

Characterisation of the Delamination Process of Nanoclays

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Abstract: Nanocomposites comprising delaminated nanoclays result in superior properties of the final product. This study aimed at monitoring the processes of intercalation and exfoliation of different nanoclay-polyol pairs performed through different dispersion protocols. X-ray diffraction, rheology and particle sizing are discussed in relation to the evolving product properties.

Keywords: Nanoclays, delamination, exfoliation, intercalation.

Introduction

Nanoclay dispersions or “nanocomposites” are obtained through the delamination (intercalation and/or exfoliation) of clay platelets in a polymer melt or monomer prior to polymerisation. Whilst in conventional composites, the clay acts as a filler material to the polymer, intercalated nanocomposites form when a small amount of polymer moves into the gallery spacing between the clay platelets to promote the swelling of stacks of clay platelets and exfoliated nanocomposites are clay platelets fully delaminated and dispersed in a continuous polymer matrix (Figure 1). Superior product properties have been reported even at low clay concentrations [1, 2, 6, 7, 8]. Better mechanical and thermal properties make them attractive for applications in the automotive industry [3] and excellent barrier properties with good transparency for packaging [4]. They are used as rheology modifiers in paints, inks and cosmetics; anti-settling, anti-sagging agent on vertical surfaces; provide better colour retention and good coverage in cosmetics and inks; they have been shown to enhance the thermal stability of greases. Hence, they are used in a wide range of industries including water treatment and controlled release of therapeutic agents. These benefits are primarily due to the clay being uniformly distributed throughout the polymer matrix resulting in a larger surface area for contact.

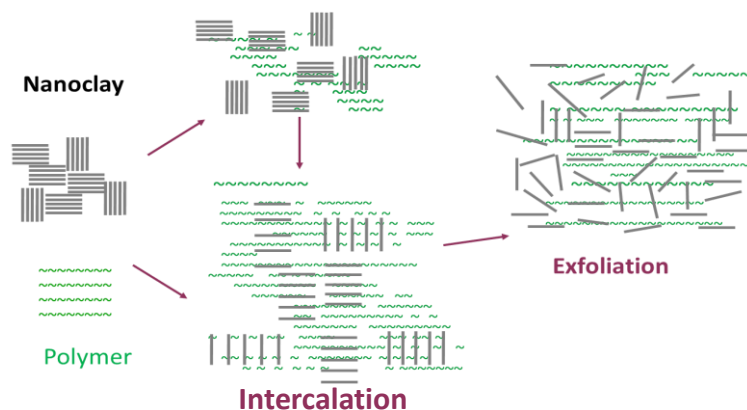


Figure 1: Schematic representation of the intercalation and exfoliation processes

been a challenge due to the difficulties in identifying appropriate experimental technique(s) to monitor the delamination process and ensure repeatability of the desired product properties.

This study has been undertaken with different partial formulations of clay-in-polyol dispersions with varying affinity and clay concentration to establish how best to characterise the delamination process and also draw conclusions relevant to formulation and process development.

Experimental

Three grades of Cloisite clays (organically modified montmorillonites from Rockwood additives, now BYK Additives Ltd), 30B, 10A and 15A were dispersed in Daltocel F555, F435, F456 (polyols from Huntsman) in different combinations to achieve different levels of affinity.

The intercalation process, studied under gentle conditions, was carried out in a stirred tank equipped with a hydrofoil, Lightnin A310 impeller. This was of a diameter of $D=0.096$ m, operated at a speed of $N=200$ rpm which corresponded to a specific power input of $P/m=0.10$ W/kg.

For exfoliation, which is a power intensive process, three process devices were used in a 0.169 m diameter glass tank with 4 standard baffles (2 kg of total dispersion):

- a stirred tank with a sawtooth impeller of $D=0.062$ m and operated at 1500 rpm, (~ 8.6 W);
- a Hielscher UP200S ultrasonic processor (S14D sonotrode) in conjunction with a $D=0.072$ m pitched blade turbine operating at 150 rpm to maintain the solids in suspension. The ultrasonic probe was operated over a range of amplitudes corresponding to 55 to 89 W.
- a stirred bead mill: WAB Multilab Mill

The X-Ray diffraction technique used to determine the inter-gallery spacing at the start and end of intercalation experiments was Hecus XRS. For rheology measurements, an Anton-Paar Rheolab QC rheometer was used. The particle sizer, Beckman-Coulter LS230, was modified to use with a custom-built flow cell and a special design external circulation loop.

Results and Discussions

Dispersion viscosity increased upon the addition of nanoclays but the rheology of samples taken during the course of intercalation did not change (Figure 2). On the other hand, X-Ray diffraction measurements, proved to be a useful tool for monitoring the evolution of the intercalation process. Figure 3.a shows diffractograms for the continuous phase, Daltocel F555, the dry clay powder, Cloisite 30B and that after the intercalation stage and results for three dispersions are shown in Figure 3.b.

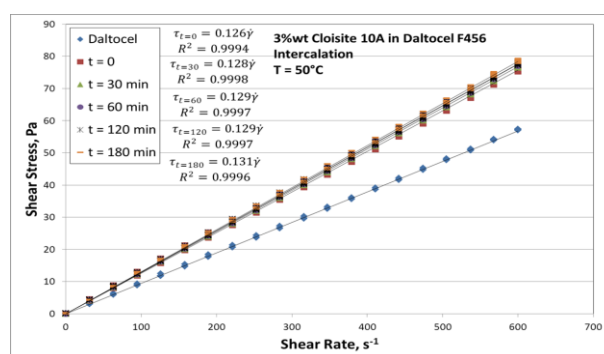


Figure 2: Rheological profile of the polyol before and after addition of the nanoclay and during intercalation

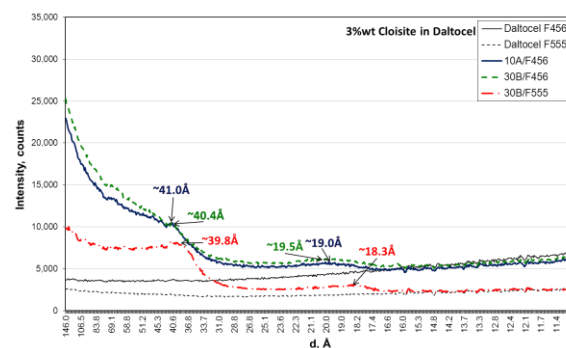
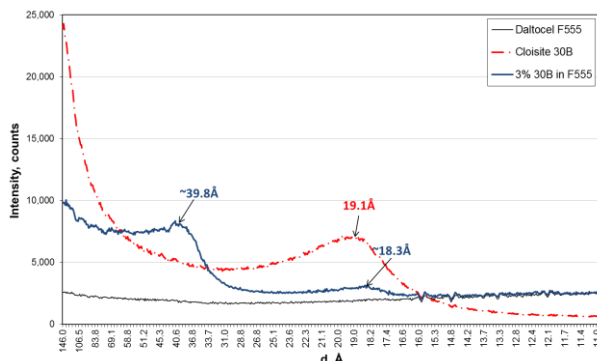


Figure 3: Inter-gallery spacings measured for (a) continuous phase, nanoclay powder and after intercalation

(b) different nanoclay and polyol pairs

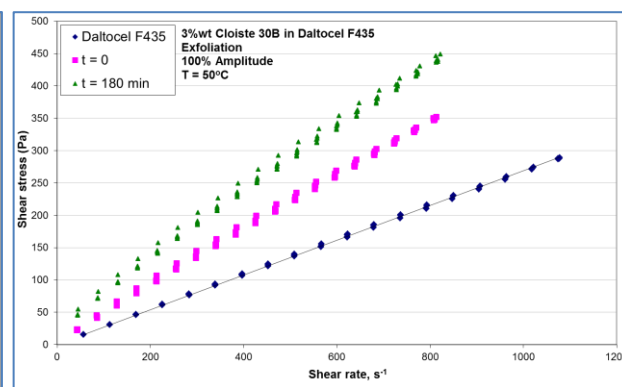
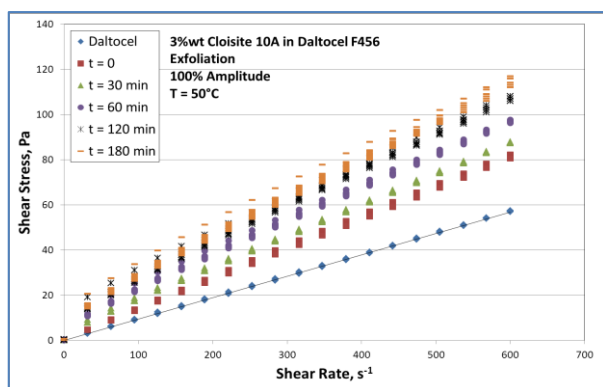


Figure 4: Evolution of the rheology of nanoclay dispersions during the course of exfoliation

During the course of exfoliation, performed using the more power intensive ultrasonicator, the rheology of the dispersion changed dramatically (Figure 4). The dispersion became highly non-Newtonian exhibiting yield stress which could best be defined by the Herschel Bulkley model in most cases and time dependent (thixotropic) properties. The extent to which this occurred depended on the nanoclay-polyol pair (Figure 4). At a given shear rate value of 600 s^{-1} , whilst the relative viscosity increase was negligible during intercalation, a significant increase was noted during exfoliation which takes place at more power intensive conditions. This also depended on the affinity between the nanoclay and polyol pair (Figure 5).

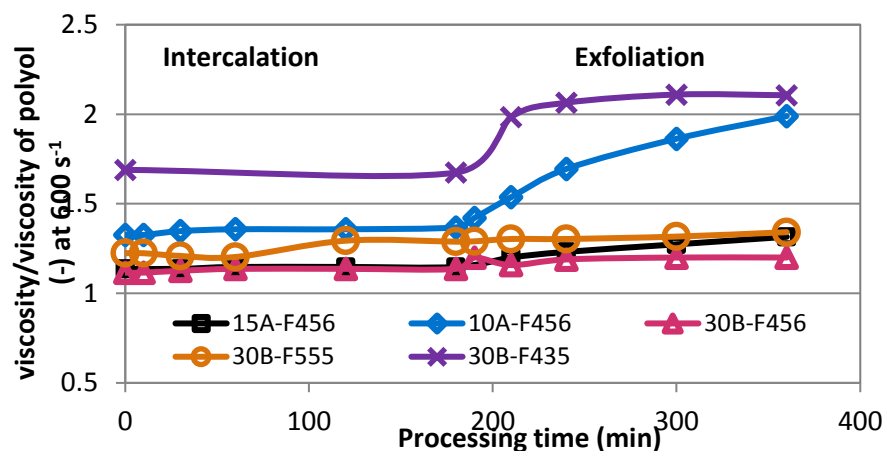
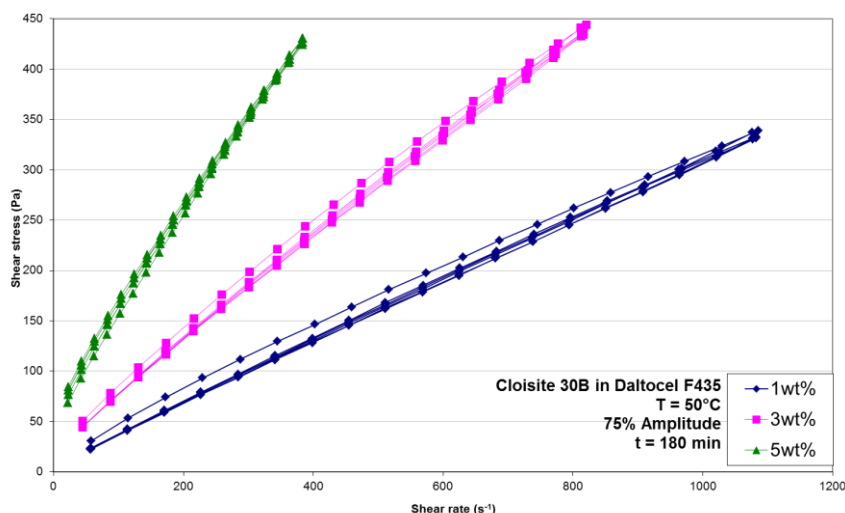
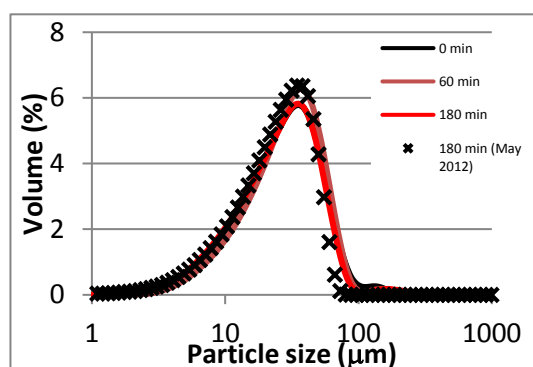


Figure 5: Relative increase of point viscosity with different nanoclay-polyol pairs during exfoliation

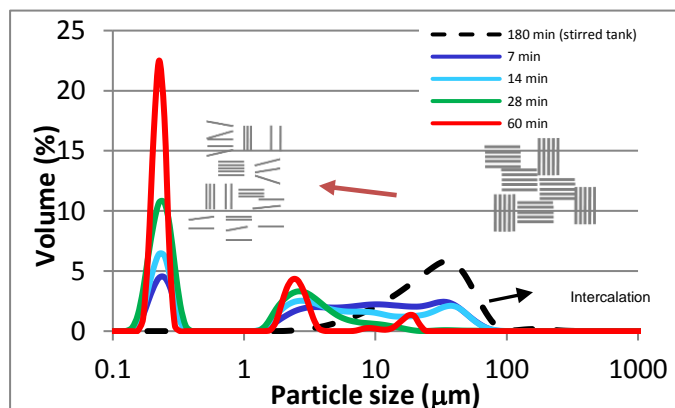


It is also worth pointing out that changes in the dispersion rheology during exfoliation can be significant with only a few % by weight increase in clay concentration (Figure 6).

Figure 6: Effect of nanoclay concentration on rheology during exfoliation



(a)



(b)

Figure 7: Evolution of particle size distribution (a) during the intercalation, (b) the exfoliation of Cloisite 10A in DaltocelF456 using the stirred bead mill

Particle size measurements taken during a 180 min intercalation process did not reveal any changes and data obtained from independently run experiments were reproducible as shown in Figure 7.a. The evolution of the exfoliation process could on the other hand be followed through particle sizing

(Figure 7.b). Whilst it is accepted that due to the aspect ratio, the results are indicative of trends rather than actual values, it is clear that this technique can also be used to monitor the exfoliation process. These changes noted in the rheology and particle size distribution during exfoliation raised the question whether the two types of measurement could be related. As can be seen from Figure 8, the trends followed by particle size and rheology results are in line with an initially steep increase in both the dispersion viscosity and volume fraction of submicron material, followed by a slower increase.

Exfoliated nanoclay dispersions showed better stability, i.e. longer shelf life compared to intercalated dispersions.

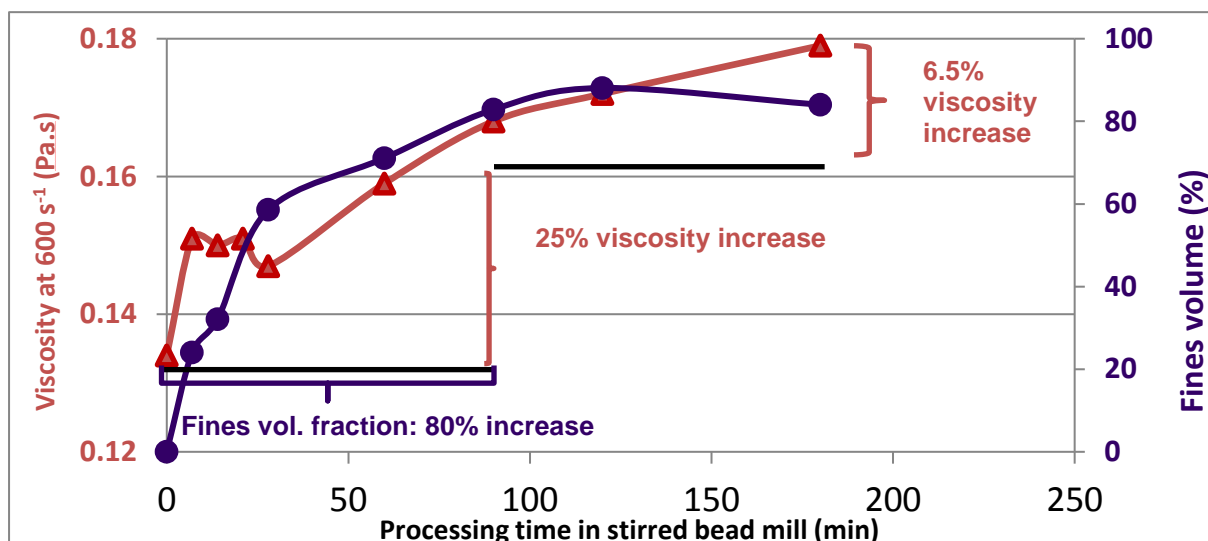


Figure 9: Evolution of Particle Size Distribution for submicron particles and rheology during the exfoliation of 3% Cloisite 10A in Daltocel F456 using the stirred bead mill

Conclusions

The delamination of nanoclays was investigated using a range of experimental techniques, namely X-Ray diffraction, rheology and particle sizing. It could be demonstrated that X-Ray diffraction technique is suited to monitor the intercalation process. Changes in rheology and particle sizing were found to be indicative of the exfoliation of nanoclays, achieved under more power intensive conditions. The particle size results were obtained through a purpose built external flow loop, and the trends followed were in line with those from rheology measurements.

The results obtained with nanoclays and polyols of different affinity and at different clay concentrations have provided useful information relating to formulation. In addition, the changes in flow properties in particular during the course of exfoliation were used for process design, with modifications resulting in significant improvements of the final product properties. Further details on these will be presented at the conference.

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