ORIGINAL CONTRIBUTION

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Rheology as a tool for the analysis of the dispersion of carbon filler in polymers

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Abstract The aim of this work is to validate the use of dynamic oscillatory measurements in the melt to characterize the dispersion of a filler in a matrix after melt blending. Polyethylene oxide (PEO) is used as a polymeric matrix. Active carbon is used as a filler at a constant filler volume content of 26.4%. The melt viscosity of the polymeric matrix is varied by melt blending of two miscible POE and polyethylene glycol (PEG) species having very different molecular weight distributions. This enables to obtain various matrix viscosities and in turn various states of dispersion of the filler that were characterized by optical microscopy and image analysis. Dynamic mechanical measurements in the melt in the terminal zone show a large increase of the moduli associated to the presence of the filler. Comparison with the results of optical microscopy shows that this increase is clearly related to the dispersion. The inter-particle distance is likely to be the leading parameter rather than the number of particles. Characterization of the amount of bound polymer shows that the amount of bound polymer is nearly independent of the matrix composition. Futhermore, the composition of the bound layer reflects the matrix composition though PEO is slightly preferentially bound on the active carbon.

Keywords Filled polymer ·
Dispersions · Oscillatory shear

Introduction

Addition of fillers into polymers is a common industrial practice. Beside their use for cost reduction purposes, fillers also enable to create new materials and bring new properties to polymers. For instance, carbon black is used to reinforce elastomers but also to enhance the electrical conductivity of polymers. Among factors that basically determe the properties of filled polymers such as the intrinsic characteristics of the filler and polymer, the composition of the blend, and the structure of the filler and the interfacial interactions (Pukanszky and Fekete 1999), the state of dispersion is known to be extremely important. Therefore, the properties are strongly connected to the interactions between the components in the system. Essentially, matrix to filler interactions and particle to particle interactions must be considered. The importance of the later is often underestimated although it determines the properties of the composite, because it may be responsible for aggregation and agglomeration. Aggregates of primary particles generally show a high degree of cohesion while agglomerates are formed from clusters of aggregates with less cohesion. Therefore, they can be destroyed by mechanical shearing or stresses in order to improve the dispersion of the filler. Indeed, agglomerates are almost invariably detrimental to the properties.

Agglomeration is a well known phenomenon in particulate-filled composites. The balance between the forces which bind together the particles and those which try to separate them, basically determines the existence and the extent of the agglomeration phenomena. Attractive forces may have various origins. Essentially, when they enter into contact, two bodies are attracted to each other

by an adhesive force. This force depends both on the particle size and on the surface energy, which can be expressed by a reversible work of adhesion. In the case of suspensions, Adams and Edmonson (1987) mention forces which depend on the extent of wetting of the particles. If particles are only partially wetted by a fluid or a polymer melt, capillary forces may act between the particles through contributions related to surface tension and to a hydrostatic component. Adams and Balachandran (1987) have analysed the role of additional electrostatic forces that may play a major role during the approach of charged particles. However, these forces disappear as soon as the particles enter into contact and Van der Waals or other attractive forces become dominant.

The reduction of the size of agglomerates requires a highly dispersive and distributive mixing that will break and distribute the particles into the polymeric matrix in an homogeneous way. For this reason, a large number of polymer–filler systems are obtained by melt blending because of the large amount of dispersive mixing that can be achieved by this way due to the high viscosity of the molten polymer. Dispersion and agglomeration of fillers take place in the melt in a competitive manner. Agglomeration phenomena are clearly related to the forces described previously with the particle size as an additional parameter. For $CaCO_3$ filled polypropylene, Pukanszky and Fekete (1997, 1998) and Fekete et al. (1999) have observed that there is a critical particle size at which adhesion exceeds the shear forces. Since most fillers have a relatively broad particle size distribution, some degree of agglomeration inevitably occurs. On the other hand, the extent of agglomeration generally decreases when the applied shear rate or/and the particle size increases.

Three main mechanisms of dispersion under flow are reported in the literature and have been thoroughly described in the case of carbon black filled polymers: rupture, erosion and collision. Simple rupture of the agglomerates occurs when the hydrodynamic stresses exceeds the cohesive stress (Dizon 1976; Rwei et al. 1992). It is characterized by a sudden splitting of the agglomerate into a small number of large fragments. Erosion is initiated at lower shear stresses and it consists of a continuous detachment of small particles from the surface of the agglomerate (Kao and Mason 1975; Powell and Mason 1982; Shiga and Furuta 1985; Rwei et al. 1991, 1992; Horwatt et al. 1992; Seyvet and Navard 2001). Collision has been identified recently by Seyvet and Navard (2000) and found to become active as soon as the concentration of agglomerates is large. Of course, these three mechanisms are general and can also be efficient for particles other than carbon black. Nevertheless, because of the particular structure of carbon black, the orders of magnitude of the applied hydrodynamic stresses are different.

Dispersion can be measured by optical microscopy. Nevertheless, the technique can hardly be used for very high loadings and in this case, dissolution of the polymer matrix prior to the analysis is required. For this reason, other techniques for the analysis of the dispersion, namely rheological methods, might be interesting. Indeed, the presence of the filler in polymers is known to induce dramatic changes of the rheological behaviour in the melt (Scott et al. 1988; Gandhi and Salovey 1988; Lin and Masuda 1990; Aranguren et al. 1992; Gahleitner et al. 1996; Amari et al. 1997; Wu et al. 2000; Yurekli et al. 2001; Zhang and Yi 2002). Especially filler-to-filler interactions may be at the origin of the appearance of a secondary plateau for the storage modulus at low frequency (Jäger and Eggen 2004). The phenomenon has been mentioned by various authors and is generally attributed to three main contributions: the hydrodynamic effect of the filler in the molten polymer, the change of the relaxation times of the matrix and the building of a filler network. Connections between the filler particles can be due to primary or secondary entanglements depending on whether bridging between particles occurs via a single macromolecule or entangled molecules (Aranguren et al. 1992).

The present study deals with the dispersion of active carbon in a polymeric matrix after melt blending. This filler is an effective absorbent primarily due to its extensive porosity and very large available surface area. It is principally used in water and wastewater treatment and in filtration of contaminated air, but electrical applications can also be considered. In this study, the relevance of dynamic measurements in the melt for the characterization of the dispersion was tested.

Experimental

Materials

The active carbon used in this study is produced from pine-tree activated by vapor. It is available in powder form. The physicochemical properties of the active carbon are presented in Table 1. Specific area and porosity have been assessed by nitrogen sorption isotherms at 77 K. The amount of acid and basic groups on the surface of the active carbon have been measured by titration as described in a recent paper by Bar-Chaput and Carrot (2005). The surface tension has been determined from the observation of the location of the filler in two immiscible solvents using Young's equation.

In order to investigate the effect of chain length on the dispersion of the active carbon in the polymer, miscible polyethylene oxide (PEO) and polyethylene glycol (PEG) blended in various proportions were used as a polymer matrix. The polymers are commercial

Table 1 Properties of active carbon

Ash content, %	3.7
pH	10
Surface area: BET (N_2), m^2/g	1100
Acid functions, $\mu mol/g$	830
Basic functions, $\mu mol/g$	760
Mineral impurities, $\mu mol/g$	85
Surface tension, mJ/m^2	50
Microporous volume (< 2 nm), cm^3/g	0.27
Mesoporous volume (2–50 nm), cm^3/g	0.57
Macroporous volume (50–200 nm), cm^3/g	0.06

grades available from Union Carbide. The molecular weight distribution of the polymers was measured by size exclusion chromatography in water at 30°C using a Waters® Alliance® GPCV 2000 system. Two Ultrahydrogel™ columns in the range 1,000–8.10^5 g/mol and 10^4–10^6 g/mol were used. The calibration was performed with PEO standards from 1,050 to 8.10^5 g/mol. Molecular weights are reported in Table 2. The two polymers show excellent solubility in water and are fully miscible in the whole composition range (Abdel-Azim et al. 1998).

Mixing

Two types of blends have been prepared. PEO/PEG blends were used to validate the analytical methods and to obtain information on the matrix behaviour and PEO/PEG/active carbon blends were used to investigate the effect of chain length on the filler dispersion. In the filled polymers, the filler loading is 26.4% in volume of dry active carbon. Because the active carbon contains water adsorbed on its surface, the moisture content was measured using a Sartorius Infrared Dryer MA40 at 140°C prior to sample preparation. All blends were prepared by melt mixing at 140°C, in an internal mixer (Rheomix® 600P Haake) equipped with roller rotors and a 70 cm^3 chamber. The rotor speed was 32 rpm, the corresponding shear rate is approximately 14.4 s^{-1}. Mixing for 10 min enabled the stabilisation of the torque.

Table 2 Molecular weights of the polyethylene oxide and the polyethylene glycol

	PEO	PEG
Mn (g/mol)	21,000	7,400
Mw (g/mol)	194,000	7,800
Ip	9.2	1.05

Amount of bound polymer

Because of the high affinity between active carbon and the hydrophilic polymers, a high amount of polymer is bound to the filler. Further analysis of the results in this paper requires a better knowledge of the amount and nature of bound species. This problem was addressed in the recent paper of Bar-Chaput and Carrot (2005). The method for the determination of the amount of bound polymer and for the analysis of the nature of the bound layer is based on a combination of dissolution of the filled polymer in water, filtering, drying and weighting together with the analysis of the solution after filtration by size exclusion chromatography. Details for the method are given in the paper of Bar-Chaput and Carrot (2005).

Optical microscopy

Though the polymers can be easily dissolved in water, classical techniques for the analysis of the dispersion were not reliable because of the weakness of the agglomerates. Optical microscopy was preferred to characterize the dispersion of the active carbon in the polymer matrix. A 200 mg sample was immersed in 50 ml of de-ionized water without stirring in order to keep the integrity of the agglomerates. The suspension was left at rest during 1 week and a clear stabilized suspension of agglomerates in water was obtained. A drop of the suspension was put between two glass slides, the later immobilize the agglomerates in water and prevent further agglomeration. The sample was then observed with a Leica DM LP optical microscope with 20× magnification equipped with video acquisition. Photographs of eight zones were taken and were converted into binary images with a fair contrast of the edges of the objects such that the granulometry was asserted with a high confidence.

Rheological testing

The rheological characterization in the melt was carried out in a strain controlled rheometer, ARES (Rheometrics), for the filled sample, and in both the strain controlled rheometer and a stress controlled rheometer, SR 5000 (Rheometrics), for the unfilled matrix. Though con-plate could give reliable results with this geometry, it would have been difficult to avoid any shaping of the samples before the measurements. Preferably, parallel plate geometry (plate diameter of 25 mm) was used for most of the blends while those containing less than 30 wt% PEO were analyzed in a Couette geometry (inner diameter of 26 mm and outer diameter of 28.5 mm) because of the low viscosity. For parallel plate geometry,

the samples were disk-shaped by compression-moulding at 80°C prior to the analysis. The temperature of the analysis was 140°C for the filled polymers and a set of temperatures from 80 to 140°C for the pure polymeric matrix without fillers. In the later case, time–temperature superposition holds. Dynamic frequency sweep experiments were conducted over a frequency range from 100 to 0.01 rad/s. Measurements were carried out in the linear viscoelastic domain at a stress of 300 Pa in the stress-controlled rheometer and a strain ranging from 5 to 20% in the strain-controlled system for the unfilled samples. For the filled polymers, a linear viscoelastic domain could be found at strain lower than 0.05%. The linearity was assessed at the highest frequency and this strain value enables sufficient torque signal for all other frequencies under investigation. All measurements were carried out under a nitrogen atmosphere to prevent degradation.

Results and discussion

Rheological behaviour of the polymeric matrix

In order to understand the effect of the polymer matrix on the dispersion of the filler, the detailed rheological analysis of the PEO/PEG miscible blends was conducted. Mastercurves of the dynamic moduli at 140°C of the various blend are plotted in Fig. 1a and b.

The activation energy for the zero-shear viscosity calculated on the time-temperature shift factors was found to be 35 kJ/mol. As expected, due to the dilution effect of short chains, both moduli decrease when the amount of PEG increases. Further analysis was conducted with the help of a discrete relaxation spectrum calculated from the experiments. The plateau modulus for pure PEO calculated from the relaxation spectrum (0.6 MPa) is lower than the value of the literature (Fetters et al. 1999) because of uncomplete data at high frequency. For the blends, the calculated plateau modulus scales as the 2.1 power of the weight fraction of the PEO in the blend (Fig. 2) according to the expected dilution effect of long chains by short species. The effect of the dilution also influences the equilibrium compliance that increases by a factor of 2.5 as soon as a small amount of PEG is added, indicating an increase of the entanglement spacing.

The zero shear viscosity was found to scale with the weight average molecular weight with an unusual exponent of 6.2 (Fig. 3). Though they have different chain ends, PEO and PEG have the same monomeric unit and they are miscible in the melt (Abdel-Azim et al. 1998), therefore phase separation cannot be invoked to explain the observed exponent. Despite the narrow range of molecular weight investigated, similar effects
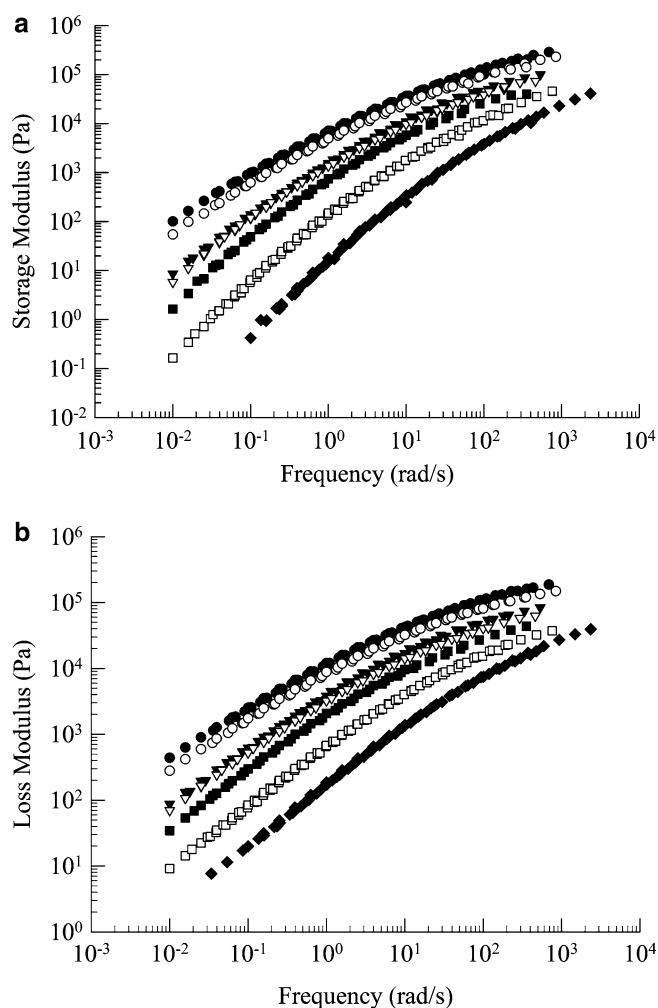

Fig. 1 Dynamic modulus of the miscible blends of PEG–PEO at 140°C: **a** Storage modulus, **b** Loss modulus. PEG content in the matrix is: *filled circle* 0%; *open circle* 10%; *filled inverted triangle* 20%; *open inverted triangle* 30%; *filled square* 40%; *open square* 50%; *filled diamond* 60%

have been reported in the literature (Rudin and Chee 1973) and were attributed to polydispersity. Following their experiments, in the present case, the bimodal distribution that is generated by mixing the broadly distributed high molecular weight PEO with the narrowly distributed low molecular weight PEG could be at the origin of the large value of the exponent. Indeed, dilution brought by short chains induces strong tube renewal effects and with respect to the dynamic dilution mechanism, for a binary blend of species with very different molecular weights, the zero-shear viscosity scales as the third power of the weight fraction of long species. When it is plotted as a function of the weight average molecular weight, the net effect is a large increase of the scaling exponent of the zero-shear viscosity.
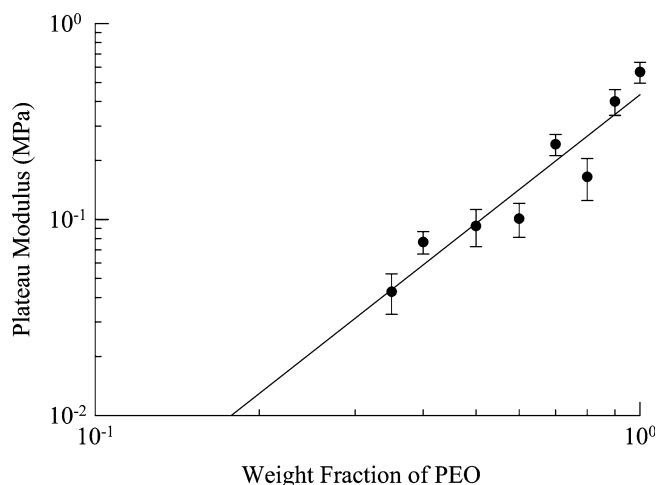
Fig. 2 Plateau modulus versus composition of the miscible blends PEO–PEG, full line indicates the 2.1 scaling

Rheological behaviour of the filled polymers

Figure 4 presents a comparison of the oscillatory data for an unfilled and filled system based on a PEO–PEG matrix containing 50 wt% of PEG. The filler content was 26.4 vol%. Data were obtained in the linear visco-elastic domain. Though it is known that such a domain is hardly attainable in the case of highly filled polymers, in the present case, strains lower than 0.05% were found to be within this domain. Figure 4 shows the dramatic increase in both moduli due to the presence of the filler. Nevertheless, all the systems show a terminal zone and a flow behaviour at low frequency. The filler increases the plateau modulus and gives rise to a broadening of the relaxation spectrum towards the longer times. The data
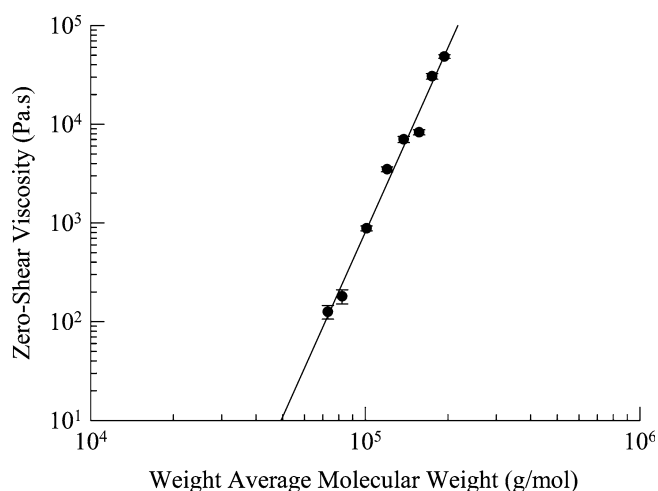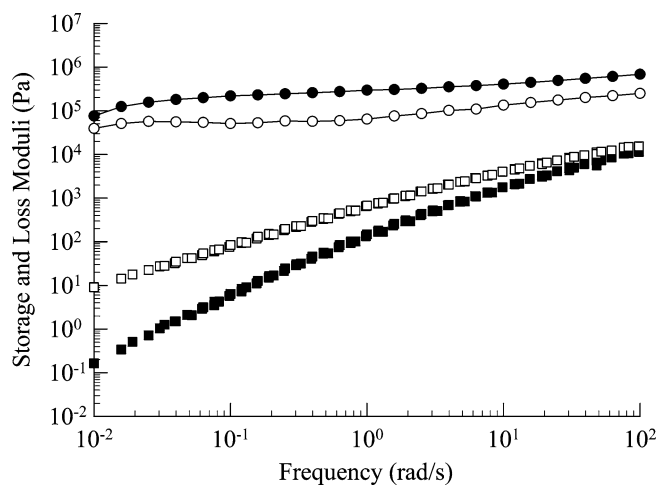

Fig. 4 Storage and loss moduli of unfilled (*filled square*, *open square*): and filled systems (*filled circle*, *open circle*) at 140°C. The matrix composition is 50/50 PEG–PEO. *Full lines* indicate the calculation with a discrete relaxation spectrum

could be represented with the help of a discrete relaxation spectrum, the calculated moduli are shown by the full lines on Fig. 4. This spectrum was used to calculate the value of the plateau in the high frequency zone.

Storage modulus of the filled polymers

Figure 5 presents the storage modulus of filled polymer with a constant filler loading of 26.4 vol% and different compositions of the matrix at 140°C. A clear effect of the filler in the low frequency range can be observed.
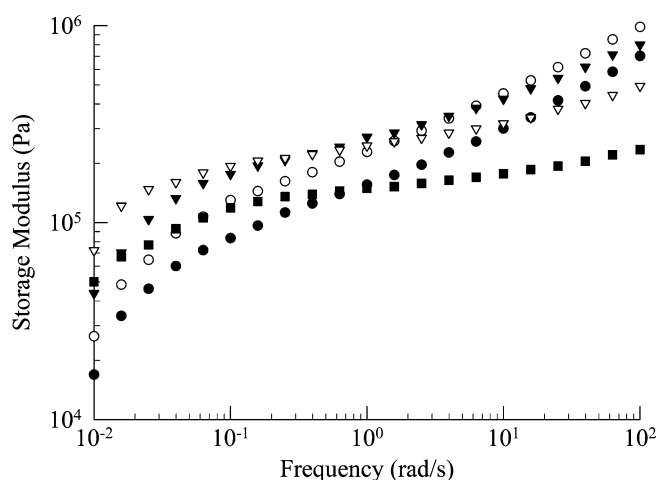

Fig. 3 Zero shear viscosity versus composition of the miscible blends PEO–PEG at 140°C, full line indicates the 6.2 scaling

Fig. 5 Storage modulus of filled systems at 140°C. PEG content in the matrix is: *filled circle* 0%; *open circle* 20%; *filled inverted triangle* 40%; *open inverted triangle* 60%; *filled square* 80%
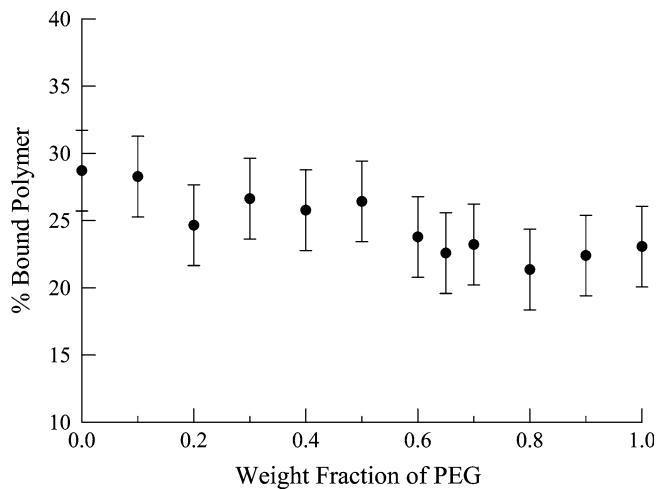
Fig. 6 Amount of bound polymer versus matrix composition

Nevertheless, in all systems, a terminal flow zone is observed. These features indicate that the presence of the filler induces the appearance of a new long relaxation time in the relaxation spectrum due to the presence of polymer bound to the filler. The contributions of the longest relaxation time to the modulus are in the same order of magnitude whatever be the composition of the matrix. This was confirmed by the analysis of the amount of bound polymer after dissolution of the PEO–PEG matrix in water which shows that this amount is high (20–30%) and nearly constant or slightly decreasing with the amount of PEG in the matrix (Fig. 6). Further analysis of the soluble fraction shows that the bound polymer has the composition of the matrix with preferable bonding of the long chains especially at low PEG contents (Bar-Chaput and Carrot 2005). It is worth noting that the presence of the filler induces a new relaxation process rather than an equilibrium plateau and therefore it can be attributed to a weak network of the filler particles. Indeed, being surrounded by bound polymer, the particles may be connected by entangled polymer chains. The mobility of the chains is restricted but disentanglement enables the mobility of the particles and the relaxation of the stress in the filler network. In connection with this restriction of the mobility of the chains by interaction with the active carbon, the variation of the plateau modulus marks the density of the temporary network due to the fillers in addition to that of the entanglements of the polymer. Similarly, starting from measurements of the yield modulus in dynamic spectroscopy, Jäger and Eggen (2004) showed that the strength of the network structure in polymer–carbon black systems only depends on the carbon black type and loading. They also observed that the characteristic time dependence of the rupture and restoration process of the network links is not related to the polymer. Therefore, they concluded that the network structure is determined by particle–particle bonds and that the polymer itself only plays a role in the overall viscoelastic properties of the material.

Analysis of the dispersion of the filler

Figure 7 presents the pictures of the active carbon dispersed in water between glass slides after dissolving the matrix. This method was found to preserve the dispersion. The dispersion was further characterized by image analysis. Results are plotted on Fig. 8 and show that when PEO is the major component, the distributions of diameters are similar with a maximum between 2 and 5 μm and very few particles with diameter larger 100 μm. The system with 30 wt% PEG presents the less agglomerates with diameter larger than 200 μm. On the contrary, large amount of PEG and especially the pure PEG matrix gives rise to a bad dispersion of the agglomerates.

Correlation between the dispersion and the plateau modulus

From Fig. 9, it can be seen that there is a clear correlation between the state of dispersion of the filler and the value of the plateau modulus in the filled system. The plateau modulus increases when the particles become thinner and better dispersed in the polymer matrix.

The explanation for this can be found in the equation that gives the modulus of a network of strands as given by Eq. 1 derived from the rubberlike elasticity:

$$G_N \propto v\,kT \qquad (1)$$

with v number of strands per unit volume, k Bolzmann constant, T temperature.

Assuming that the plateau modulus is due to a contribution of the filler particles to the temporary network as entanglement points in addition to entanglements between polymer chains, the plateau may be expressed by:

$$G_N \propto NkT \qquad (2)$$

with N number of particles per unit volume. For a nearly spherical shape of the particles, this relation could be rewritten as:

$$G_N \propto \frac{6\phi}{\pi D^3} kT \qquad (3)$$

with ϕ volume fraction of filler, D the particle diameter.

Figure 10 shows that Eq. 3 does not hold and that the number of particles is not the proper parameter in Eq. 1. Indeed, the plateau modulus is found to scale to the −1.4 power of the diameter instead of the −3 power.

Fig. 7 Suspension in water after dissolution of the polymer matrix in water. PEG content from left to right and from top to bottom: 0, 30, 50, 80, and 100%. Width of the pictures: 600 µm
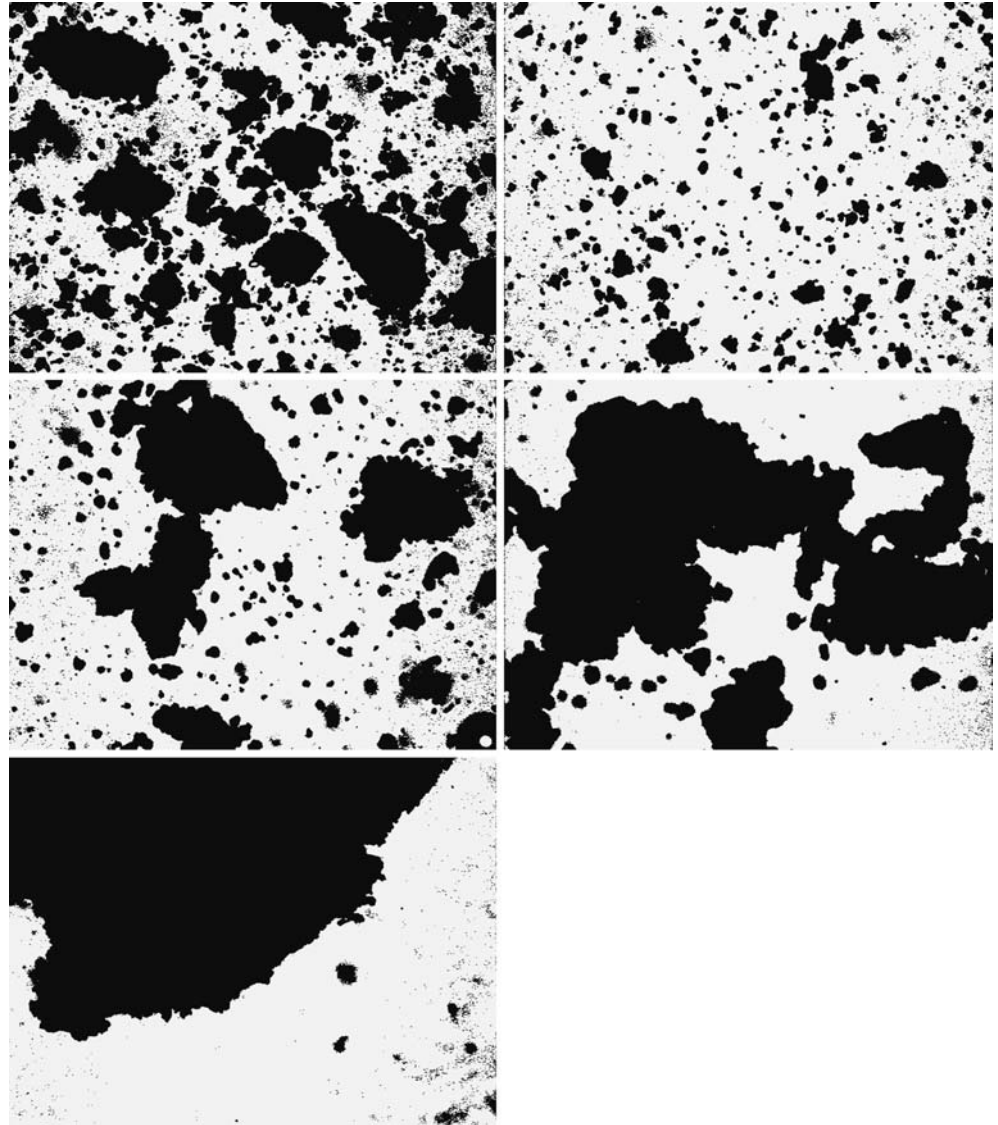
A better correlation could be obtain by returning to the classical definition of the plateau from the rubber elasticity. The number of strands per unit volume is used instead of the number of particles and it is related to the interparticle distance:

$$G_N \propto kT \frac{1}{D} \left\{ \left(\frac{\pi}{6\phi} \right)^{1/3} - 1 \right\}. \tag{4}$$

The dependence of the plateau modulus with the reciprocal of the particle diameter as predicted by Eq. 4 is in better agreement with the scaling that is observed experimentally. Therefore, the interparticle distance may be the preferred parameter that describes the interactions between particles from the rheological point of view. Deviation from the scaling of Eq. 4 could be due to the non-sphericity of the particles or to the polydispersity of sizes.

Influence of the viscosity of the matrix on the dispersion

As mentioned before, Fig. 9 shows two distinct behaviours. For weight fraction of PEG below 30%, the filler is well dispersed in the matrix with a small average diameter and few agglomerates while the plateau modulus is high. On the other hand, when the fraction of PEG in the matrix increases to over 30%, the dispersion worsens and the higher the amount of PEG, the worse is the dispersion with an increasing number of agglomerates of large size. Because, the analysis of the amount of bound polymer does not
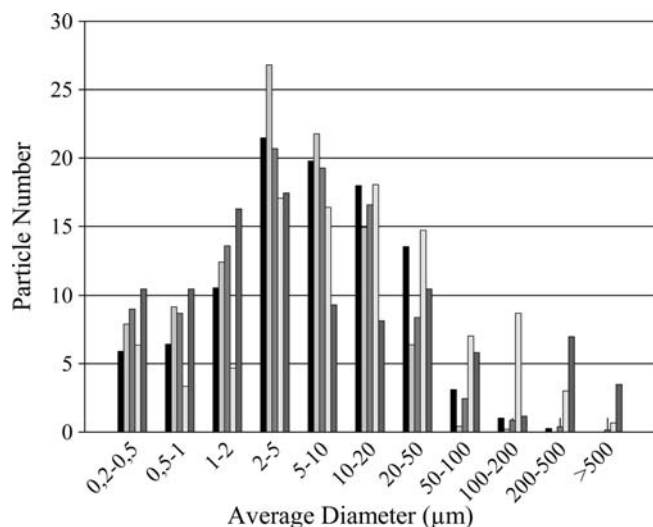
Fig. 8 Histograms for the particle sizes of active carbon in various matrix with PEG contents (from left to right in each class): 0, 30, 50, 70, and 100%

Fig. 10 Correlation between the number average diameter of the particle and the plateau modulus of the filled polymer. *Full line* indicates the −1.4 scaling

show significative difference between the samples with different matrix compositions, good adhesion between the active carbon and the polymer can be assumed. This implies good transfer of the hydrodynamic stresses. Thus, in the case of active carbon and the polymeric matrix under investigation, the dispersion of the agglomerates during the mixing step is mainly due to a rupture mechanism. When the matrix viscosity is large, the hydrodynamic stress exceeds the adhesive forces in the agglomerates and the filler is well dispersed. On the opposite, for high amount of PEG, the viscosity of the matrix decreases and the efficiency of the rupture mechanism becomes low because the hydrodynamic stresses are weaker than the cohesive forces.

Conclusions

In this paper, it is shown that oscillatory measurements in the melt can be a useful tool to get information on the dispersion of a filler in a polymer matrix. Especially, it has been observed that in the case of active carbon dispersed in a polymer matrix composed of miscible PEO and PEG, the presence of the filler is responsible for the building of a temporary network. Comparison with the characterization of the dispersion performed by optical microscopy coupled with image analysis shows that the plateau modulus associated with this network is directly connected to the state of dispersion of the filler. The interparticle distance seems to be the relevant parameter rather than the number of particles per unit volume. It is similar to the length of a strand in the

Fig. 9 Number average diameter of the particle (*open square*) and plateau modulus of the filled polymer (*filled circle*) as a function of the matrix composition
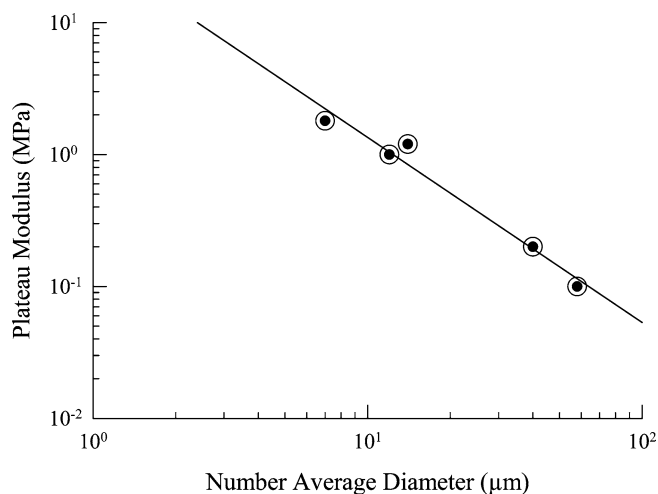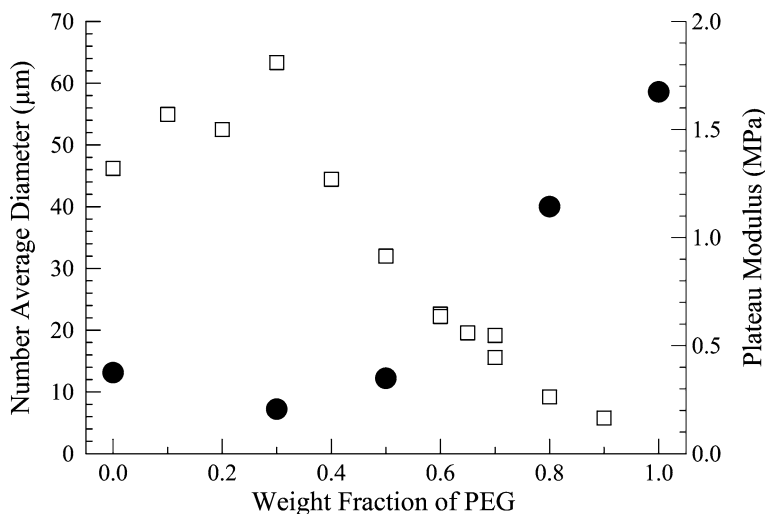
classical definition of the plateau modulus from the rubberlike theory.

Finally, the analysis of the state of dispersion of the filler in miscible blends of PEO and PEG with various composition shows that the viscosity of the matrix during the mixing stage in the melt plays a decisive role. This indicates that the dispersion occurs mainly by a rupture mechanism and that the ratio of the hydrodynamic stress to the cohesive stress into the agglomerates is the leading parameter. Indeed, measurements of the amount of bound polymer did not show significant differences from one sample to another and the adhesion of the particle to the matrix is good whatever be the composition.

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