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A rheological method to compare the degree of exfoliation of nanocomposites

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Abstract

A method to quantify the shear thinning effect for polymer–clay nanocomposites has been developed. It relies on the shear thinning exponent *n*. The method allows to compare the extent of delamination of platelet stacks based on a routine polymer characterization experiment. Since technical properties of nanocomposites are closely linked to delamination or exfoliation, the method helps to predict the level of properties of a nanocomposite. The method is expected to become a highly useful analytical tool in the development of nanocomposites from thermoplastic polymers and virtually all kinds of platy, fibrous, or dendritic filler materials with high aspect ratio.

Keywords: Nanocomposites; Rheology; Organoclay

1. Introduction

Polymer–clay nanocomposites are the subject of intense research efforts. Numerous papers and patent applications have been published on the subject, and a concise survey has recently been given [1]. The key objective in preparing polymer clay nanocomposites is to achieve exfoliation or delamination of the large stacks of silicate nanoplatelets into single layers or tactoids of a small number of layers. Only then the enormous aspect ratio of the platelets can fully contribute to the nanocomposite property profile. Consequently, in developing and optimizing nanocomposites one needs to know the degree of exfoliation of a particular sample and compare it to other samples, which have been prepared under a similar, but distinctively different set of parameters. Literature discloses a number of methods for this purpose, see, e.g. chapter 4 of [1].

Wide angle X-ray scattering (WAXS) is a very popular method for this purpose. It quantifies the gallery height between adjacent silicate platelets and thus proves the widening of this distance as matrix polymer intercalates between the galleries. This is an unequivocal means to prove the formation of intercalated nanocomposites with gallery heights up to about 4 nm, which is the resolution limit of typical instruments used. Several authors [1] consider the complete disappearance of WAXS signals of a polymer clay nanocomposite a proof for complete or almost complete exfoliation of the nanoplatelets. The authors disagree with that proposition. While perfect exfoliation in a polymer matrix would indeed lead to the disappearance of the WAXS signal, other changes of physical state of the layered silicate could as well be responsible for the loss of layer periodicity or WAXS signal to noise ratio. Hence the disappearance of a WAXS signal is not a convincing proof for the formation of a perfectly or almost perfectly exfoliated polymer–clay nanocomposite.

Transmission electron microscopy (TEM) is the method of choice to visualize the exfoliation of platelet stacks. However, due to its extremely high resolution TEM only probes a very small volume, which may or may not be representative of the total composite. Moreover sample preparation for TEM analysis is difficult and time consuming. Therefore, the method is too costly for routine characterization of nanocomposites.

Melt rheology has been discussed in chapter 15 of [1] and several papers [2–10] as a method to characterize polymer–clay nanocomposites. Pronounced shear thinning has been found to be a characteristic feature of truly nanodispersed composites. Under certain experimental conditions even pseudo-solidlike rheological behaviour [4] has been

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detected, possibly resulting from edge to face interactions of silicate platelets or platelet tactoids. These edge to face interactions help to build and mechanically stabilize the mesoscale cardhouse structure of platelets in the nanocomposite. At higher shear rates or prolonged action of slow shear forces the platelets do increasingly align in parallel leading to the observation of pronounced shear thinning [5]. In several publications [1–9] it has been shown, that there is a qualitative relation between the extent of shear thinning and the concentration of organoclay platelets.

To our knowledge there is no publication, yet that discloses an approach to quantify shear thinning in order to compare exfoliation and nanoscale dispersion of nanocomposites. The purpose of this paper is to communicate such an approach developed in our laboratories.

2. Experimental

All nanocomposites investigated were made from poly(butylene terephthalate) (PBT) as matrix polymer. Commercial grade Celanex® CX2003 was employed in all melt compounding experiments, because it is available in large quantities with narrow melt viscosity specifications. This assures that the rheological behaviour of the various samples is the result of the nanocomposite structure, but not of matrix polymer molecular weight or polydispersity variations.

Purified as well as organically modified montmorillonites were obtained from Southern Clay, Gonzales/Texas, and Sued-Chemie, Moosburg/Germany. Clay concentrations were kept constant at 4% by weight of silicate. This was done because shear thinning is a function of clay concentration [1–10]. Powdery clay and polymer were mixed, carefully dried overnight in a vacuum oven and compounded in a Haake melt kneader on the 50 g scale. Standard processing conditions applied were 15 min kneading time at 250 °C and 80 rpm (samples a–d). Composite samples were introduced into the rheometer in the form of melt pressed plates of 25 mm diameter and 1 mm thickness.

Some comparison samples were prepared by the in situ polymerization method. The clay was dispersed in 1,4-butanediol. Then this dispersion was copolymerized with dimethylterephthalate to form PBT with the clay present in situ during the polymerization reaction (samples e and f). These in situ polymerized nano-composites also comprised 4 wt% of silicate. Samples of this in situ polymerization batches were melt pressed into specimen and characterized in the same manner as the melt compounded samples.

In order to obtain meaningful mechanical test data some samples were scaled up to the kg scale. The compounding was done on a Leistritz LSM 30/34 twin screw extruder (samples g–i). Moderate shear and (comparatively) long residence time was employed as a direct consequence from the work reported in Ref. [11]. Tensile bars were injection molded and their respective elastic modulus determined in an Instron instrument according to ISO 527 at 1 mm/min elongation rate and a strain of $\Delta l/l < 0.25\%$.

Rheological measurements were performed using a Physica MCR 300 rheometer with a CTD 600 thermo chamber. Plate–plate geometry with plate diameter of 25 mm was employed. Samples of 1 mm thickness were inserted and heated to 240 °C. Data were taken in the range between 0.1 and 100 s^{-1} shear rate.

Since the cardhouse of nanoplatelets might be destroyed by a high shear amplitude, it is necessary to use a very low amplitude (see Section 3). The measurements were made with a constant shear amplitude of 1%. It was confirmed at low shear rates that at 1% amplitude the sample viscosity did not change over time as a result of silicate platelets aligning in parallel.

Scanning electron micrographs (SEM) were taken in order to complement rheological and tensile measurements. Smooth cut sample surfaces were etched under vacuum in an oxygen plasma. This treatment lead to the selective removal of a few hundred nanometer of polymer matrix close to the surface, leaving behind the three dimensional platelet cardhouse as top layer. The plasma etching was done within the SEM instrument and the remaining silicate platelet scaffold micrographed immediately afterwards.

3. Results and discussion

Fig. 1 shows the alignment of organoclay platelets at higher shear amplitudes in the plate–plate geometry. Sweep No. (1) taken at 1 rad and 240 °C at increasing amplitude shows a plateau viscosity up to a deformation of approximately 10%. At higher amplitude the viscosity decreases drastically. Sweep No. (2) was taken immediately

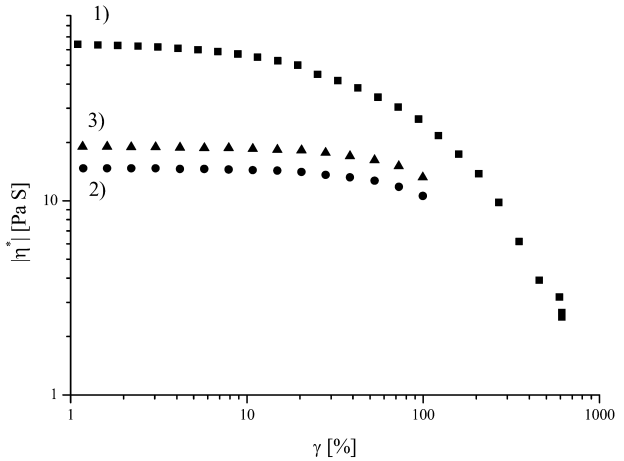

Fig. 1. Consecutive amplitude sweeps of the very same nanocomposite sample, showing shear induced alignment of the nanoclay platelets in sweep No.(1) resulting in significantly diminished low shear viscosity in sweep No. (2). Thermal randomization of the platelet alignment restores some of the viscosity loss, as proven by sweep No. (3) taken after a 60 min hold time.

after the first one with the same sample under identical conditions. The initial low shear viscosity observed in sweep No. (1) is not restored, a clear indication that the platelets are more or less aligned as a result of higher amplitude shear. After a 60 min hold time at 240 °C a third sweep was taken. Quite unexpectedly this sweep No. (3) shows a somewhat increased low shear viscosity again. The alignment of the platelets induced in sweep No. (1) has disappeared by thermal randomization over the 1 h hold period.

The flow curves (apparent viscosity η vs. shear rate ω) taken under low amplitude measurement conditions were fitted to the power law expression:

$$\eta = A\omega^{(n)}$$

with η, apparent viscosity; A, a sample specific pre-exponential factor; ω, the oscillation frequency of the rheometer equivalent to shear rate; n, the shear thinning exponent

In order to determine A and n a plot of $\log(\eta)$ vs. $\log(\omega)$ was made and fitted to a straight line. The shear thinning exponent n is the proposed semi-quantitative measure of nanodispersion of the sample. If a linear double logarithmic plot results, the intercept A is close to the experimentally measured viscosity at $\omega = 1\ s^{-1}$. In most cases, however, curved plots of $\log(\eta)$ vs. $\log(\omega)$ resulted. Then the straight line was fitted to the data at the lowest shear rates, in order to determine n. The rationale for this is that at low shear rates the rheological response is most representative for the unperturbed, i.e. unoriented, platelet structure in the composite. At higher shear rates, experimentally realized, via higher oscillation frequencies of the plate–plate-rheometer, the solid-like cardhouse cannot follow the shear induced disturbance. The dynamics is then controlled by the liquid polymer melt.

Fig. 2 shows the results obtained with four different nanocomposite samples. Unmodified PBT CX 2003 shows perfect Newtonian behaviour at the comparatively low shear rates employed here, resulting in a shear thinning exponent $n = -0.02$ (not shown in the figure). Addition of purified but not organically modified montmorillonite does not affect any change in the shear thinning behaviour (sample a). Again the flow curve is practically horizontal and $n = -0.04$. In contrast, the three samples comprising organically modified clay platelets do show pronounced shear thinning. The respective values of the exponent n vary between $n = -0.56$ and -0.86. Clearly the shear thinning exponent allows a quantitative discrimination between the samples. Two questions, however, do arise:

1. Is the shear thinning exponent truly dependent on the nano-and mesoscale composite structure formed by the (partially) exfoliated platelets? Or did different processing conditions lead to those differences in the flow behaviour of the matrix polymer?
2. Does the shear thinning exponent n correlate with other, independently obtained information on the nano-and mesoscale structure of the composites?

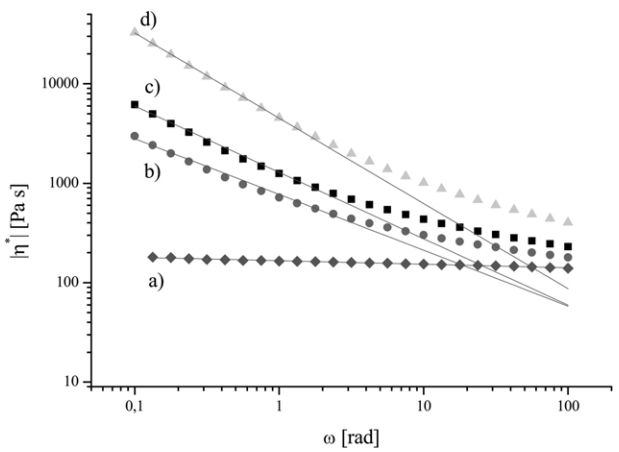

Fig. 2. Flow curves η vs. ω of different nanocomposite samples prepared by melt kneading under identical processing conditions: (a) PBT plus purified montmorillonite $n = -0.04$. (b) PBT plus organoclay No. 1 $n = -0.56$. (c) PBT plus organoclay No. 2 $n = -0.67$. (d) PBT plus organoclay No. 3 $n = -0.86$. Neat PBT (not shown) $n = -0.02$.

In order to address question No. 1 the rheological characterization of sample (d) was repeated at different temperatures within the interval 240 °C $< T <$ 270 °C. Fig. 3 shows the result, which is surprising at a glance: upon variation of the temperature between 240 and 270 °C one would expect strong differentiation in the rheological behaviour of a polymer composite. In fact there does not seem to be any influence of the temperature at low shear rates. Only at shear rates close to 100 s^{-1} the viscosity decreases with temperature. Therefore the time temperature superposition principle does not apply, which has been demonstrated earlier with other nanocomposite samples [12].

At a closer look this finding indicates platelet exfoliation. If the platelets form a nanoscale network or cardhouse structure, then the rheological behaviour of the composites should be solidlike (as indicated in Ref. [4]) with only minor

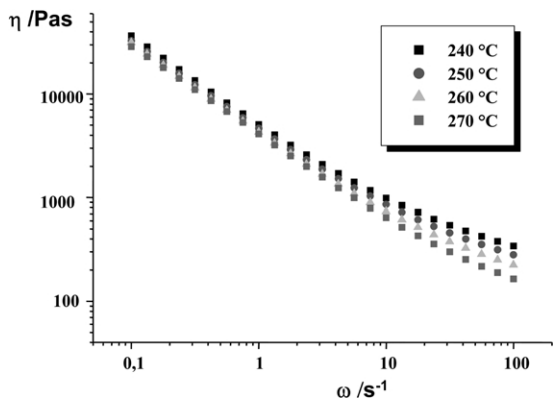

Fig. 3. Flow curve η vs. ω for nanocomposite (d) measured at different temperatures.

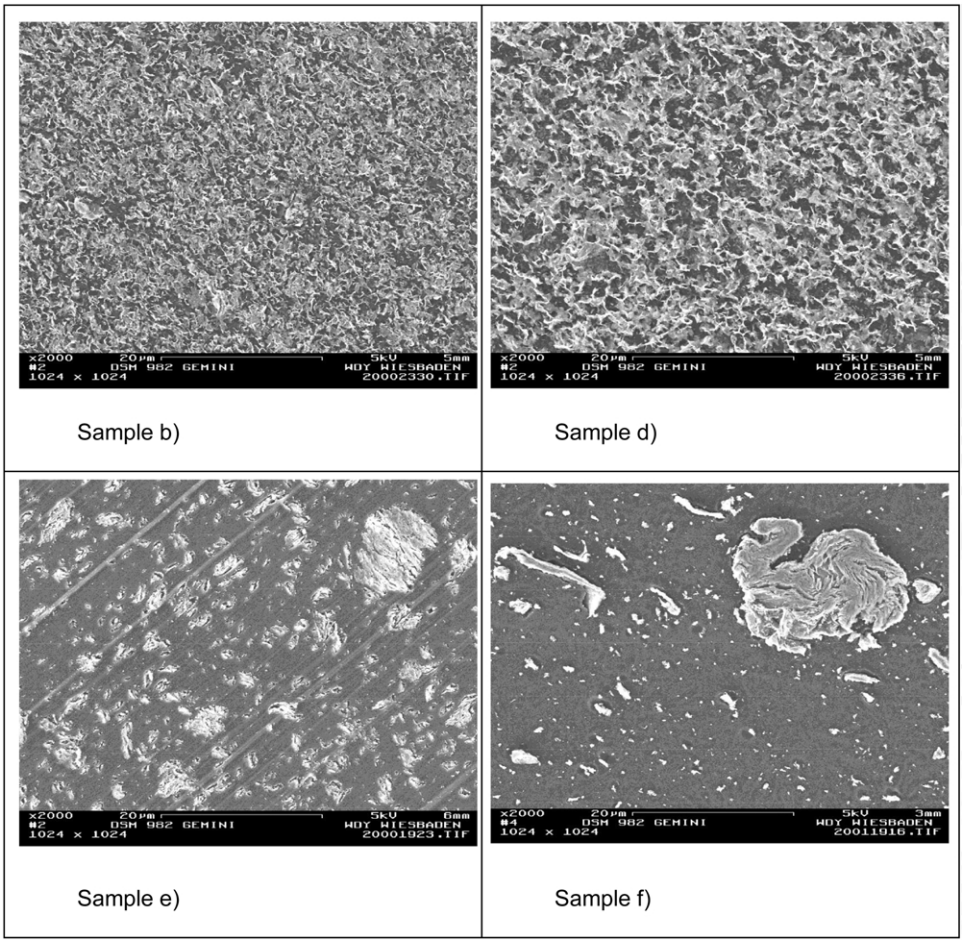

Fig. 4. SEM pictures: samples (b) and (d) are as in Fig. 1. Sample (e) was prepared by in situ polycondensation in the presence of organoclay No. 1 as for sample (b). It has a shear thinning exponent of $n = -0.12$. Sample (f) was prepared by in situ polymerization in the presence of purified but not organically modified montmorillonite. It has a shear thinning exponent of $n = -0.02$.

influence of temperature at low shear rates. At higher shear rates the rheology will be determined by the polymer matrix. Thus the composite will behave much like a liquid with the well known strong influence of temperature on viscosity.

We will try to answer question No. 2 with the help of scanning electron microscopy (SEM) and mechanical properties of the composites. Fig. 4 shows some SEM photographs taken from representative samples at a magnification of 2000. Samples (b) and (d) in the first row are the same composites as in Fig. 2 with shear thinning exponent of $n = -0.56$ and -0.86, respectively. Samples (e) and (f) in the second row are comparison samples made by in situ polymerization. For sample (e) a slight shear thinning with $n = -0.12$ was observed. Sample (f) showed Newtonian behaviour with $n = -0.02$.

Samples (b) and (d) comprise a smooth, finely dispersed nanoscale scaffold. Both of these samples showed considerable shear thinning in melt rheology. Sample (e) with only moderate shear thinning is not nearly as well dispersed. Huge stacks of platelets might be discerned on the SEM picture. Sample (f), behaving essentially Newtonian, contains large aggregates of up to ~ 10 μm diameter. It is not a nano composite

SEM cannot differentiate between samples (b) and (d), despite the significant difference in their respective shear thinning exponent n. The reason for this might be that both samples are in fact delaminated beyond instrument resolution. Fig. 5 is a higher magnification SEM picture of sample (b). It demonstrates that the platelet appear to have

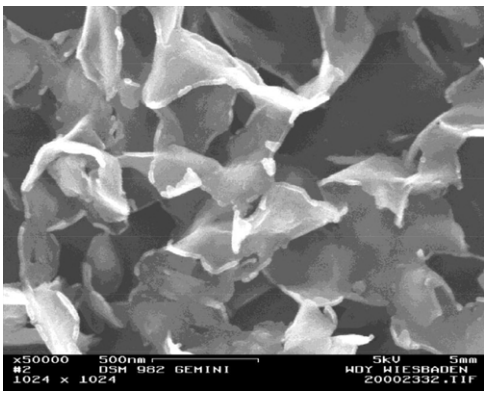

Fig. 5. Higher resolution SEM picture taken from sample (b).

Table 1
Shear thinning exponent and tensile modulus for samples prepared in a Leistritz LSM 30/34 twin screw extruder

Sample	Composition	Shear thinning exponent n	Tensile modulus (GPa)
(g)	PBT control	−0.03	2.5
(h)	PBT plus organoclay No. 1 (sample b)	−0.65	3.2
(i)	PBT plus organoclay No. 3 (sample d)	−0.86	3.5

Note that there is a certain impact of compounding conditions (twin screw extruder vs. laboratory scale melt kneader) on the shear thinning exponent, n for sample (i) is identical to sample (d) prepared with organoclay No. 3. In contrast, n for sample (h) is 20% higher as compared to sample (b), both prepared from organoclay No. 1.

an almost uniform height of $h \approx 30$ nm, which closely corresponds to the instrument resolution. In conclusion, REM analysis confirms the quantitative character of the shear exponent n, well exfoliated samples display a higher magnitude of n, while absence of exfoliation results in n close to zero

In terms of mechanical properties of nanocomposites an increase in elastic modulus has been reported to be a prominent effect (see, e.g. chapters 6 and 7 in Ref. [1]). The better the silicate platelets are exfoliated, the stronger is the reinforcement effect on the resulting nanocomposite at a given mineral content. In order to obtain kg scale samples for injection moulding and mechanical testing, the compositions of samples (b) and (d), respectively, were melt compounded on a pilot extruder. Table 1 shows the relation between shear thinning exponent n and tensile modulus for these specimen. Note that the shear thinning exponent n for the sample (i) remained unchanged at $n = -0.86$ as compared to sample (d), which is of the same composition. In contrast, samples (h) and (b) are characterized by slightly different values of n, despite having the same composition. This indicates the influence of melt compounding conditions (laboratory scale melt kneader vs. twin screw extruder) on the degree of exfoliation.

In Table 1 a clear correlation between the shear thinning exponent n and the tensile modulus is observed: the higher the exponent n, the more efficient is the reinforcement of the respective composite.

4. Conclusion

In the preceding paragraph it was demonstrated that the shear thinning exponent n is a semi-quantitative measure of the degree of exfoliation and delamination. The term semi-quantitative means that there is no unequivocal relation between the shear thinning exponent n and the degree of delamination. It also means that the average number of nanoplatelets per tactoid for a given nanocomposite cannot be calculated from n. Rather the shear thinning exponent may be used for direct comparison of the exfoliation quality of nanocomposite samples prepared under intentionally varied conditions (e.g. nanoclay content, intercalant chemistry, compounding or polymerization conditions, etc.).

The properties of nanocomposites such as mechanical strength, gas permeation barrier, or suppression of heat and mass transfer during combustion do depend on the degree of exfoliation of the silicate platelets. Therefore, the shear thinning exponent n may help to identify interesting samples at a stage, where technical testing cannot yet be applied. It is a valuable complement to the nanocomposite characterization methods known in the art. The method relies on standard polymer test equipment, thus facilitating the data acquisition as compared to WAXS and TEM. Its particular advantage is that it probes bulk properties on a small laboratory scale. This means that the result on the one hand is representative for a macroscopic sample volume, which is important from an engineering point of view. On the other hand, sample preparation may be done on the gram scale, which simplifies and speeds up development.

The method has been introduced here using examples of polymer–clay nanocomposites only. Its full range of applicability is expected to be much broader. Any composite prepared from a thermoplastic polymer and platy, fibrous, or even dendritic filler materials with high aspect ratios should display a similar melt rheological behaviour. Analogous shear thinning behaviour has been observed in our laboratory for composites prepared from graphite platelets and dendritic forms of carbon black as nanofillers. It is also reported for polycarbonate/carbon nanotube composites [13], where the extent of shear thinning has been directly linked to the percolation threshold for electroconductivity.

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References

[1] Pinnavaia TJ, Beall GW, editors. Polymer–Clay Nanocomposites. New York: Wiley; 2000.
[2] Krishnamoorti R, Vaia RA, Giannelis EP. Chem Mater 1996;8:1728–34.
[3] Krishnamoorti R, Giannelis EP. Macromolecules 1997;30:4097–102.
[4] Ren J, Silva AS, Krishnamoorti R. Macromolecules 2000;33:3739–46.
[5] Krishnamoorti R, Ren J, Silva AS. J Chem Phys 2001;114:4968–73.

[6] Solomon MJ, Almusallam AS, Seefeldt KF, Somwhangthanaroj A, Varadan P. Macromolecules 2001;34:1864–72.
[7] Lim YT, Park OO. Rheol Acta 2001;40:220–9.
[8] Galgali G, Ramesh C, Lele A. Macromolecules 2001;34:852–8.
[9] Hyun YH, Lim ST, Choi HJ, Jhon MS. Macromolecules 2001;34: 8084–93.
[10] Krishnamoorti R, Mitchell CA. J Polym Sci B 2002;40:1434–43.
[11] Dennis HR, Hunter DL, Chang D, Kim S, White JL, Cho JW, Paul DR. Polymer 2001;42:9513–22.
[12] Reichert P, Hoffmann B, Bock T, Thomann R, Muelhaupt R, Friedrich C. Macromol Rapid Commun 2001;22:519–23.
[13] Pötschke P, Fornes TD, Paul DR. Polymer 2002;34:3247–55.