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Rheological Aspects of PP-TiO_2 Micro and Nanocomposites: A Preliminary Investigation

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Summary: The linear rheology of PP-TiO_2 composites was investigated as a function of the filler particle size. Small amounts ($\phi = 4.5\%$) of micron and nano-sized TiO_2 spherical particles were added to the polymer by melt compounding. In spite of the low particle volume fractions and the weak polymer-filler interactions, relevant changes have been observed in the linear viscoelastic behaviour of the nanostructured formulations. Microstructural analyses performed through electron microscopy have shown a good degree of dispersion of micron-sized particles. Conversely, the presence of a relevant number of TiO_2 nanoparticle clusters has been detected for the nanocomposite. The structure of these aggregates seems to be strongly responsible for the rheological behaviour of these last materials in comparison with microstructured ones. Relevant similarities between the viscoelastic properties of nanocomposite and the flow feature of many soft glassy materials have been noticed, and a simple physical picture has been proposed in order to interpret the rheological response of studied nanocomposites.

Keywords: nanocomposite; polypropylene; rheology; structural relaxation

Introduction

It is difficult to disperse inorganic nanoparticles in non-polar polymers due to the incompatibility in surface characteristics between the hydrophobic matrix and the hydrophilic oxide surface. The employ of surface-modification agents is generally required in order to reach a good dispersion of the filler.[1] Nevertheless, the mechanical properties and the flow behaviour of polymer significantly change even if negligible interactions exist between the filler and the organic matrix. When small amounts of inorganic (hydrophilic) particles are added to a hydrophobic polymer matrix, the derived hybrid structure can be depicted as particle aggregates dispersed in a polymer matrix,[2] especially if the filler is nanosized at least in one direction. Interactions between individual particles within aggregates, as well as among aggregates, hinder relative motion between material planes, modifying both the solid-state and the melt-state behavior of the host polymer. In highly filled polymer based composites, filler interactions are so strong that relevant solidlike yield phenomena can be observed even at temperatures above the melting temperature of the polymer. This behavior is often attributed to the existence of a filler network that spans large sections of the polymer matrix.[3,4]

Generally, two filler particles can interact only if their separation distance is small enough in comparison with their size. In order to estimate interparticle distances, we can assume that, if N monodisperse spherical particles with radius R are randomly distributed in a volume V, the distance between the particles centres can be approximated to $d = (V/N)^{1/3}$. Introducing the particle volume fraction $\phi = Nv/V$

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($v =$ volume of individual particle), the wall-to-wall distance D can be evaluated as:

$$D = \left[\sqrt[3]{\frac{4\pi}{3\phi}} - 2\right] R \qquad (1)$$

The expectation of the critical percolation threshold for such a system is $\phi \sim 0.52$. For diluted systems such as ones we are interested in, D has the same order of magnitude of R and it scales linearly with the particle radius. Therefore, if the filler particles are well dispersed within the host polymer, nanometric interparticle distances are expected for nanocomposites.

When the filler particle size, at least in one dimension, approaches the mean radius of gyration of host polymer chains, a large fraction of polymer is in contact with the filler, any chain being able to interact simultaneously to more than one particle.[5] The relative motion among chains may be retarded by the polymer confinement between nanoparticle and/or aggregate surfaces. Such an effect also exists in composites with much larger fillers (e.g. micron size), but the volume of perturbed matrix is limited to the interfacial boundary layer, representing a negligible fraction of the total volume of material.[6] Moreover, in systems characterized by weak polymer-particle interactions such as those studied in this work, a relevant tendency of small particles to clamp together under the push of Van der Waals forces can lead to flocculation. Besides the simple distortion of flow lines, the presence of flocs can have a profound effect on the composite rheology due to the increase in effective phase volume and the formation of a pseudo-network between flocs or chain of particles.[7]

The unique continuum level properties resulting from the nanoscale interactions have attracted considerable recent interest, and many studies have focused on the design of high performance composite materials. However, due to the complicated nature of molecular interactions, there is a lack of general agreement upon nanocomposite rheology, and the most successful rheological models introduce various simplifying assumptions that are difficult to validate.[8,9]

The overall objective of this work is to study of the linear rheological behavior of PP-TiO_2 micro and nanocomposites. A poor affinity between the host polymer and the filler characterizes the studied materials. An attempt to relate the relevant differences among the flow behavior of the composites to their microstructures was carried out. In line with this aim, electron microscopy, both in scanning and transmission mode, was used in order to visualize the morphology of the samples. The coupling of microscopic and rheological techniques represents a powerful approach in order to study the behavior of complex fluids such as those studied in this work, characterized by strong relationships between flow and microstructure.

Experimental Part

A commercial grade polypropylene (Moplen HP563N, by Basell) was used as the polymer matrix. The homopolymer has a quite narrow molecular weight distribution ($M_w/M_n \sim 1.5$), a density of 0.9 g/cm^3 at 23 °C, MFI of 10 g/10 min (230 °C/2.16 kg), and a melting temperature of 152 °C. Micro and nanosized titanium dioxide (TiO_2) powders (from Sigma Aldrich) were used as reinforcement filler. The basic properties of the particles are listed in Table 1, as given by the manufacturers.

A Haake co-rotating twin screws extruder (Thermohaake, Rheomex PTW 24/p) was used to compound the materials. Due to consolidated strong correlations between rheological properties and composition of hybrids, first a masterbatch was prepared and then it was diluted in order to reach the desired compositions. Moreover, TGA checks (TA instruments, Q5000) were performed upon all the samples employed for rheological analyses.

The polymer matrix and the powder filler, previously dried under vacuum for three hours at 100 °C, were dosed by using

Table 1.
Main properties of reinforcement fillers.

Filler	Density @ 25 °C	Surf. Area (m^2/g)	Avg. part. Size (nm)
Micro TiO_2	4.26 g/mL	0.14÷0.04	<44000
Nano TiO_2	3.9 g/mL	190÷290	~15

two distinct metering feeders, the filler being added directly in the melt polymer. The presence of three mixing blocks along the screws ensured a good degree of dispersion of the powders. The materials were collected as rods by using a capillary die (D = 1 mm, L/D = 10). A temperature profile ranging between 160 °C and 190 °C was set along the extruder, and the materials were quenched in cold water at the die exit. The screw speed was set to 60 rpm, and the residence time of the materials within the extruder was estimated in about three minutes. Gaseous nitrogen was insufflated during the charging of materials to prevent oxidative phenomena. The pure PP used as the reference material for rheological investigations was extruded under the same conditions, in order to compare the effect of the fillers on polymer matrices subjected to the same thermo-mechanical history. A summary of the prepared composites is shown in Table 2.

The incompatibility in surface characteristics between the host polymer and the inorganic particles allows neglecting any relevant polymer-particle networking mechanism in order to interpret the flow behaviour of the studied composites.

Rheological measurements were performed on a strain controlled rotational rheometer (Rheometric Scientific^{TM}, Ares L.S.). Dynamic oscillatory shear tests were carried out by using either 25 mm or 50 mm diameter parallel plates in a dry nitrogen atmosphere at T = 190 °C. The linear viscoelastic limits were found to vary with filler amount and particle size, and the strain amplitudes of frequency scan measurements were accordingly varied between 0.7% (for PPTi-45N) and 5% (for pure PP and PPTi-45M). Due to typical microstructure evolutions occurring during thermal treatments of nanocomposites,[10,11] samples were equilibrated in the rheometer at the test temperature of 190 °C for about two hours before testing. Stress relaxation tests were performed in order to get a direct insight into the dynamics of the composites. A single step strain at time t = 0 was applied and the transient shear stress $\sigma(t)$ was monitored as a function of time. The reported stress relaxation data were verified to be in the linear regime.

The microstructure of the composites was investigated by observing the same samples used during rheological investigations. The specimens were cooled after rheological tests by using gaseous nitrogen, and the disks were removed from the plates of rheometer and treated for morphological analyses. Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed. Samples for SEM (Leica, mod. 420) observations were cryo-fractured and coated with gold to generate electric current on their surfaces. TEM (Philips, mod. EM 208) observations were performed upon microtomed 100–150 nm thick samples cut from the disks recovered after rheological measurements and analyzed to evaluate the cumulative size distributions (CSD) and the average sizes (R_N) of the inorganic phase.

Table 2.
Composite composition and sample code names.

Sample name	Particle type	Volumetric fraction ϕ (%)
PP	—	—
PPTi-45 M	Micro TiO_2	4.5
PPTi-45N	Nano TiO_2	4.5

Results and Discussion

The SEM micrographs of micro and nanocomposites at $\phi = 4.5\%$ are compared in Figure 1.

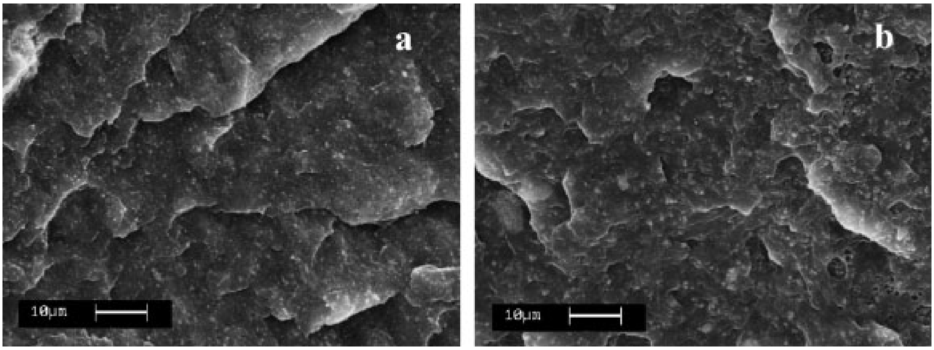

Figure 1.
Microstructures of the micro (a) and and nanocomposites (b) at $\phi = 4.5\%$.

Both the samples are well dispersed on mesoscale, but the presence of nanoparticle clusters characterizes the PP45N. This is clearly shown in the TEM micrograph reported in Figure 2, where a magnification of one of these aggregates is reported: several hundreds of individual TiO_2 nanoparticles group to form closely packed clusters with irregular shape.

The stress relaxation moduli of neat reference PP, PP45M and PP45N before and after a two-hours thermal annealing are compared in Figure 3, while in Figure 4 the micrographs of the samples before (4.a) and after (4.b) the thermal conditioning are shown.

As expected on the basis of the low particle volume fractions, the effects due to the presence of the microparticles on the viscoelasticity of the composite are negligible, when comparing with the viscoelasticity of the neat polymer. Moreover, no annealing effects were observed for the microcomposite, and both the moduli have been resulted stable during a quiescent annealing process. Conversely, the presence of clusters strongly affects the linear rheology of the nanohybrid formulation. Faster relaxation modes ($t < 5 \times 10^{-1}$ s) are only slightly affected by the ageing, but the presence of a rough plateau of G(t) characterizes the behaviour of the annealed

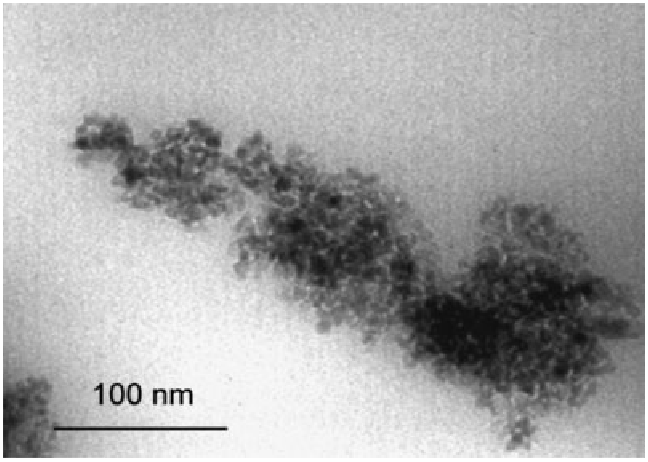

Figure 2.
TEM micrographs of a TiO_2 nanoparticle cluster.

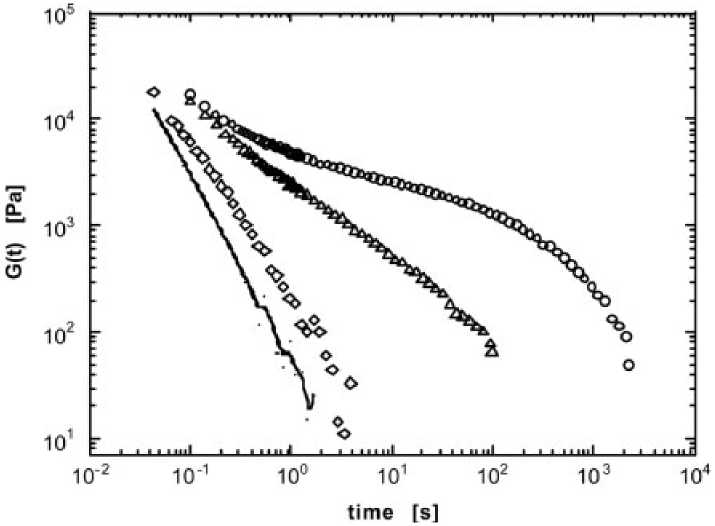

Figure 3.
Stress relaxation moduli of PP45M (diamonds), PP45N before (triangles) and after (circles) a two-hours thermal annealing, and neat polymer (solid line).

sample. This behaviour could be ascribed to the existence of a dynamic population, much less relevant in the not annealed sample, slowing relaxation kinetics and responsible for the pseudo-solidlike response of annealed PP45N. In other words, rheological behaviour should be related to the formation of big particle clusters during time, as clearly shown by TEM analyses.

In order to qualitatively assess the effects related to the applied thermal annealing upon the PP45N microstructure, an analysis of TEM micrographs was carried out and the cluster areas, A, were measured by assuming them as roughly ellipsoidal. Thus, taking the cluster sizes, R, as $R \sim \sqrt{A}$, the cumulative cluster size distributions, CSD, and the cluster number average size, R_N ($\Sigma N_i R_i / \Sigma N_i$, where N_i is the number of clusters with size R_i) were determined.

The CSD of the PP45N before and after the annealing treatment are compared in Figure 5.

The thermal conditioning causes an increase of the cluster sizes, as indicated by the lowering of the cumulative CSD curves. In particular, the number average

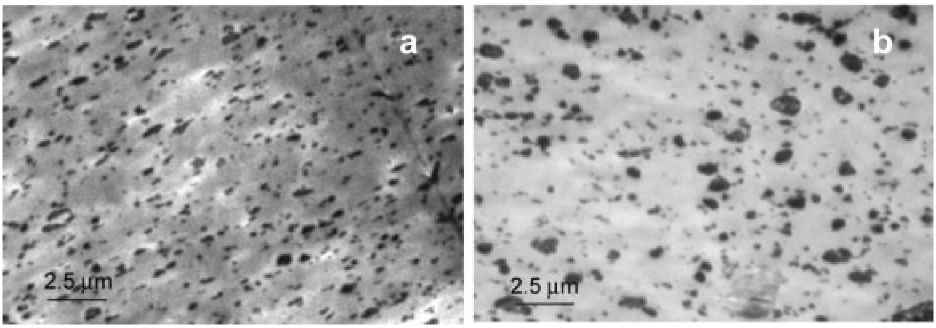

Figure 4.
TEM images of PP45N sample before (a) and after (b) the annealing are shown.

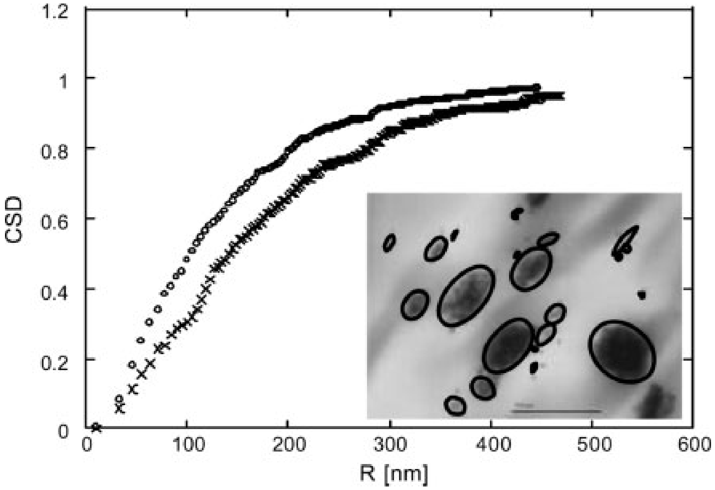

Figure 5.
Cumulative cluster size distribution functions for PP45N before (circles) and after (crosses) a two-hours thermal annealing. An example of cluster analysis is shown in the insight.

size increases from R_N~125 nm to R_N~170 nm. The presence of big aggregates (up to R~500 nm) can be noticed also for the not annealed sample. Moreover, the regularity of both the curves indicates a wide dispersion of cluster sizes.

The linear viscoelastic behaviour of PP45M and PP45N is shown in Figure 6 together with that of the neat PP. In order to extend the investigated range of frequencies through the frequency scans, typical relationships among the linear viscoelastic functions have been used for the sample PP45N. Derived functions G(t) was Fourier transformed in the linear regime to yield the frequency-dependent storage and loss moduli:[12]

$$G'(\omega) = \omega \int_0^\infty \sin \omega t G(t) dt \tag{2}$$

$$G''(\omega) = \omega \int_0^\infty \cos \omega t G(t) dt \tag{3}$$

The rheology of the two hybrids is clearly different. As expected on the basis of the low filler volume fractions and the weak polymer-particle interactions,[13] only a slight increase of G′ and G″ has been detected for the sample PP45M with respect to the host polymer. Conversely, an increase of orders of magnitude of both moduli characterizes the linear viscoelastic behaviour of the nanocomposite. In particular, G′ is greater than G″ in the whole range of frequency investigated, and a weak power law dependence at low frequencies of both the moduli can be observed. Nevertheless, both the absence of an unambiguous plateau and the relaxation occurring at $\omega \sim 10^{-3}$ rad s^{-1} indicates the untruly solid-like characteristic of PP45N.

The rheological behaviour of studied nanocomposites seems to be consistent with the features of many soft glassy materials such as colloidal gels, foams and emulsions. In these structurally disordered materials, the presence of slow glassy dynamics characterizes the low-frequency behaviour. The energy barriers that such materials have to cross are very large with respect to typical thermal energies. Therefore, the system adopts a disordered (metastable) configuration, but it slowly evolves toward states having the least free energy.[14] If the slow dynamic population responsible for the solid-like feature has a continuous distribution of relaxation times, a weak power law dependence of the moduli at low

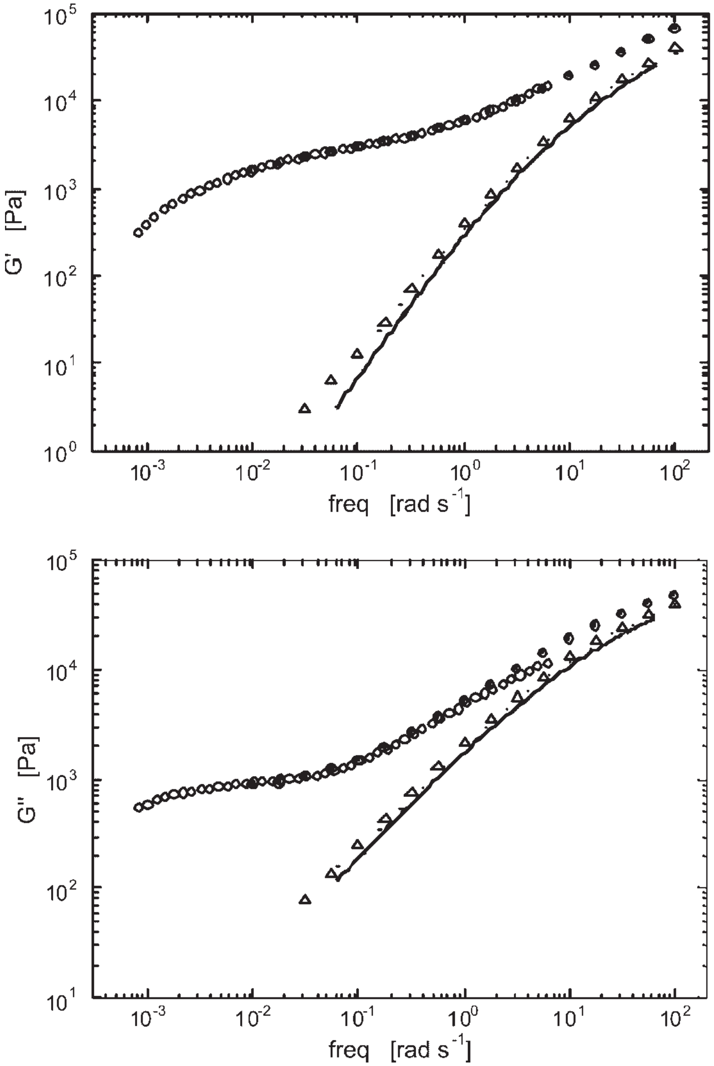

Figure 6.
Comparison between linear viscoelastic moduli of microcomposite (triangles), annealed nanocomposites (filled circles) and host polymer (solid line). The data for PP45N have been extended to low frequencies (empty circles)by Fourier transforming the G(t) (Equations 2 and 3) after the annealing.

frequencies may emerge, at least until the slowest specie is relaxed. Cipelletti and co-workers have found a progressive structural relaxation of fractal colloidal gels during time, and an unexpected final decay, compatible with the relaxation of the bigger clusters, has been observed through dynamic light scattering (DLS) experiments.[15]

On the basis of previous considerations, a simple physical picture can be proposed in order to interpret the rheological response of studied materials:[16,17] both the polymer matrix and the filler contribute independently to the total rheological response of the nanocomposite, the particle clusters representing the fraction responsible for the pseudo-solidlike behaviour emerged during the rheological tests. Due to a direct dependence of the structural relaxation time of a cluster on its size, the wideness of cluster size distribution implicates the existence of a continuous spectrum of relaxation times. The enveloping of the relaxations of each family of clusters having similar sizes could explain the weak power law dependence detected for both $G'(\omega)$ and $G''(\omega)$, the ultimate relaxation at 10^{-3} rad s^{-1} being related to the structural relaxation of the bigger nanoparticle clusters. Finally, the absence of relevant rheological effects detected for the microcomposite may be related to the absence of particle aggregates able to deform and relax. In these systems, the reaching of the percolation threshold is an indispensable requisite to significantly affect their flow behaviour.

Conclusions

In this work, the flow properties of PP-TiO_2 composites have been studied as a function of the particle filler size. In particular, the linear viscoelastic behaviour of micro and nanocomposites with low particle volume fractions has been compared. Despite of the small amount of filler and the weak polymer-particle interactions, relevant increases of both the elastic and the viscous moduli have been noticed for the nanocomposite, while negligible effects have been detected for the microcomposite. The presence of TiO_2 nanoparticle clusters detected through electron microscopy investigations seems to be responsible for the rheological behaviour of nanostructured formulations.

The similarities emerged between the viscoelastic properties of nanocomposite and the flow features of many soft glassy materials have suggested a simple interpretation of rheological data. The whole flow behaviour could be roughly approximated as the combination of two distinct dynamic populations with different kinetic: the host polymer (fast) and the clusters (slow), able to deform and relax. The slowing of relaxation kinetics related to the presence of clusters characterizes the rheology of the nanocomposite. Conversely, the micron-sized TiO_2 particles cannot significantly modify the flow properties of the ultimate hybrid, at least for the small filler amounts considered in this work. For such systems, relevant rheological effects are expected only at very high particle volume fractions ($\phi > 0.5$), when percolation phenomena start occurring.

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