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Study Rigid Amorphous Fraction in Polymer Nano-Composites by StepScan and HyperDSC

Introduction

It is known that there is a rigid amorphous fraction (RAF) in semicrystalline polymers. The RAF exists at the interface of crystal and amorphous phase as a result of the immobilization of a polymer chain due to the crystal. There is debate on whether the crystal melts first and then RAF devitrifies or the RAF devitrifies before the crystal melts. It can not be answered easily because these two things often happen in the same temperature range. Also, the RAF fraction sometimes exists at the surface of silica nanoparticles in the polymer silica nanocomposites material. However, unlike semi-crystalline polymers, the silica nanoparticle does not undergo any transition at the temperature when RAF devitrifies. So polymer silica nanocomposites offer a good opportunity to study the devitrification of RAF¹.

Some studies have indicated a second glass transition from RAF in dynamic measurements. To the author's best knowledge, there is no evidence of a second T_g in polymer nanocomposites from DSC experiments. In order to identify RAF in DSC, absolute heat capacity measurement is very important. A formula has been well established for the determination of RAF in semicrystalline polymers based on accurate heat capacity measurement as described by Wunderlich, see² for a review.

Here, heat capacity measurement has been performed in order to detect a possible second T_g on nanocomposites of polymethyl methacrylate (PMMA) with silicon oxide nanoparticles of different shape. StepScan™ DSC was used for determination of precise heat capacity and HyperDSC® to prevent degradation and identify devitrification of the RAF at elevated temperatures.

Experimental

Precise heat capacity curves were obtained using a PerkinElmer® Diamond DSC. Heat capacity was determined from StepScan, a special variant of temperature modulated DSC³. Measurements were performed using samples of about 20 mg, 3 K steps at heating rate 6 K/min and isotherms of about 1 minute. The temperature range, if not otherwise indicated, was 30 to 170 °C. The instrument was calibrated as recommended by GEFTA using indium and zinc at zero heating rate for temperature and sapphire for heat capacity. Due to the low underlying heating rate, 3 K/min, deviations from the zero rate calibration were less than 0.2 K and not further considered. Uncertainty of heat capacity was about 2%. HyperDSC measurement was performed at 400 K/min in order to prevent the degradation of polymer up to about 360 °C.

Result

A sketch of the polymer silica nanocomposite material is presented in Figure 1. Three phases are present including silica nanoparticles, mobile amorphous polymer phase and rigid amorphous phase at the particle interface.

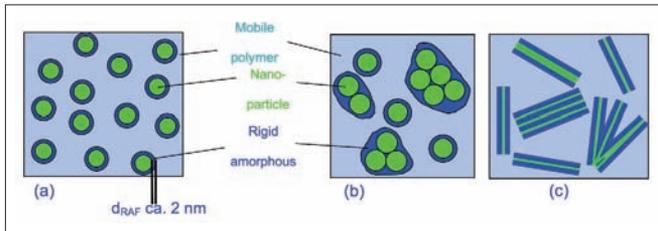


Figure 1. Sketch of spherical (a, b) and layered (c) nanoparticles covered by a layer of immobilized polymer (RAF). Total deagglomeration of the particles is assumed in (a); a more realistic situation is shown in (b) and (c).

For semicrystalline polymers it is well known that the observed step in heat capacity, ΔC_p , at the glass transition is often less than expected from crystallinity. Wunderlich et al. therefore introduced the concept of a rigid amorphous fraction (RAF):

$$RAF = 1 - \text{crystallinity} - \Delta C_p / \Delta C_{p, \text{pure}} \quad \text{eq. (1)}$$

where ΔC_p and $\Delta C_{p, \text{pure}}$ are the heat capacity increments at the glass transition for the semicrystalline and the amorphous polymer, respectively. The ratio of both step heights represents the fraction of the polymer contributing to the glass transition, which is called mobile amorphous fraction (MAF).

For polymer nanocomposites sometimes a reduced step height (relaxation strength), ΔC_p , at glass transition is observed too. Similarly an immobilized or rigid amorphous fraction can be determined from heat capacity according eq. 1 replacing the crystalline by the nanoparticle fraction.

$$RAF = 1 - \text{filler content} - \Delta C_p / \Delta C_{p, \text{pure}} \quad \text{eq. (2)}$$

In order to apply eq. 2 precise heat capacity data in the temperature range of the glass transition of the polymer nanocomposite are needed. In Figure 2 the measured specific heat capacities for the PMMA based nanocomposites are shown. The curves were calculated in respect to the sample mass (polymer + nano particles). As for semicrystalline polymers a slight increase in glass transition temperature was observed for all nanocomposites after carefully drying at reduced pressure. The glass transition temperature of the nanocomposites was determined as the half step temperature from the StepScan DSC measurements. The values are slightly different compared to scan measurements at 10 K/min because of the different time scale of the experiment.

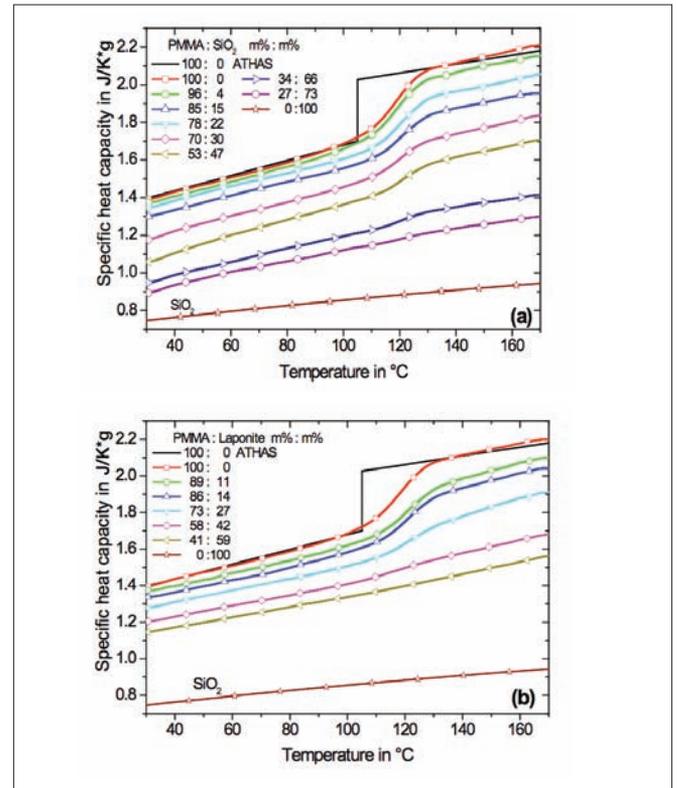


Figure 2. Specific heat capacity of nanocomposites in respect to sample mass. (a) – PMMA with spherical SiO₂ nanoparticles, (b) – PMMA with Laponite RD™. Specific heat capacity for SiO₂ is shown too. The black lines represent reference data for PMMA from ATHAS⁴. Diamond DSC, StepScan mode.

Next, the amount of RAF in the PMMA nanocomposites was quantified applying eq. 2. The step in heat capacity at the glass transition for the different samples was determined as usual at T_g and normalized by the step in heat capacity for the pure polymer. The results for the PMMA and PS nanocomposites are shown in Figure 3.

According eq. 2 the diagonal in Figure 3 represents the case when no RAF is present. In other words, a two phase system (filler + polymer) which is expected if there is no interfacial immobilization. The data for the PS nanocomposite are close to this line. For the PMMA nanocomposites, the decrease of the

normalized relaxation strength is much steeper than the diagonal. From the normalized relaxation strength the different fractions according eq. 2 can be obtained. The upper arrow at 27 m% filler corresponds to the filler fraction. The lowest indicates the mobile amorphous fraction (MAF) contributing to the calorimetric relaxation strength at glass transition. The difference between the measured values and the diagonal (middle arrow) represents the immobilized (rigid) fraction (RAF) which can be calculated according eq. 2.

Straight lines in Figure 3 correspond to a constant ratio between RAF and filler fraction. In other words, it is assumed in ideal cases that each filler particle is covered by the same amount of RAF (all according mass). This assumption is not well justified by the data of Figure 3. The mass percentage of the RAF normalized by the filler content is shown in the inset as a function of the filler mass fraction. If all nanoparticles were covered by the same immobilized layer one would expect to find a constant ratio between the RAF and the filler content. The slight decrease of the ratio indicates a decrease of the RAF per nanoparticle with increasing filler concentration. This is most probably due to agglomeration of the particles as indicated schematically in the inset. Then the effective surface is no longer proportional to filler content and the points in Figure 3 should follow a line parallel to the diagonal. For the highest filler fractions this seems to be the case.

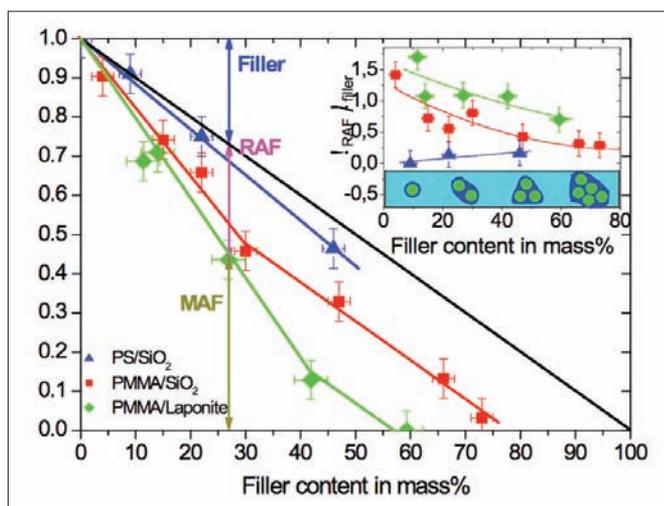


Figure 3. Calorimetric relaxation strength as a function of nanofiller content. The vertical double arrow indicates the amount of RAF for PMMA at 27 m% Laponite RD™ filler. Symbols: Δ – PS with spherical SiO₂ nanoparticles; \square – PMMA with spherical SiO₂ nanoparticles; \diamond – PMMA with Laponite RD™ clay nanoparticles. The inset shows the percentage of the RAF versus filler content, see text.

In order to check the behavior of the RAF layer and to detect a possible second glass transition we performed heat capacity measurements up to the degradation of the polymer. StepScan DSC was used first to obtain precise heat capacity data up to the beginning of degradation. Measurements were performed up to degradation temperature but because of the

isotherm after each 3 K temperature step, heat capacity could be obtained until the heat flow during the isotherm was not stable anymore. RAF devitrification is expected to appear as a second step in heat capacity towards liquid heat capacity. But there is no step like or gradual transition observed up to 250 °C where the polymer starts to degrade at slow heating.

Influence of degradation on the heat capacity determination can be reduced by using high heating rates. To shift the beginning of degradation to higher temperatures, HyperDSC⁵ measurements at 400 K/min heating rate were performed. Also, the fast scanning rate increases the sensitivity of the measurement. So if there was a second glass transition due to the RAF, it would be more easily detected by fast scanning experiments.

At 400 K/min heating rate, the polymer in the nanocomposite does not degrade up to about 360 °C. But there is again no second glass transition visible below 360 °C (Figure 4). This means that the interaction between the polymer matrix and the nanoparticles is so strong that heating even up to such high temperatures is not enough to remove the anchors and to allow relaxation and devitrification of the RAF.

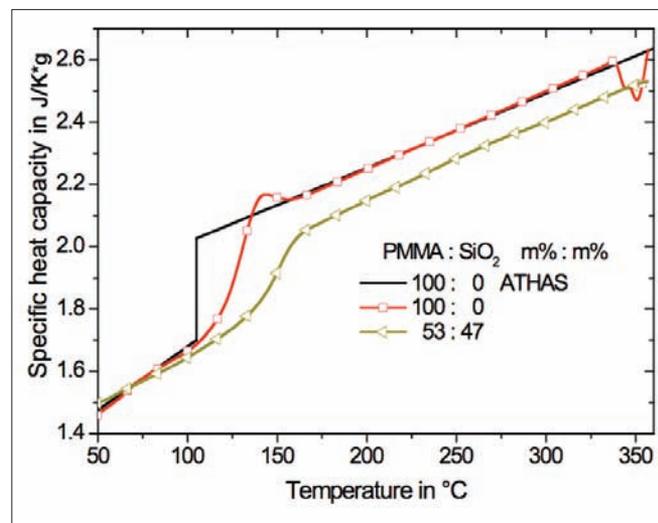


Figure 4. HyperDSC measurements at 400 K/min heating rate for pure PMMA and the nanocomposite filled with 47 m% spherical SiO₂ nanoparticles. Sample mass 0.5 mg. The black lines represent reference data for PMMA from ATHAS⁴.

Interaction between PMMA and SiO₂ at the interface of the nanoparticles is expected to be weaker than a covalent bond, which is present in polymer chains leaving the crystal and proceeding in the amorphous region between the lamellae. If the non covalent bond between the inorganic nanoparticle and the PMMA does not allow devitrification before degradation of the polymer to occur it is very unlikely that in semicrystalline polymers the RAF devitrifies as long as the polymer chains are covalently anchored to the rigid polymer crystals. Most likely, the polymer crystals must melt or gain mobility in another way before the RAF can relax and devitrify.

Conclusion

StepScan method was used to determine the heat capacity at the glass transition of the polymer accurately. Based on that, the existence of an immobilized fraction in PMMA SiO₂ nanocomposites was demonstrated. It was found that the interaction between the SiO₂ nanoparticles and the PMMA is so strong that no devitrification occurs before degradation of the polymer. The nonexistence of a second glass transition was further confirmed by HyperDSC.

The results obtained for the polymer nanocomposites support the view that the reason for the restricted mobility must disappear before the RAF can devitrify. For semicrystalline polymers this means that rigid crystals must melt before the RAF can relax. Only for semicrystalline polymers with significant chain mobility inside the crystals, may RAF devitrify before melting.

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