Effects of interfacial interactions and of crystallization on rigid amorphous fraction and molecular dynamics in polylactide/silica nanocomposites: A methodological approach

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ABSTRACT

We employ a partly new experimental approach to polymer nanocomposites (PNCs) based on a semi-crystalline matrix, in order to distinguish between phenomena affiliated, on the one hand, to interactions between polymer and nanoparticles, and, on the other hand, to polymer crystals. Thus, effects of silica nanoparticles and of crystalline fraction (*CF*) on glass transition and segmental dynamics in poly (L—lactic acid) were investigated by means of differential scanning calorimetry (DSC) and broadband dielectric relaxation spectroscopy (DRS). Analysis of results involves combination of measurements on initially amorphous and on semicrystalline (annealed) samples. No change in the glass transition temperature by the filler is observed by DSC, whereas the heat capacity step decreases in the PNCs. The segmental α relaxation (dynamic glass transition) in DRS becomes, however, faster and weaker in the PNCs. Results are rationalized in terms of the rigid amorphous fraction (*RAF*) due to filler (interfacial polymer, *RAF_{filler}*) and due to polymer crystals (*RAF_{crystal}*). *RAF_{filler}* and *RAF_{crystal}* were disentangled from the total *RAF* via two assumptions: (a) assuming the same *RAF_{crystal}* to *CF* ratio in the neat matrix and the PNCs, and (b) assuming the same *RAF_{filler}* in amorphous and semicrystalline samples. Changes of the various polymer fractions with composition show similar trends in DSC and DRS. *RAF_{filler}* was found to increase with filler fraction, with a saturation for the largest loading (20 wt%), assigned to filler aggregation confirmed by morphological characterization. Both *RAF_{crystal}* and mobile amorphous fraction, *MAF*, were found within experimental error almost constant with filler loading. The overall results suggest that interfacial interactions (*RAF_{filler}*) in combination with changes in semicrystalline morphology dominate polymer dynamics in semicrystalline PNCs.

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1. Introduction

Polymer nanocomposites (PNCs) are in the center of interest of materials science the last decades [1—3]. The use of fillers in the nanoscale offers the great benefit that small amount of fillers are sufficient to induce tremendous improvements in desired properties [4]. This effect is widely thought to arise, mainly, from the large surface to volume ratio of the nano-fillers and, consequently, a high fraction of polymer at interfaces with nanoparticles [3]. This *interfacial polymer fraction*, called also *rigid amorphous fraction* (*RAF*) at interfaces, *RAF_{filler}* (Scheme 1a), has been studied experimentally by differential scanning calorimetry (DSC) [5], among

other techniques, showing reduction of the heat capacity step at glass transition. Thus, *RAF_{filler}* is considered as immobile [6—9]. Reported effects on glass transition temperature, on the other hand, are controversial [9,10]. Additional support, regarding immobilization of the interfacial polymer, has been supplied by dielectric relaxation spectroscopy (DRS) techniques, where results often show a suppression in the strength of the segmental α relaxation process (related to glass transition) in PNCs, as compared to the unfilled matrix [11—14]. Similarly to DSC, interfacial polymer is considered responsible for this suppression by DRS. As expected, for fine filler dispersion *RAF_{filler}* increases with filler content almost linearly [7,8], even for very high loadings ($\geq$0.5 wt) [15,16], while particles aggregation is usually accompanied by a saturation in *RAF_{filler}* [7,15].

However, in a significant number of studies on PNCs during the last decade interfacial polymer shows for some polymers retarded

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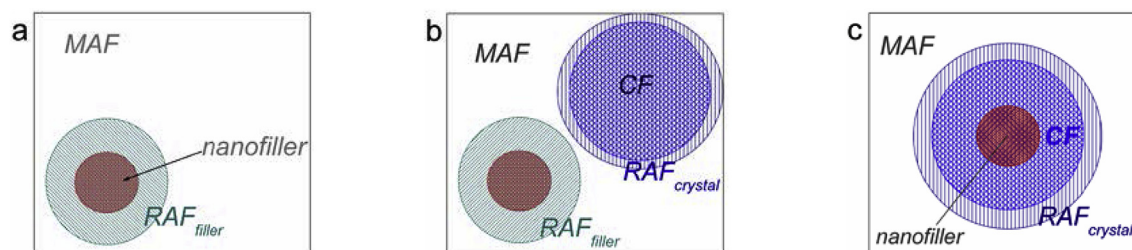
Scheme 1. Simplified models for the various polymer fractions in (a) amorphous (2—phase model, *MAF*—*RAF*) and (b,c) semicrystalline nanocomposite samples (3—phase model, *MAF*—*RAF*—*CF*) [6]. *MAF* is the mobile amorphous fraction, *CF* is the crystalline fraction, *RAF_filler* is the rigid amorphous fraction at interfaces with the nanofiller, and *RAF_crystal* is the rigid amorphous fraction around crystals. (b) describes the case of fillers that do not act as crystallization nuclei [7,8], while the opposite situation is described in (c), i.e. fillers act as crystallization sites [17].

mobility by DRS. In particular, next to the α relaxation, characteristic for the bulk, a slower and less cooperative process has been recorded [18]. This relatively new process has been identified mainly in PNCs based on rubbers interacting strongly with filler surface [18—22], as the quite flexible chains of such polymers are capable to adopt large numbers of contact points at the surface of the fillers [23—25]. More recently, similar results have been reported also for thermoplastic polymers [15,16,26], where the strength of polymer-particle interaction [26], on the one hand, and the availability of potential contact points (morphology of nanoparticles surface) [11], on the other hand, play a key role.

The situation becomes more complex when PNCs are based on semicrystalline polymers, where an additional contribution to *RAF* arises from serious constraints imposed on polymer chains in the vicinity of crystals (*RAF_crystal*, Scheme 1b) [6,8,27—31]. From the methodological point of view, the total *RAF* in semicrystalline PNCs can be directly measured by means of the missing calorimetric (glass transition) or/and dielectric response (α relaxation). For separating the two contributions to *RAF* in previous work the assumption was made that the amount of *RAF_crystal* is proportional to crystalline fraction, *CF*, and that their ratio is the same in unfilled polymer and the respective PNCs [8,32]. The latter can be partly controlled by properly selected (optimized) measurement conditions [5,8]. We should also keep in mind, with regard to this concept, that *RAF_crystal* may change with temperature of measurement [29]. Recently, an alternative route to disentangle the two *RAF*s has been described [14], by performing DSC measurements on the same PNCs first in the amorphous state (e.g. by quenching from the melt state) and then in the semicrystalline state (e.g. after crystallization annealing). *RAF_filler* is obtained from the first type of measurements (Scheme 1a). Next, under the assumption that *RAF_filler* remains unchanged during crystallization, *RAF_crystal* is obtained from the second type of measurements, *RAF_crystal* = *RAF* − *RAF_filler*. Please note, however, that also this assumption is questionable, as results by DRS indicate that *RAF_filler* may be temperature dependent [22,24]. In addition, redistribution (reorganization) of nanoparticles in the matrix during evolution of crystallization has been reported using SAXS [33].

The two methods described above for separating the two contributions to *RAF* by employing both DSC and DRS measurements are applied in the present study on PNCs of poly (L-lactic acid) (PLLA) and fumed silica (aerosil) nanoparticles, in the loading range from 2.5 to 20 wt% silica. Recently, we employed this methodology in a special case, namely in PLA filled with fixed amounts of nano-inclusions of 1-3D geometry (nanotubes, nanosheets, spherical nanoparticles) [17]. All fillers were shown to act as nucleating agents, so that *RAF* was suggested to correlate there exclusively with crystals (*RAF* = *RAF_crystal*, Scheme 1c). By applying here the methodology on PLLA/silica PNCs in a wide range of filler contents, we attempt to separate effects on *RAF_filler* and on molecular

dynamics imposed by polymer-filler interactions (direct effects) from those imposed by crystallinity (indirect effects). We disentangle the total *RAF* into *RAF_filler* and *RAF_crystal* by the two methods mentioned above, on the basis of measurements on both amorphous and semicrystalline PNCs in the one, and of measurements on both neat and filled PLLA samples annealed under the same conditions in the other. We discuss the assumptions the two methods are based upon, as well as their limits of applicability, and compare to each other results obtained by them. Finally we calculate the various polymer fractions in the PNCs by both DSC and DRS and discuss comparatively results by the two techniques.

The main effort in previous work on PLA/silica PNCs was to increase the low degree of crystallinity and crystallization rate of PLA [34—38]. Good quality of filler dispersion proved essential for that [34,39], and various routes of mixing polymer and filler were explored, such as melt mixing [34,36], solutions mixing [17], condensation of silica sol [35,40], and surface modification (both inorganic [36,38] and by grafting of organic oligomers [34,35,40,41]). In most of these studies, low filler contents up to 5 wt% were used [35,36]. Studies on PNCs with larger loadings (up to 20 wt%) are rare [34,39,40], and, in that case, maximum improvement in mechanical properties and in crystallinity has been reported for silica loadings between 2 and 5 wt% [34,36]. Only in a few studies, limited to platelet-like fillers (nanosheets) [14,31,42], methodologies comparable to that of the present work were employed.

2. Experimental

2.1. Materials

Poly (L-lactic acid) (PLLA, Purac Biochem, *MW* ~700 kDa) was mixed with addition of 2.5, 10 and 20 wt% silica (SiO_2, aerosil, A200, Degussa AG, primary nanoparticles of ~12 nm in diameter) using the solvent casting method, described in detail in previous work [17]. The solvent was evaporated at elevated temperature and the nanocomposite films (0.5—1.0 mm in thickness) were obtained by employing a thermal press operating at 200 °C. Neat PLLA was also dissolved and a film of ~1 mm in thickness was obtained after solvent evaporation and thermal pressing. Immediately after pressing, the samples were immersed into cold water, this procedure resulting in solid and fully amorphous samples. The latter was confirmed by both DSC and WAXS measurements [17].

2.2. Scanning electron microscopy (SEM)

Filler dispersion in the polymer matrix was examined by field emission Scanning Electron Microscopy (SEM) by means of a FEI NovaSEM 230 apparatus, operating at room temperature under high vacuum mode and using a Through Lens Detector (TLD) at a