Influence of the Nanoscale Morphology on the Micro- and Macromechanical Behavior of Composites

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SUMMARY: The development of polymer nanocomposites with enhanced physical and mechanical properties also allows an evaluation of the intrinsic properties of the nanoscale constituent. However, as the absolute size of the reinforcement decreases, the particle surface area increases and particle-particle as well as particle-matrix interactions during processing become more prominent. These interactions can induce significant variations in the microstructure of the composite matrix which need to be considered when evaluating the composite performance. Rheological studies can highlight the complex interactions between the nanoscale reinforcements and the polymer molecules. Not only the degree of dispersion and the alignment of the filler within a given system are important factors governing the resulting properties of the composite. Elongational flows during processing for example can lead to a significant load transfer from the melt to reinforcements with a high aspect ratio which can dramatically alter the microstructure of a semicrystalline thermoplastic matrix. Such variations in the microstructure are reflected in an altered micromechanical deformation behavior of the composite. In order to correctly interpret the properties of a given nanocomposite and to be able to predict the behavior of a system as a function of filler type and content these interactions need to b

KEYWORDS: nanocomposites, processing, rheology, structure-property relationships

INTRODUCTION

Although the terms *nanomaterial* and *nanocomposite* represent a fairly new and exiting field in materials science, such materials have already existed for a century in the polymer industry and have always existed in nature. A nanocomposite is defined as a composite material with at least one of the dimensions of one of the constituents on the nanometer scale. Carbon black (CB)-filled rubber for automotive applications is an excellent example for the established implementation of this concept in technical products. The recent drive behind the development of nanocomposites is based on the fact that the properties of a material become increasingly insensitive to flaws at the nanoscale, enabling the exploitation of the unique physical and mechanical properties of very small objects in large-scale components.

Natural materials such as bone, tooth, and nacre are very good examples of the successful implementation of this concept. Such composites exhibit many levels of hierarchical structures from macroscopic to microscopic length scales. Despite these complicated structures, the smallest building blocks in such materials are generally on the nanometer scale and, more importantly, it is a nanoscale reinforcement embedded in a matrix. The concept of creating both structural and functional multi-phase nanocomposites with an improved performance is currently exploited in all types of matrices such as metals, ceramics and polymers. The same accounts for the filler particles, which can be organic or inorganic, and cover a wide range of materials. The resulting composites exhibit a multitude of enhanced properties, both physical (for example, electrical and thermal conductivity) and mechanical (stiffness and strength), so that the material cannot easily be classified as a structural or functional composite. The terms *i* , as opposed to plain *filler*, are equally frequently used for the nanoscale component without a clear distinction.

Although significant advances have been made in recent years to overcome the problems associated with the manufacture of polymer nanocomposites, processing remains a key challenge to utilize the properties of the nanoscale reinforcement. A primary difficulty is the achievement of a good dispersion and distribution of the filler in the composite, independent of filler type and aspect (length-to-diameter) ratio. Without a proper dispersion, filler aggregates can act as defects, which limit the mechanical performance, and these agglomerates can also adversely influence the physical properties such as optical transmissivity of the matrix.

When dispersing particles with diameters below 1 µm in a medium of low viscosity, diffusion processes, particle-particle as well as particle-matrix interaction forces play an important role in the dispersion process. It is not only the absolute filler size but rather the specific surface area (hundreds of m^2/g) and the resulting interfacial area which significantly influence the filler-matrix interactions during processing. In turn, one would expect these interactions to induce variations in the microstructure of the polymer matrix, which, in the case of semicrystalline matrices for example, have significant implications on the resulting mechanical behavior of the composite in themselves. Therefore, the matrix microstructure must be critically assessed when evaluating the performance of polymer nanocomposites.

OUTLINE

The Polymer Engineering group at the University of Bayreuth is actively pursuing the development of polymer nanocomposites. The aim is not only to produce novel materials with enhanced properties but also to establish the structure-property relationships of these materials for applications ranging from the electronic to the automotive and aerospace sector. It is important to understand the interactions between the various types of nanoscale fillers with a given matrix under given processing conditions to be able to predict the resulting composite behavior. In addition, only a complete evaluation of the composite microstructure allows a determination and evaluation of the intrinsic properties of the nanoscale constituent.

Given the multitude of different nanoscale fillers (carbon black, carbon nanofibers and nanotubes, layered nanoclays, silicate nanotubes, …) with vastly different properties which are theoretically predicted and, in many cases, experimentally verified, the selection of a suitable material for a given application is crucial. For example, the potential of carbon-based nanomaterials for components requiring the achievement of sufficient electrical conductivity for anti-static applications has been established. On the other hand, layered silicate nanoclays are suited for the development of polymer nanocomposites with improved barrier properties. In contrast, phosphorus-containing molecular additives can be used to produce effective and environmentally friendly flame-retardant polymers.

Independent of the type, shape and aspect ratio of a given nanoscale filler, composite processing leading to a good dispersion and alignment of the filler in a polymer is crucial. For example, the direct physical mixing of a given polymer and nanoscale reinforcement may not form a nanocomposite. This situation is analogous to a polymer blend, and in most cases, separation into discrete phases takes place. In immiscible systems, the limited physical interactions between the two components lead to poor mechanical and physical properties of the final composite. However, the surface chemistry of commonly used layered silicate nanoclays for example can be modified to allow strong interactions of the clay with a given polymer matrix during processing, which can lead to the desired dispersion of individual nanoscale layers.

In this presentation, a variety of different polymer nanocomposites for both structural as well as functional applications will be discussed. It is demonstrated that the processing behavior of such systems has a pronounced influence on the resulting morphology and properties of the final product. Furthermore, the processing parameters can be optimized to further enhance the desired properties of the composites, an approach that can lead to very specialized products.

Structural nanocomposites:

- Carbon nanofiber-and silicate nanoclay-reinforced thermoplastic nanocomposites (standard extrusion and injection molding techniques)
- Carbon-nanofiber/nanotube-reinforced thermoplastic composite fibers (melt-spinning)

Functional nanocomposites:

- Carbon nanotube-filled thermosets for anti-static applications
- Phosphorus-containing molecular additives for flame retardant thermosets

INJECTION-MOLDED THERMOPLASTIC NANOCOMPOSITES

There are at least three general experimental methods to produce polymer nanocomposites: mixing in the liquid state, solution-mediated processes and in-situ polymerization techniques. The direct melt blending approach is much more commercially attractive than the latter two methods, as both solvent processing and in-situ polymerization are less versatile and more environmentally contentious.

A number of thermoplastic nanocomposites have been prepared by twin-screw extrusion compounding and subsequent injection-molding of the prepared masterbatches.

The semicrystalline thermoplastic matrices range from commodity polymers such as polypropylene (PP) to technical thermoplastics such as polyamide (PA) and, finally, to high-performance thermoplastics such as poly(ether ether ketone) (PEEK). In addition, a range of commercially available nanoscale reinforcements have been evaluated, layered silicates (LS), silicate nanotubes (SN) as well as carbon nanofibers (CNF). Depending on the surface area of the nanoscale material, filler loading fractions of up to 15 wt% have been realized using standard processing machines up to the kilogram scale.

The processing behavior of these masterbatches for future large-scale production has been investigated by shear rheological experiments, both with a stress rheometer at low shear rates and with the extruder at high shear rates, respectively. As Fig. 1 highlights, the addition of up to 15 wt% of carbon nanofibers to a PEEK matrix does not significantly alter the processing behavior of this composite system. The nanocomposites show a similar shear thinning as the pure matrix in the shear rate regime typically encountered during extrusion and injection-molding. This behavior also reflects the good degree of dispersion achieved during the twin-screw extrusion process for this material combination.

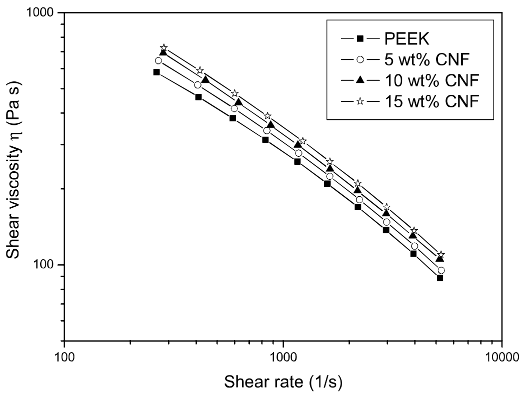
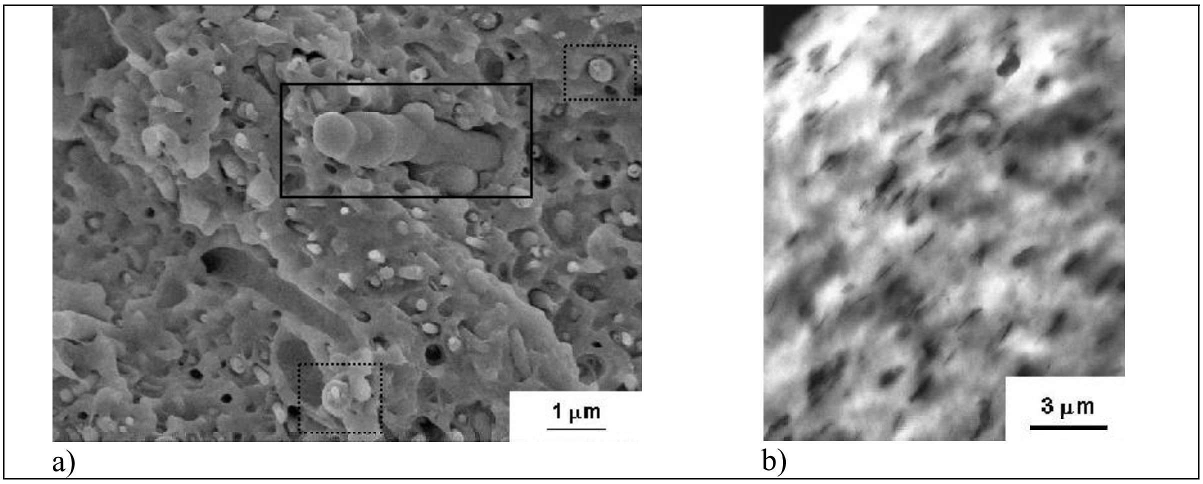


Fig. 1 Shear viscosity of PEEK-CNF masterbatches as a function of the shear rate

In all cases, a good dispersion of the nanoscale reinforcement in the thermoplastics has been achieved. However, in the case of most layered silicate nanoclays an intercalated structure appears to dominate, only seldom a certain degree of exfoliation is observed in the final products. Moreover, the shear-intensive processing has led to a partial orientation of the filler particles with a high aspect ratio. This alignment is a result of the interactions between the reinforcement and the polymer molecules during processing and reflects the typical molecular orientation in injection-molded samples. The scanning electron micrograph in Fig. 2 a) verifies the good dispersion and partial alignment of carbon nanofibers in a PEEK matrix at a loading fraction as high as 10 wt%.[1] Similarly, layered silicate nanoclay PA-6 composites also exhibit a good dispersion and preferential orientation with the direction of flow during processing, Fig. 2 b).[2]

Furthermore, the transmission electron micrograph highlights the dominating appearance of intercalated stacks of silicate nanoclays, although individual fully exfoliated layers can be seen. The orientation of the nanoclay corresponds to the molecular orientation as a function of the processing conditions. For example, in these PA-6 nanocomposites there exists a clear dependence of the mechanical properties on the specimen thickness.[2] This skin-core dependence in turn is reflected in the micromechanical deformation behavior which depends on the orientation of the nanoclays.

In addition to the morphology of the nanoscale reinforcement the matrix microstructure must be assessed in order to fully understand the micromechanical deformation behavior of the nanocomposite. For example, under standard injection-molding conditions, the carbon nanofibers do not induce a variation in the crystalline morphology of the PEEK matrix [1], whereas they act as heterogeneous nucleation sites in a semicrystalline polyproplyene.[3]



a) b)

Fig. 2 a) Scanning electron micrograph of fracture surface of PEEK nanocomposites containing 15 wt% CNF and b) transmission electron micrograph of PA6 nanocomposite containing 5 wt% LS

Only a fundamental characterization of the composite microstructure allows an evaluation of the composite properties such as stiffness and yield stress as a function of filler type and loading fraction with regard to the intrinsic properties of the nanoscale phase. This is especially important when attempting to compare the effective reinforcement capability of different nanoscale fillers and to understand complex composite properties such as the tribological wear behavior. [4]

MELT-SPUN NANOCOMPOSITE FIBERS

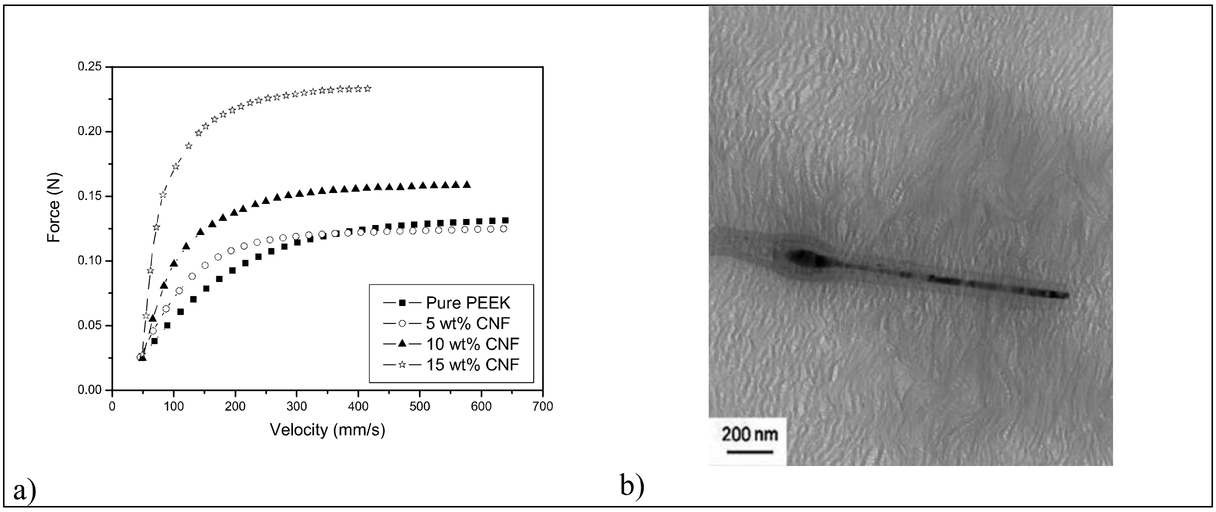
The most promising current approaches towards increasing the orientation of nanoscale reinforcements within a matrix include the optimization of the extrusion die and stretching the composite melt to form films and fibers. The enhancement of the mechanical performance of thin polymer fibers for example is considered as one key application for the use of nanoscale fillers since the small size of the final composite inhibits the use of conventional reinforcements.

However, the influence of the nanoscale phase on the microstructure of the matrix can become even more pronounced when the composite melt is subjected to elongational flows.

An example of the strong interaction between carbon nanofibers and the PEEK matrix melt during elongational deformation experiments is shown in Fig. 3). As can be seen, there is a significant increase in the force required to draw a composite melt strand as it exits a die with increasing nanofiber content.[5] The load transfer from the melt to the aligned reinforcement during processing alters the spinning behavior of this composite system and can induce significant variations in the resulting matrix microstructure as the system cools down.

Fig. 3 b) highlights the local variations in the matrix microstructure of a melt-drawn PP film containing 0.5 wt% of carbon nanofibers.[3] X-ray diffraction methods especially are suited to characterize both the microstructure of the spun product as well as the in-situ deformation behavior of such nanocomposites.

A range of thermoplastic polymer composite fibers containing carbon nanofibers as well as different carbon nanotubes has been melt-spun and analyzed with regard to the resulting microstructure and mechanical deformation behavior.[6,7] The results presented for these different systems highlight the importance not only to characterize the microstructure of the final composite but also to study the in-situ micromechanical deformation behavior as a function of reinforcement type and content. Again, only a complete understanding of the complex interactions between a given reinforcement and matrix and the chosen processing conditions allows the evaluation of the intrinsic properties of the nanoscale phase and, even more importantly, the desired prediction of nanocomposite properties for technical applications.



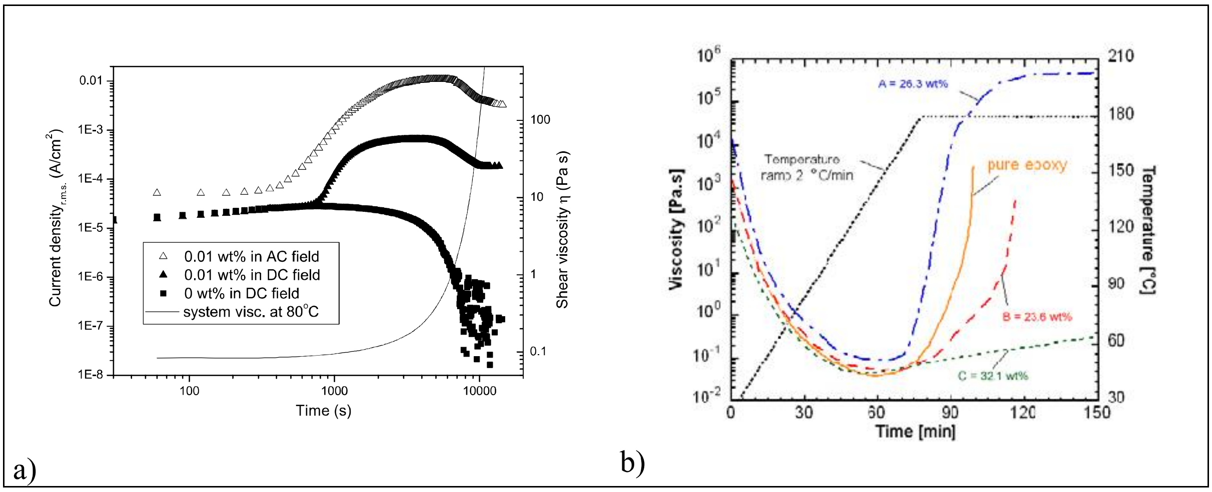
a) b)

Fig. 3 a) Draw-down force as a function of draw-down velocity of PEEK-CNF masterbatches and b) TEM image of highly-oriented PP film containing CNF

THERMOSET FUNCTIONAL NANOCOMPOSITES

Multi-wall carbon nanotubes have been exploited as electrically conductive fillers in an epoxy matrix.[8-11] The degree of nanotube entanglement and agglomeration and, therefore, the resulting composite microstructure and conductivity can be tailored by adjusting the processing conditions. Here, only a complete evaluation of the kinetics of the phase separation process allows a subsequent optimization of the final composite properties. For example, the agglomeration process of initially well-dispersed CNT can be controlled by the application of electric fields during curing[11], an approach that enables the formation of oriented nanotubes networks which maintain an increased degree of transmissivity of the matrix.

As shown in Fig. 4 a), the CNT network formation in epoxy composites can be monitored by in-situ experiments during curing. The current density of the composite can be measured between two electrodes dipped into the dispersion. The application of both DC and AC electric fields during curing induces the formation of oriented nanotube networks. On the other hand, in-situ rheological experiments can highlight the influence of molecular additives on the processing behavior of epoxy composites and can be used to define critical additive concentrations which will limit the application of such systems in liquid resin technologies such as resin transfer molding or resin infusion. An example of this approach is shown in Fig. 4 b), where the viscosity of an epoxy system with different molecular additives (leading to 3 wt% of phosphorus in the composite) during curing is shown. Such experiments can clearly distinguish between the different chemical reactivity of the additives in this case. In turn, these variations in the curing behavior are reflected in the degree of cross-linking in the final product and the resulting mechanical properties.



a) b)

Fig. 4 a) In-situ current density measurements of carbon nanotubes-epoxy composites and b) viscosity of epoxy composites as a function of different molecular additives

CONCLUSIONS

In order to correctly interpret the properties of polymer nanocomposites a detailed investigation of the composite microstructure is necessary. Standard polymer processing techniques can induce a partial orientation of the nanoscale phase which, in turn, can have a significant influence on the matrix microstructure. Such variations in the composite microstructure can lead to an altered micromechanical deformation behavior. It is therefore crucial to understand the complex interactions between the filler particles and the polymer matrix during processing in order to be able to predict the properties of a given nanocomposite system for a given processing technology.

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