Talc Filled Thermoplastic Composites: Melt Rheological Properties

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Abstract:
The effects of composition and resulting morphology on the rheology of thermoplastics filled with different talc platelets were studied in the 0-22% range of volume fraction, Φ. The sufficiently filled polymer composites exhibit a rheological behavior which significantly differs from the pure polymers used in this work, a linear low density polyethylene, a low density polyethylene and a polyamide 12. The changes in the rheological behavior are influenced by the size, the concentration and the surface treatment of plate-like talc particles. They also depend on the chemical nature and viscous and elastic characteristics of the polymer matrix. In particular, the effect of platelet orientation on the viscoelastic properties of reinforced composites was pointed out. For sufficiently filled systems, a low frequency response indicative of a pseudo solid-like behavior is obtained only during the first frequency sweep. In fact, the low frequency storage modulus, G', is constant. With repeated frequency sweeps, more platelets were aligned in the flow direction, thus the low frequency storage modulus gradually decreases and becomes dependent on frequency, ω. The low frequency complex viscosity η^* also progressively decreases with repeated frequency sweeps. In addition, for these systems, the low shear viscosity η build up in an unbounded manner because of the existence of particle-particle interactions. There are stresses below which there is no flow indicating the existence of yield values. Steady shear elastic properties are also studied, especially in the case of systems showing an apparent yield stress.

Zusammenfassung:
Der Effekt der Zusammensetzung und resultierender Morphologie auf die Rheologie von Thermoplasten, welche mit Talgplättchen gefüllt sind, wurden in einem Bereich von 0 - 22 Volumenprozent, ϕ, untersucht. Die stark gefüllten Komposite zeigen ein rheologisches Verhalten, das von dem der reinen Polymere (LDPE und Nylon 12) abweicht. Die Veränderungen im rheologischen Verhalten werden von der Grösse, der Konzentration und der Oberblächenbeschaffenheit der plättchenförmigen Talgpartikel beeinflusst. Ausserdem hängen sie von der chemischen Beschaffenheit und den viskosen und elastischen Eigenschaften der Polymermatrix ab. Insbesondere wird der Einfluss der Plättchenorientierung auf die viskoelastischen Eigenschaften der plättchenverstärkten Komposite untersucht. Für ausreichend gefüllte Systeme wird eine niederfrequente Antwortfunktion, welches für das Verhalten eines Pseudo-Festkörpers kennzeichnend ist, nur während des ersten Frequenzsweeps gefunden. Der Speichermodul, G', ist im Bereich kleiner Frequenzen konstant. Bei Wiederholung der Frequenzsweeps wurden mehr Plättchen orientiert, so dass der Speichermodul bei kleinen Frequenzen allmählich abnimmt und frequenzabhängig wird. Die komplexe Frequenz, η^*, nimmt bei einer Wiederholung der Frequenzsweeps ebenfalls ab. Zusätzlich zeigt die Vikosität dieser Systeme bei kleinen Scherraten aufgrund von Partikel-Partikel Wechselwirkungen einen markanten Anstieg. Es existieren Spannungen, unterhalb derer kein Fliessen vorliegt, was auf die Existenz einer Fliessgrenze hindeutet. Elastische Materialeigenschaften für die stationäre Scherung werden ebenfalls untersucht, insbesondere für solche Systeme, welche eine scheinbare Fliessgrenze besitzten.

Résumé:
La rhéologie de thermoplastiques chargés de différentes plaquettes de talc est étudiée en fonction de la composition et de la morphologie de ces systèmes sur une plage de fractions volumiques de talc, Φ, s'étendant de 0 à 22%. Les composites suffisamment chargés présentent un comportement rhéologique qui diffère très largement de celui des polymères purs utilisés dans cette étude, un polyéthylène linéaire basse densité, un polyéthylène basse densité et un polyamide 12. Les changements observés dans le comportement rhéologique sont influencés par la taille, la fraction volumique et le traitement de surface des plaquettes de talc. Ils dépendent aussi de la nature chimique et des propriétés élastiques et visqueuses de la matrice polymère. En particulier, l'effet d'orientation des plaquettes sur les propriétés viscoélastiques des composites renforcés est mis en évidence. Pour des systèmes suffisamment chargés, une réponse indiquant un comportement pseudo-solide est obtenu seulement lors du premier balayage en fréquence. En effet, le module élastique, G', à faibles fréquences est constant. Avec des balayages en fréquence répétés, de nombreuses plaquettes s'alignent suivant la direc-

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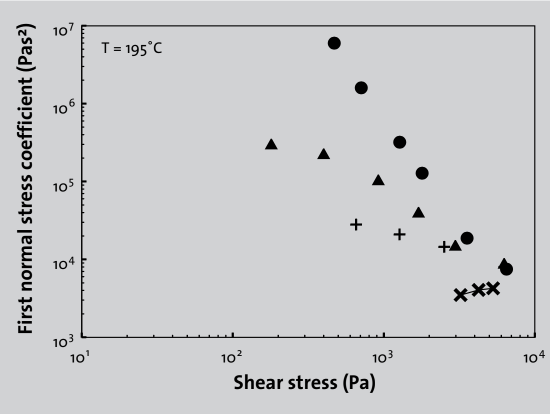


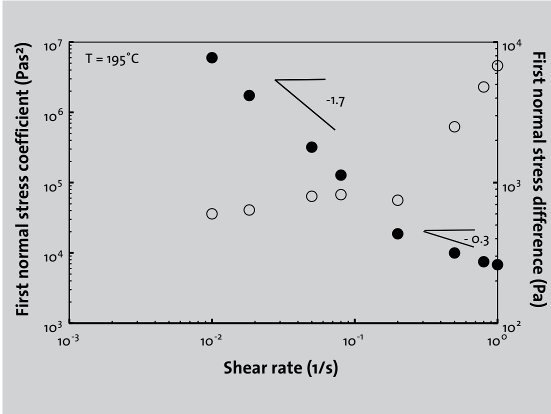


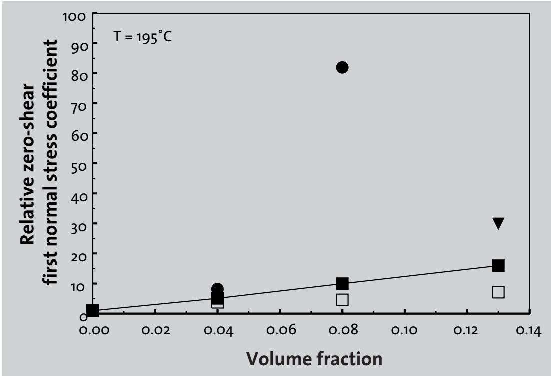
Figure 9 (left above): Variation of the talc1/LLDPE first normal stress coefficient versus shear stress at different volume fractions (✗ 0%, + 4%, ▲ 8%, ● 13%).

Figure 10 (right above): First normal stress difference and coefficient as a function of shear rate.

Figure 11 (right below): Relative zero-shear first normal stress coefficient at different volume fractions.

es, the first normal stress coefficient increases with increasing particle loading. For moderately filled polymers, we observe a low shear plateau, hence, we can determine the zero-shear first normal stress coefficient Ψ_1. It is not the case for filled polymers showing an apparent yield stress, for example LLDPE filled with 13% of talc1 (Fig. 9). Figure 10 reflects the dependence of the first normal stress coefficient and the first normal stress difference on shear rate, for LLDPE filled with 13% of talc1. These curves show two regions. In the first region ($\dot{\gamma} \leq 0.2\ s^{-1}$), Ψ_1 scales as $\dot{\gamma}^{-1.7}$ and N_1 slightly increases as the shear rate is increased. In the second region, ($\dot{\gamma} > 0.2\ s^{-1}$), Ψ_1 scales as $\dot{\gamma}^{-0.3}$ and N_1 is almost proportional to shear rate squared. The variation of the first normal stress difference for this system is very similar to those obtained for suspensions with silicone oil and fillers [28] or nanocomposites [29]. Finally, in the Fig. 9, we can remark that beyond a certain shear stress value, denoted τ_C, the talc volume fraction has a negligible influence on elasticity: at $\tau_C \approx 10\,000$ Pa, the elasticity level of talc1/LLDPE composites is close to the elasticity level of pure LLDPE. τ_C is slightly superior to 10 000 Pa for LDPE or PA12-based composites, hence τ_C is dependent of the nature of the matrix.

Figure 11 shows the talc volume fraction dependence of the relative zero-shear first normal stress coefficient, which is the ratio of the zero-shear first normal stress coefficient of the filled system to that of the matrix. Whatever the system, the relative zero-shear first normal stress coefficient increases with the increasing amount of talc. Figure 11 shows that, at every volume fraction, the relative zero-shear first normal stress coefficient of talc3/LLDPE is smaller than that of talc1/LLDPE. The effect of the high shape factor tends to raise the value of the relative zero-shear first normal stress coefficient. In this study, this effect is predominant in comparison with the effect due to the presence of smaller particles, which significantly reduces the first normal stress difference, as extensively discussed by Shenoy [30]. Figure 11 also shows that at $\Phi = 13\%$ talc1/LDPE



system and especially talc1/PA12 system have relative zero-shear first normal stress coefficients which are largely smaller than this of talc1/LLDPE system. In the case of polyamide, the surface particle treatment leads to a weak reduction of the coefficient respectively to untreated particles [9].

6 CONCLUSION

The investigation reported herein allows to correlate, at least qualitatively, morphology and rheological properties of talc filled thermoplastics. Three matrices, with different natures, structures or rheological properties, and three talc plate-like fillers, with different granulometries or surface properties are chosen for this study. So, in relation to the morphology of these filled systems observed at rest, the shear viscous properties, but also the shear elastic properties, have been studied. The changes in shear viscous properties with particle size, shape, surface treatment and volume fraction have already been observed and analyzed for other filled systems. For instance, for sufficiently filled systems, the complex viscosity reduction with repeated frequency sweeps associated to a plate-like filler orientation and the existence of an apparent yield stress which appears with particle-particle interactions are two phenomena of a great interest for industrial applications, in particular for permeation resistance to hydrocarbons. On the other hand, the outcomes concerning the elastic shear properties of talc filled thermoplastics are original and bring a new lighting on rheology of filled polymers. The influence of matrix nature, structure and rheological properties on rheological properties of talc filled thermoplastics have also been investigated.

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