

## Rheology of polymer nanocomposites – are there unique effects for exploitation?

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### ABSTRACT

Polymer nanocomposites are of great industrial and scientific interest, since they offer the potential for tailoring at a new scale. Greatly improved properties are reported at very small reinforcement contents. Different mechanisms contribute to this effect. One is conventional composite mechanics effects from a stiff phase in a soft or liquid matrix phase. Another suggested mechanism emphasizes the formation of regions of lowered polymer matrix mobility. Recently, it was suggested that nanoscale reinforcement may interact with the matrix so that entropic effects become increased. The physical or chemical molecular network of the molten or rubbery matrix phases becomes extended by interaction with the reinforcement. The mechanisms are discussed, in particular with respect to two cases, cellulose nanocomposites and layered silicate nanocomposites.

### INTRODUCTION

Polymer nanotechnology is a favored research area, in terms of funding and correspondingly increasing numbers of scientific publications. The risk for over-exploitation is obvious. The term “nano” has strongly positive value, but can be used in contexts where it is not motivated. Such an example is clay nanocomposite studies where the clay particles are still at the scale of tens of micrometers. Although the polymer matrix may penetrate into the

particle, properties are not controlled at the nanoscale.

The Noble-prize winner Richard Feynman is credited with pointing out the potential of nanostructured materials during an after-dinner speech in 1959<sup>1</sup>. He continues to explain that the main driving force for the development of materials where the structure is organized at a very fine scale, is to increase the property span of materials.

Toyota received considerable attention when they published a study in 1993 where the properties of polyamide composites filled with conventional clay (layered silicates) were significantly improved, although the reinforcement content was very low<sup>2</sup>. The reinforcement mechanisms were not clarified in the original paper, and numerous studies have been published since where the unique features of a nanostructured material or liquid is disregarded in the discussion.

The objective of the present study is to discuss different mechanisms, which may influence the non-linear viscoelasticity and failure behavior of polymer nanocomposites. Two examples will be briefly discussed in the light of different contributing mechanisms.

### COMPOSITE MECHANICS MODELS

A stiff reinforcement phase in a softer matrix phase provides reinforcement to the combined composite material. Classical

elasticity theory forms the basis for most micromechanics models describing reinforcement effects in the composite. One may note that most models have been applied to the case of a glassy polymer containing stiffer reinforcements in the form of particles, platelets, fibres or ellipses. If the matrix is in the rubbery phase, many simplified models are no longer valid since the large difference between matrix and reinforcement stiffness violates one of the basic assumptions.

One may note that in the case of layered silicate nanocomposites, the composite mechanics contribution to reinforcement cannot be neglected. The aspect ratio of silicate layers is very high, probably higher than 100. The modulus in the plane of the silicate is probably around 20 times the modulus for a glassy polymer.

#### EISENBERG'S MODEL

In 1995, Tsagaropoulos and Eisenberg published a study on the viscoelastic behavior of polymers filled with nanoscale silica particles<sup>3</sup>. The focus of their study was on the influence of filler particles on the mobility of polymer chains. It is apparent that with nanoscale fillers, this becomes an important problem. In rubbers, carbon black is extensively used as fillers, and the particles are of nanoscale dimension. Studies on these polymer composites have resulted in an interpretation as follows. An immobile layer is present at the surface of the particle. The thickness of this immobile polymer layer is typically 5-20 Å<sup>4</sup>. There is also a partially immobilized layer of thickness 25-90 Å. The importance of this phenomenon is also likely to exist both as the matrix is in the liquid and in the rubbery phase. The mobility of a polymer molecule interacting with a solid surface is dramatically reduced. In the glassy state, phenomena associated with molecular mobility will also be influenced, although less dramatic.

Tsagaropoulos and Eisenberg study the glass transition behavior in various polymers reinforced by nanoscale silica particles. Dynamic mechanical thermal analysis is used, and the focus is on phenomena at the glass transition temperature and above. The main observation is that a second peak is observed at elevated temperature, above the matrix T<sub>g</sub>. This is interpreted as a second glass transition, caused by the partly immobilized polymer matrix phase. Effects were observed due to molar mass of the polymer and due to the chemical nature of the polymer. The main conclusion is that reinforcement effects in these particle nanocomposites should be influenced by the presence of a polymer matrix where the molecular mobility is either completely or partly hindered. The proportions of matrix phases which are immobilized, partly immobilized or unmodified will depend on particle size, volume fraction and extent of dispersion (particle agglomeration is an important phenomenon).

#### STERNSTEIN'S MODEL

Sternstein and Zhu recently published a study<sup>5</sup> closely related to the previously discussed one in terms of experimental focus). However, the conclusions with respect to reinforcement mechanisms are completely different.

The starting point is that non-linear viscoelastic phenomena are present in nanoparticle filled polymer systems. Those effects cannot be explained by agglomeration or particle network formation. Instead, focus is placed on the filler-matrix interface. In particular, interaction between matrix molecules and the particle surface is considered. It is pointed out that chemically cross-linked rubbers behave similarly above T<sub>g</sub>, with respect to non-linear viscoelasticity, as nanoparticle-filled polymer melts. For both classes of materials, the chain conformation statistics controlling material behavior are the same.

Experiments are carried out on particle composites with different surface treatments, and with different molar mass on the polymer matrix. The effects of these parameters on modulus are very strong. These effects cannot be well explained in the light of composite mechanics or immobilized polymer layer models.

Sternstein is instead basing the explanation on the modification of chain conformations in the physical polymer networks. Trapped entanglements are created so that physical entanglements are created. The “effective” cross-link density of the network increases, and therefore the modulus increases. Nanofillers provide a high surface area for particle-matrix interactions, and the effects are dramatic.

#### FIBER NETWORK MODELS

In 1995, Favre, Chanzy and Cavaille published an interesting study<sup>6</sup> where they demonstrated unique mechanical properties of a composite from cellulose whiskers at the nanoscale and a thermoplastic matrix in the rubbery state. The effect was due to network formation between the high aspect ratio whiskers. As a consequence of high aspect ratio and nanoscale dimension, only very low fiber volume fraction was required.

#### CELLULOSE NANOCOMPOSITES

In a previously published study<sup>7</sup>, a thermoplastic polyurethane was reinforced by microcrystalline cellulose (MCC). MCC has an aspect ratio of about 10 (length/diameter) and a diameter of around 30 nm. The stress-strain curves of the resulting materials are presented in Figure 1. A strong improvement in properties with MCC addition is observed. Not only is modulus and strength improved, but also strain-to-failure. This is very unusual as rubbers are reinforced with stiffer particles or fibers. Commonly, strain-to-failure is reduced when micro-scale reinforcement is used since the reinforcement debonds from the soft matrix at higher strains. The

difference in modulus creates a strain concentration at or near the reinforcement-matrix interface. If separation takes place, a larger crack is formed and the material fails.

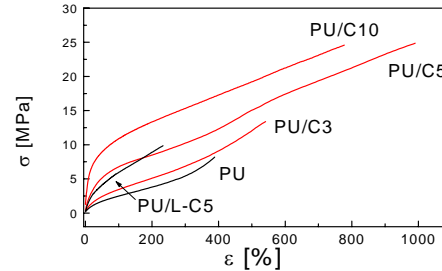


Figure 1. Nominal stress-strain curves for polyurethane (PU) and polyurethane-MCCcellulose nanocomposites (PU/C). The numbers refer to weight fraction cellulose. PU/L-C5 is the curve for a microcomposite.

From the point of view of composite mechanics, the behavior in Figure 1 is unexpected. Quantitative comparisons are difficult to make since we have limited information on the MCC orientation distribution. But the large strain to failure is impossible to explain in a context of microcomposite studies in the literature. Eisenberg’s model needs to be replaced by Sternstein’s since it cannot explain effects from interfacial treatment and molar mass.

Let us consider Figure 2. Storage modulus is presented as a function of temperature for the thermoplastic polyurethane (PU, lowest curve) and for PU with 3, 5 and 10 percent by weight of MCC. The lack of strong reinforcement at low strain conditions (Favre et al<sup>6</sup> observed one order of magnitude increase in rubbery state modulus) excludes the fiber network explanation. But the effects at high temperature are interesting. The increase in modulus becomes stronger at higher temperatures. This is in the region where increased molar mass of the polymer matrix is expected to show some effect. The softening is much weaker for high content MCC. This is consistent with Sternstein’s

explanation. For this particular case, the MCC may act as a chain extender for the thermoplastic PU network. Thus, the effective molar mass of the matrix is increased. With respect to failure properties, the cellulose reinforcement at nanoscale is likely to contribute, as well as the increased effective molar mass of the PU matrix. Isocyanate is likely to show strong interaction with cellulose, chemical reaction between the isocyanate and the surface hydroxyls of MCC is even possible.

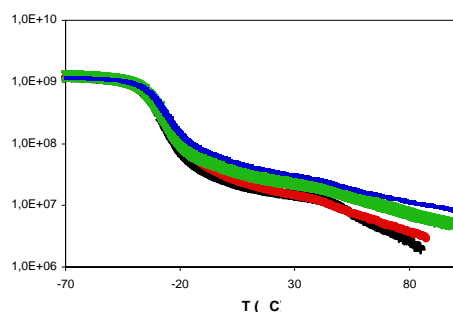


Figure 2. Storage modulus as a function of temperature for PU (lowest curve) and PU with 3, 5 and 10 wt% MCC (higher curves).

## CONCLUSIONS

Polymer nanocomposites are interesting materials since they offer the potential to extend the property range of polymeric materials. New reinforcement mechanisms can be utilized and effects from several scales may be combined. Composite mechanics effects, makes it possible to utilize the high aspect ratio and stiffness of layered silicates so that high reinforcement is obtained at low silicate content. The formation of immobilized polymer layers and the large surface area of nanoparticles leads to significant changes in physical and chemical properties of the composites, ie diffusion resistance and fire retardancy effects. Strong molecular interaction between rubbery or liquid matrices with

nanoparticle or nanofibril surfaces also leads to strong effects. This can be exploited in rubbery matrix nanocomposites with improved failure properties. The reason may be that the filler acts as a chain extender, increasing the effective molar mass of the matrix and altering the entropic behavior of the polymer network. At the same time, rubber composite survival to large extension induces strong orientation of reinforcements such as MCC.

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