The Use of Synchrotron Radiation to Improve Polymer Systems

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Introduction

It is well established that, above a certain threshold value for the molar mass M_c, the terminal viscosity of polymer melts scales with molar mass to the power 3.4. The strong increase of the viscosity with increasing molar mass is related to the presence of physical entanglements. The viscosity/molar mass rule implies that polymers of low molar masses are preferred for processing; however, high molar masses are required for materials' properties rendering the production of polymer products an area of unfortunate compromises.

One way to improve the properties of polymeric materials other than increasing its molar mass is to use additives such as nanofillers. This nanocomposite approach has advantages over traditional composites, especially when the length scale of the morphology and the fundamental length scale of the physics of a given property coincide [1]. Well-known examples are (exfoliated) clays and carbon nanotubes (CNT). However, no significant improvements in properties have been observed yet [2], though it may be too early to discard the theoretical potential of nanofillers, as many hurdles are still to overcome, especially regarding the dispersion and the processing of these materials. Mackay et al. [3] reported recently on a drop in the viscosity of nanoparticle-filled polymer melts produced by blending organic nanoparticles, synthesized by intramolecular crosslinking of single polystyrene chains, with linear polystyrene. This observation is in contradiction with the expression derived by Einstein describing the increase of the viscosity as a function of the volume fraction of fillers and the matrix viscosity, suggesting that this expression does not appear to hold in the case of nanoparticles. The decrease in the viscosity was attributed to excluded free volume induced around the nanoparticles. This is, however, accompanied with a significant decrease in the glass transition temperature, which is detrimental for the final properties.

We found a significant improvement of both processing and performance for a silica nanoparticles-filled polypropylene (PP). To facilitate dispersion of the nanoparticles, we developed a novel approach by using solid-state modification of porous, semi-crystalline PP powder with the *in-situ* preparation of silica nanoparticles by sol-gel chemistry [4]. In this presentation, we will show how shear-induced crystallization studies using small-angle X-ray scattering (SAXS) to probe the structure development were very useful to elucidate the mechanism for the improvement in processing and performance.

The next subject is related to the preparation of tough heterogeneous systems based on brittle amorphous polymers such as polystyrene and poly(methyl methacrylate) (PMMA). The macroscopic response is the consequence of the material's intrinsic behavior and it is the combined effect of strain softening and strain hardening that determines whether a polymer deforms in a brittle or ductile manner [5]. The toughness of amorphous polymers can be improved by adding a second, rubbery phase, while between the inclusions of this second phase small ligament thicknesses are preferred.

Consequently, the size of the rubbery phase should be small (~ 50 nm), since then even with moderate fractions, the interparticle distance remains below a critical value and does not allow for craze formation [6], while a high transparency remains. To work as impact modifier, cavitation should occur easily in the dispersed phase, since then release of the triaxial stress state and delocalization of strain is obtained. The capability to cavitate depends on crosslink density and size, but when a particle is precavitated no practical limit exist [7].

To minimize the resistance against cavitation, a low elastic modulus (and glass transition temperature T_g) should be used and maximum toughness is expected for nanosized core-shell particles with a non-entangled core that promotes cavitation and a rubbery shell that supports the matrix ligament during straining, thereby increasing the strain hardening modulus [8]. A possible route to prepare such systems may be the self-assembly process of diblock copolymers in the monomer into micellar morphologies followed by an *in-situ* polymerization of the monomer. By optimizing the block copolymer constituents, architecture, and composition, the morphology of the system can be set beforehand. In-situ SAXS-experiments were used to follow the structure development during preparation, but also to investigate the microscopic mode of deformation.

Methods and Materials

PP/silica nanocomposites were prepared according to the procedure described in reference 4. *In-situ* SAXS-studies were performed on the DUBBLE beamline at the ESRF, France. SAXS patterns were recorded using a gas-filled multiwire 2-D detector [9] and a camera length of 2.5 m.

A Linkam shear cell was used to apply well-defined thermomechanical history. The crystallization temperature was set at 130 ℃, such that the crystallization times are relatively long for quiescent conditions. The temperature profile used was: (1) heating at 30 ℃/min from T_{room} to T_{melt} = 220 ℃; (2) holding T_{melt} for 5 min to eliminate memory effects; (3) cooling at 30 ℃/min to T_{cryst} = 130 ℃ after which immediately SAXS images were collected. The melt was sheared for 5 s at a shear rate 60 s^{-1}. SAXS images were collected before, during and after cession of the applied shear. Details of the preparation of the PMMA and PS samples with the block copolymers are given in [10]. The test samples were stretched using a home-built tensile device in which both clamps could move in opposite directions. The tensile speed was 0.05 mm/min (for details see [10]).

Results and discussion

The dynamic viscosity, $\eta^*(\omega)$, of silica-filled PP was measured as a function of frequency for different compositions and Fig. 1 shows the results of measurements at 180 ℃. The first, striking observation is the large decrease of the viscosity with increasing silica concentration up to approx. 0.5 wt%, after which it increases again. Shear-induced crystallization studies were performed, since flow orients and stretches especially the high

molar mass chains. The degree of the orientation depends on the strength of the flow, the molar mass (distribution) and the temperature [11]. Fig. 3 shows a series of 2-D SAXS-patterns of pure PP and PP nanocomposites. The SAXS images at time t = 0 correspond to the amorphous melt and show a weak, diffuse scattering, indicating the absence of any detectable structure or orientation. The scattering patterns obtained after 180 s clearly reveal the appearance of meridional maxima, originating from oriented structures in the melt. Most remarkably, this is true for the neat PP and nanocomposites, but *not* for the 0.5 wt% silica system. To explain the decrease in the viscosity of the silica-filled polymer melt, we advance the concept of selective physisorption of polymer chains of the highest molar mass on the nanoparticle surface, while the low molar mass PP constitutes the surrounding molten matrix (See Fig. 3) [12].
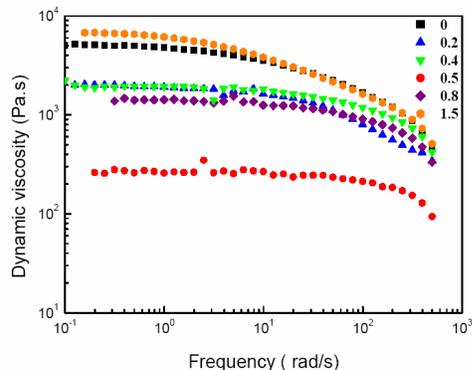

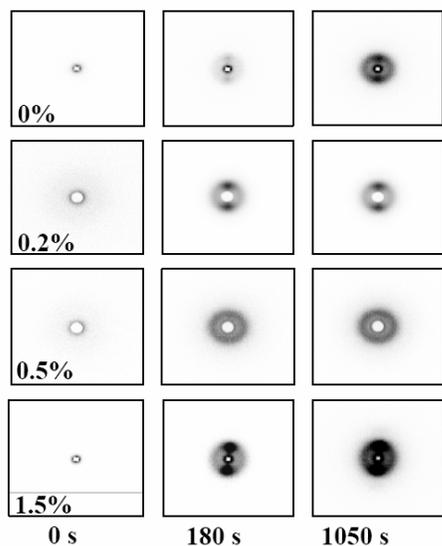*Fig.1. The dynamic viscosity of PP/silica nanocomposites versus frequency at a 1 % strain and 180 ºC.*

Fig. 2. 2-D SAXS-images of PP/silica nanocomposites after a step shear of 60 s⁻¹ for 5 s at 135 ºC.

The occurrence of macrophase separation as shown in Fig. 4 can be suppressed by copolymerization of PS with 0.5-5 mol % of *p*-(hexafluoro-2-hydroxy isopropyl) styrene (HFS) to induce hydrogen bonding between matrix and polyacrylate-block copolymer, which enhances the miscibility and lead to randomly distributed polyolefin particles surrounded by a homogeneous PBA/PS matrix [10]. The macroscopic strain at break depends to a large extent on the diblock copolymer content and the degree of demixing between the rubber shell and PS matrix. Brittle behavior was observed for PS blends which contain more than 3 mol % HFS and show complete miscibility between the PS matrix and acrylate shell. The degree of demixing controls

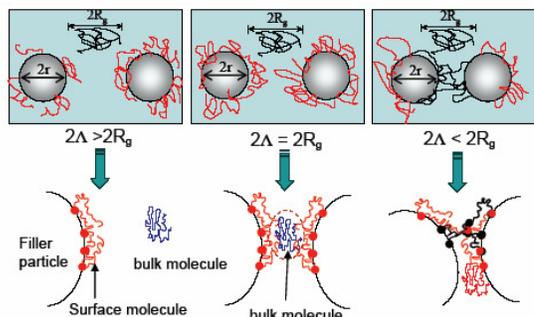the microscopic deformation mode. i.e. crazing versus cavitation-induced shear yielding.

Fig. 3. Schematics showing the adsorption process and the effect of silica concentration (interparticle distance (Λ)) on the particle-particle and particle-polymer interactions.
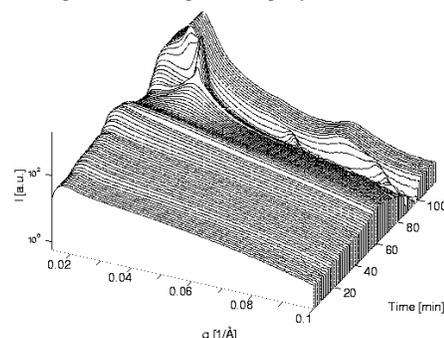

Fig. 4. 3-D SAXS patterns during polymerization of methyl methacrylate (MMA) in presence of a diblock copolymer showing macro- and microphase separation (see ref [13]).

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