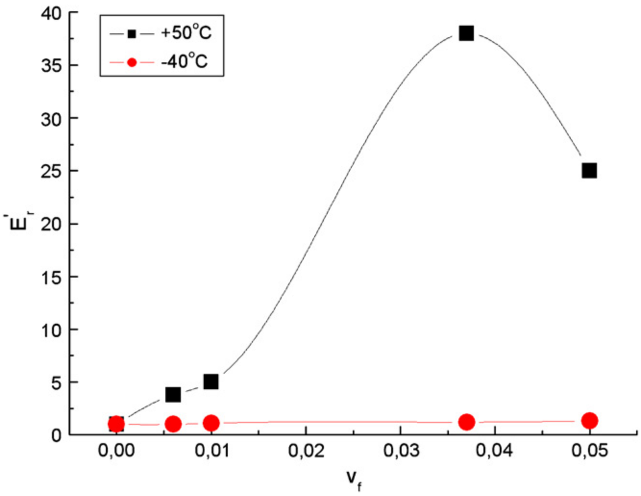

Fig. 2. Relative Young modulus, E'_r vs. filler volume fraction, v_f, for PVAc/HAP composites measured at 1 Hz at −40 °C and at +50 °C.

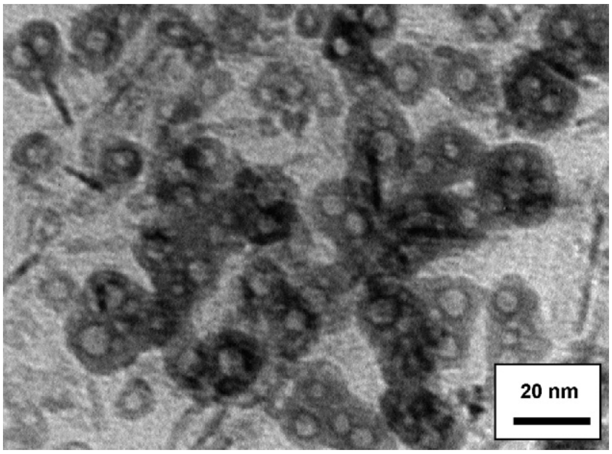

Fig. 3. TEM micrograph of the PVAc/HAP nanocomposite. HAP particles 3–7 nm in size are embedded in the PVAc immobilized layer and this "core–shell" inclusions are dispersed in the PVAc matrix.

Alternatively, one can use the reptation model to describe the observed immobilization effect [11,12]. This approach considers each macromolecule constrained in a tube-like region with the diameter D. The constraints imposed on the molecular mobility are by the virtue of neighbouring entanglements and molecular friction. Additional constraint for chain mobility can be caused by the presence of a solid surface. In the case of nanofillers with large specific surface area, this effect may become dominant. The closer the chains to the filler surface the stronger the immobilization and the higher the restriction of the reptation motion. It seems likely that there is a significant increase of the relaxation time and decrease of the tube diameter, D [15].

4. Conclusions

Dependence of the E' and tan δ on the filler volume fraction was investigated for PVAc filled with HAP nanoparticles over the temperature interval from $-40\,^{\circ}\mathrm{C}$ to $+80\,^{\circ}\mathrm{C}$. At $-40\,^{\circ}\mathrm{C}$, concentration dependence of E' agreed reasonably well with the predictions based on the Kerner model. At $+50\,^{\circ}\mathrm{C}$, the model of immobilized entanglements and change of conformation statistics of chains near the filler surface had to be considered to explain the observed several fold increase of E' caused by the addition of a small amount of HAP. It was demonstrated that the large specific surface area of the nanosized filler is capable of immobilizing large amount of entanglements causing the steep increase of E' even at small nanofiller content. Alternatively, this phenomenon can be described using the reptation theory considering an increase of the relaxation time and a reduction of the tube diameter due to interaction between chains and solid surface.

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