

MECHANICAL PROPERTIES OF FUNCTIONALIZED GRAPHITE OXIDE PP NANOCOMPOSITES

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ABSTRACT

In this paper the mechanical properties including creep resistance of polypropylene nanocomposites with octadecylamine functionalized and reduced graphitic oxide. The properties are compared with other carbonaceous nanofillers. Generally an increase in the mechanical properties especially the creep resistance is observed. This could partly be explained by the increase in the degree of crystallization that occurs because of the nucleating effect of the nanofillers. Generally the best mechanical properties were achieved using octadecylamine functionalized and reduced graphitic oxide despite the lacks of complete exfoliation.

1. INTRODUCTION

Graphene polymer nanocomposites are subject to extensive research due to the excellent mechanical properties of graphene. Graphene is often on laboratory scale produced from graphite oxide (GO), which again is produced from graphite subjected to strong water-free oxidizing agents. The GO contains a waste of different carbonyl groups, such as carboxylic and hydroxyl groups. These groups can be used to further functionalize the graphite oxide.

P. Song treated GO with a water-based emulsion of maleic anhydride-grafted-isotactic polypropylene to prevent agglomeration before reduction with hydrazine and finally melt blending with PP. The mechanical properties were significantly improved and the best mechanical properties were achieved by addition of 1% reduced GO. [1]

F. Qiu et al. covalently functionalized graphene with stearic acid and they found that dispersion in polypropylene was highly improved. [2]

In a study by GO was functionalized with alkyl amines with different chain length [3]. In this study functionalization with octadecylamine resulted in the largest improvement in mechanical properties. Rui-Ying Bao et al. also found improvement in mechanical properties by adding ODA functionalized GO.[4]

B. Yuan formed a covalent bonding between GO and maleic anhydride grafted polypropylene. With less than 1 % addition of the nanofiller a significant enhancement in the thermal properties was observed. [5]

S. H. Kim produced polypropylene-grafted thermally reduced GO as the compatibiliser between the polypropylene matrix and the graphene nanoplatelets (GNPs). They observed an increase in Young's modulus of 25% when adding 1% of GNPs; however higher loadings lead to inferior mechanical properties. [6]

K. Kalaitzidou et al. produced PP nanocomposites with graphite nanosheets and found improved mechanical properties with increasing load. They compared GNP with other fillers and the flexural modulus and impact strength were superior using GNP. [7]

Most works on polypropylene nanocomposites use melt mixing, however, some attempts have been on in-situ polymerization. [8, 9]

In this work graphitic oxide is functionalised with octadecylamine and chemically reduced. A master with polypropylene and the nanofiller batch is processed using a batch compounder and the master batch is further used to produce the nano composite material.

2. EXPERIMENTAL

2.1. Materials

Isotactic polypropylene homopolymer (iPP, HP365FB, MW = 230 000 g/mol., melt flow index: 12 g/10 min) was obtained from Borealis. HP400R also an isotactic PP homopolymer (melt flow index 25g/10 min at 230°C) was from LyondellBasell. Maleic anhydride grafted polypropylene (MAPP) compatibilizer (G-3015) was obtained from Eastman (USA).

Natural Graphite, Grade SP-1 was purchased from Bay Carbon Inc., PrintexL6 powder comes from Orion Engineered Carbons and carbon nanofibers (CNF, PP-24-XT-PS) comes from Pyrograf. Octadecylamine ($C_{18}H_{39}N$, ODA, MW = 269.52 g/mol) was procured from Merck Schuchard (Germany). Hydrazine hydrate (35% soln. in H_2O , grade 98%) and Hydrogen peroxide (H_2O_2) were procured from Sigma Aldrich (Germany).

2.2. Production of octadecylamine reduced graphitic oxide (ODArGO)

Graphite oxide (GO) was produced by a modified Hummers method. 40 ml conc. H_2SO_4 + 6.6 ml 65 % HNO_3 was mixed in a 150 ml beaker and cooled in ice-water bath. Stirring was maintained during the whole time, that is about 4 h. 1 g of graphite was added and was stirred for 30 min. 6 g $KMnO_4$ was added slowly to avoid excess heating. Ice was removed from ice-water bath and mixture was slowly allowed to heat to room temperature. Mixture was slowly heated to 40 °C for about 1 h. Water was added slowly to the mixture up to ~6-800 ml. 10 ml of 30 % H_2O_2 was added slowly and the solution became yellowish-brown. Suspension sedimented until next day and excess solution is decanted and new water up to 6-800 ml was added. The mixture was bath sonicated for 1h and ultra-centrifuged to remove water. The addition of water, bath sonication and ultra-centrifuged was repeated several times. After this ethanol (EtOH) was used instead of water and cleansing with ethanol was repeated twice. The product is named GO-EtOH. Chemical functionalization of GO was done using octadecylamine (ODA). ODA solution was prepared by dissolving 0.010 moles of ODA (1.5 g) in ethanol (150 mL) at room temperature, and then magnetically stirred for 30 min. 1 g of GO powder was dispersed in 250 mL of ethanol to achieve a nominal concentration of 4.0 mg/mL. The ODA solution was then added into the GO suspension and the mixture was refluxed at 100 °C for 24 h under constant magnetic stirring. During the ODA functionalization, the colour of the GO solution gradually changed from yellow to black. This change indicated a significant chemical change through functionalization (Dimievet al., 2012). The reduction process was performed using hydrazine hydrate. Typically, 3.75 mL of hydrazine hydrate was added into ODA functionalized GO suspension and the mixture refluxed at 100 °C for 24 h under constant magnetic stirring. Then, the suspension was vacuum filtered and washed thoroughly using ethanol and water to remove any entrapped or unreacted ODA and hydrazine respectively, and ODA-r-GO powder was obtained.

2.3. Compounding, extrusion and injection moulding of nanocomposites

First a masterbatch with 10 wt-% nanofiller were produced in a micro-compounder and afterwards the masterbatch was diluted with PP in the extruder. The masterbatch was made by mixing the polypropylene beads, maleic anhydride grafted PP (MAgPP) and the nanofillers by hand and then fed in to a micro-compounder (MC 15 cc, Xplore Instruments) consisting of a co-rotating twin-screw extruder. The melt compounding temperature was set to 185 °C and screw speed at 75 rpm. The compounding time was 20 min for the nanocomposites that were tested.

The final nanocomposites were produced by mixing 10 % masterbatch with 90% polypropylene and feeding it to the extruder. Extrusion were done using a Prism Eurolab 16 co-rotating twin-screw extruded set at 200°C from hopper to die. Twin screw speed was 300 rpm.

Injection moulding was done in a Haake MiniJet from Thermo Scientific. The cylinder temperature was 220°C, the mould temperature 70°C and the injection pressure was 600 bars.

2.4. Characterization

The complex viscosity of the masterbatch was measured at 200 °C on a TA DHR-3.

Mechanical properties was measured on an Instron 5944 equipped with a clip-on extensometer. Creep strain was measured at 22°C at a constant load of 23 MPa.

Storage modulus was measured in 3-bending mode on TA Q800 heated at 3 °C/min from RT to 100 °C running at 1 Hz.

DSC analysis was performed on a TA Q2000 at 10°C/min from 40 to 200 °C in a heat, cool, heat cycle. XRD analysis was performed on a Panalytical Empyrean XRD using Cu Ka.

3. RESULTS AND DISCUSSION

3.1. Rheological measurements

The viscosity of the masterbatch (HP365FB, compatibiliser and 10 % ODA-r-GO) was measured for various compounding times to find the best compounding time, which is a compromise between cost, degradation of the polymer and the mixing. In Figure 1 the viscosity is shown for the composite with 10 % ODA-r-GO and also the polymer with compatibiliser alone. The degrading effect of the heat and compounding is clearly seen for the pure polymer where the viscosity drops significantly. However, looking at composite, it can be seen that the better dispersion achieved for prolonged compounding times compensated for the lower viscosity of the polymer. Going from 20 min to 30 min compounding time did not increase the viscosity of the composite. So a compounding time of 20 min was chosen for the further experiments. The polymer (HP365FB) was also changed to a polymer (HP400R) with more antioxidants that was more resistant to degradation during compounding.

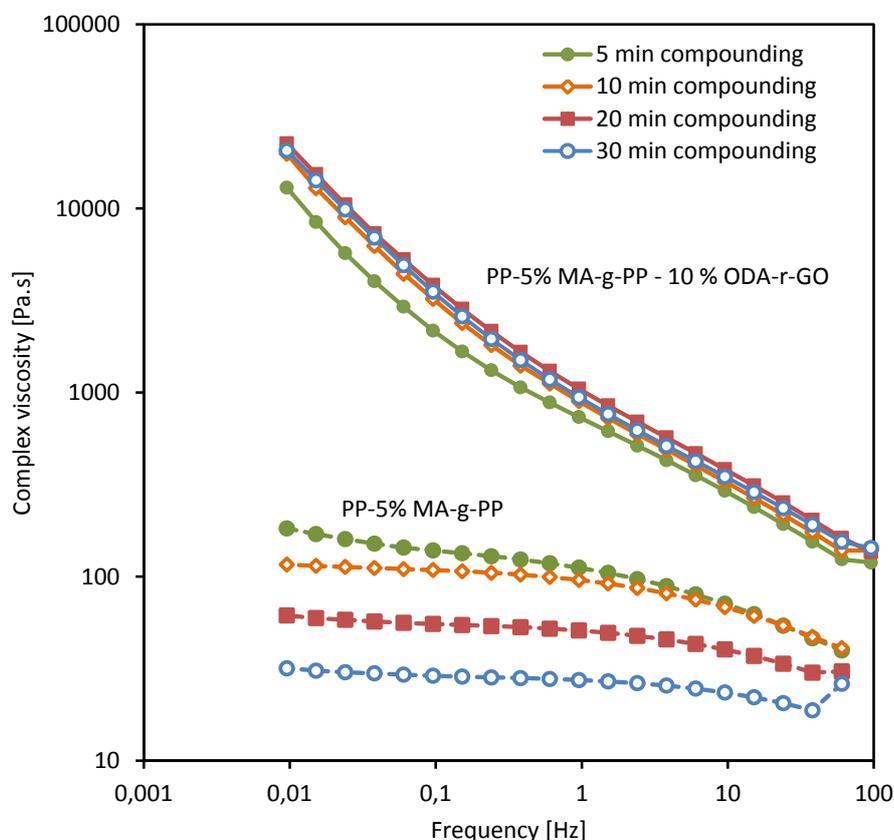


Figure 1: Complex viscosity of masterbatch with 10 wt-% ODA-r-GO of the PP with the compatibilizer alone after compounding a various times.

3.2. Morphological characterization of nanocomposites

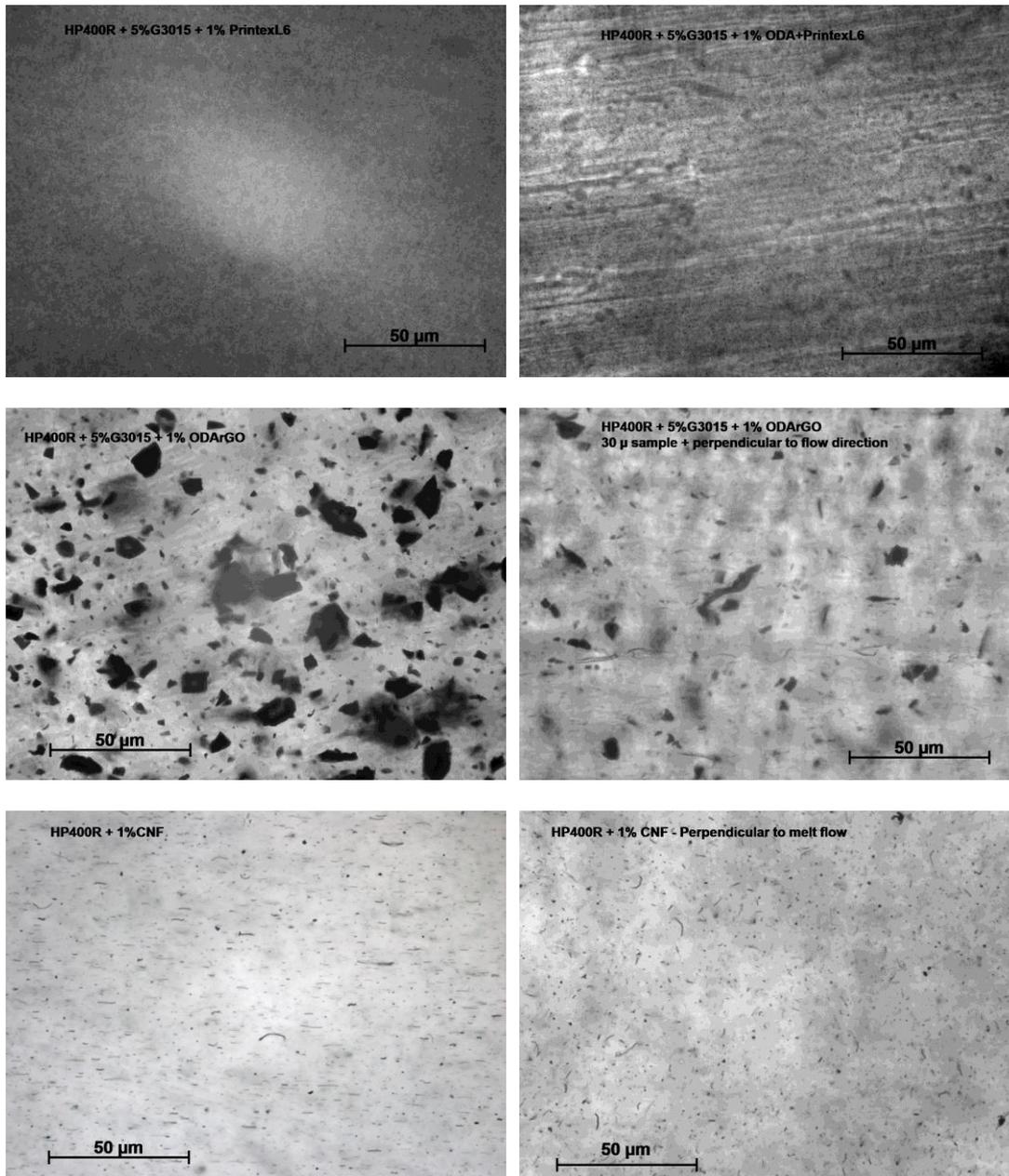


Figure 2: LOM picture of nanocomposites. The LOM samples are about 100 μm thick.

In Figure 2a and b is seen the PP nanocomposites with unmodified and ODA-modified PrintexL6. According to Z. Ranjbar [10] the primary carbon black particle size is 18 nm, however the agglomerates are much larger. The agglomerates are just visible in the LOM pictures of nanocomposites. They seem to be very uniformly dispersed. In figure c and d is seen the ODA-r-GO PP nanocomposites. The dispersion seems quite homogenous; however the graphene or graphite flakes are quite large. The platelets seem to be aligned in the flow direction of the melt during injection moulding. Looking at Figure 3 it can be seen that the octadecylamine modified and reduced graphitic oxide is heavily intercalated as the interplanar distance is much larger. The [001] peak for GO at 10° is normally observed at this position. [1, 4, 5] After octadecylamine-modification and reduction the [001] planar distance increases which can be explained by the intercalation with the

alkylamine. At the same time a broad and weak peak appears which is typical for randomly ordered (turbostatic) graphitic. [11] This indicates that the reduced graphitic nanofiller are not fully exfoliated. This is also true for the nanocomposites as a peak from the modified and reduced graphitic oxide is still visible at 8°. The LOM pictures of nanocomposites with carbon nanofibers can be seen in Figure 2e and f. The dispersion seems very homogenous and the nanofibers seem to be aligned with the flow of the melt. The average fibre diameter should be 100 nm [12], thus we should only be able to see the larger fibres.

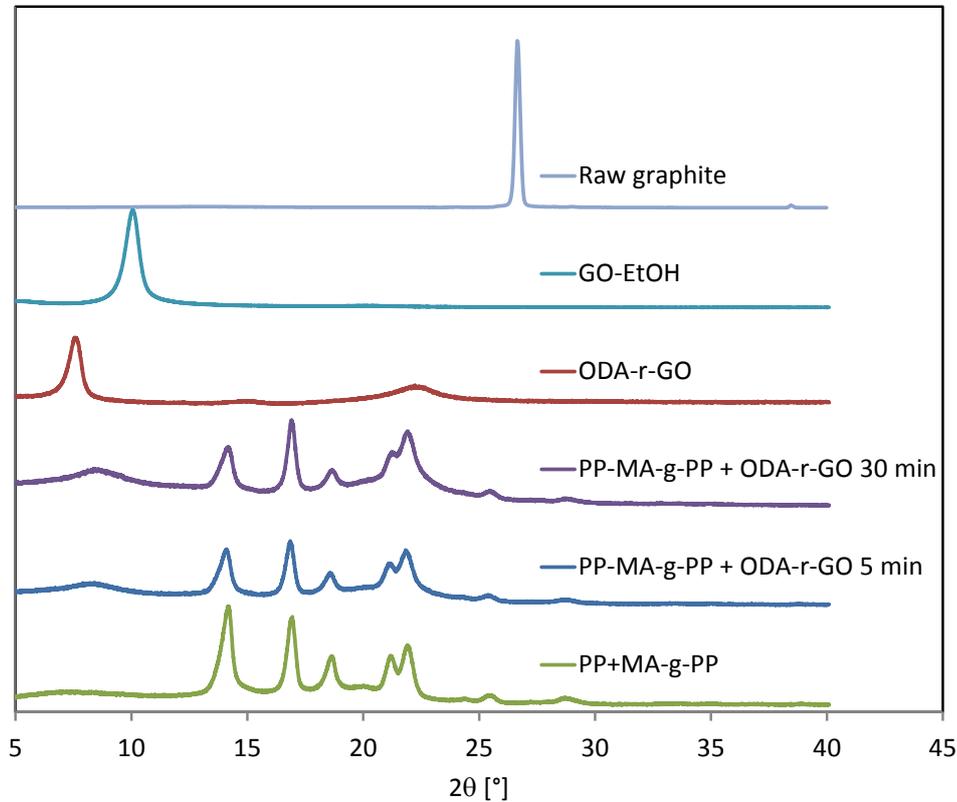


Figure 3 XRD spectra for graphite, the various graphitic nanofillers and the nanocomposites with added graphitic nanofiller.

In Figure 3 the XRD spectra for PP is also visible. The spectra correspond to the α -form of crystalline iPP. However the 16.95° peak is substantially higher which indicates a preferred orientation of the crystallites due to the preferred orientation of the graphene-nanoparticles due to the flow of the melt. [13]

3.3. Mechanical testing

Adding CB and ODA-r-GO increase the modulus as in Figure 4. Surprisingly no increase in the modulus is seen adding CNF despite the good dispersion and alignment of the fibres in the flow direction which is also the direction of the normal stresses during testing. However, the CNF has a beneficial effect on the strain at creep. Generally the best mechanical properties seem to be achieved with ODA-r-GO, despite what seems to be an inferior dispersion and lack of complete exfoliation. Tensile testing was only done until a strain of 50% and no fracture at that strain was observed. In Figure 5 it can be seen that the influence of the temperature on storage modulus for the CNF nanocomposites deviates from the other nanocomposites showing a low storage modulus comparable to neat PP at low temperature and a storage modulus at high temperature comparable to the other nanocomposite materials.

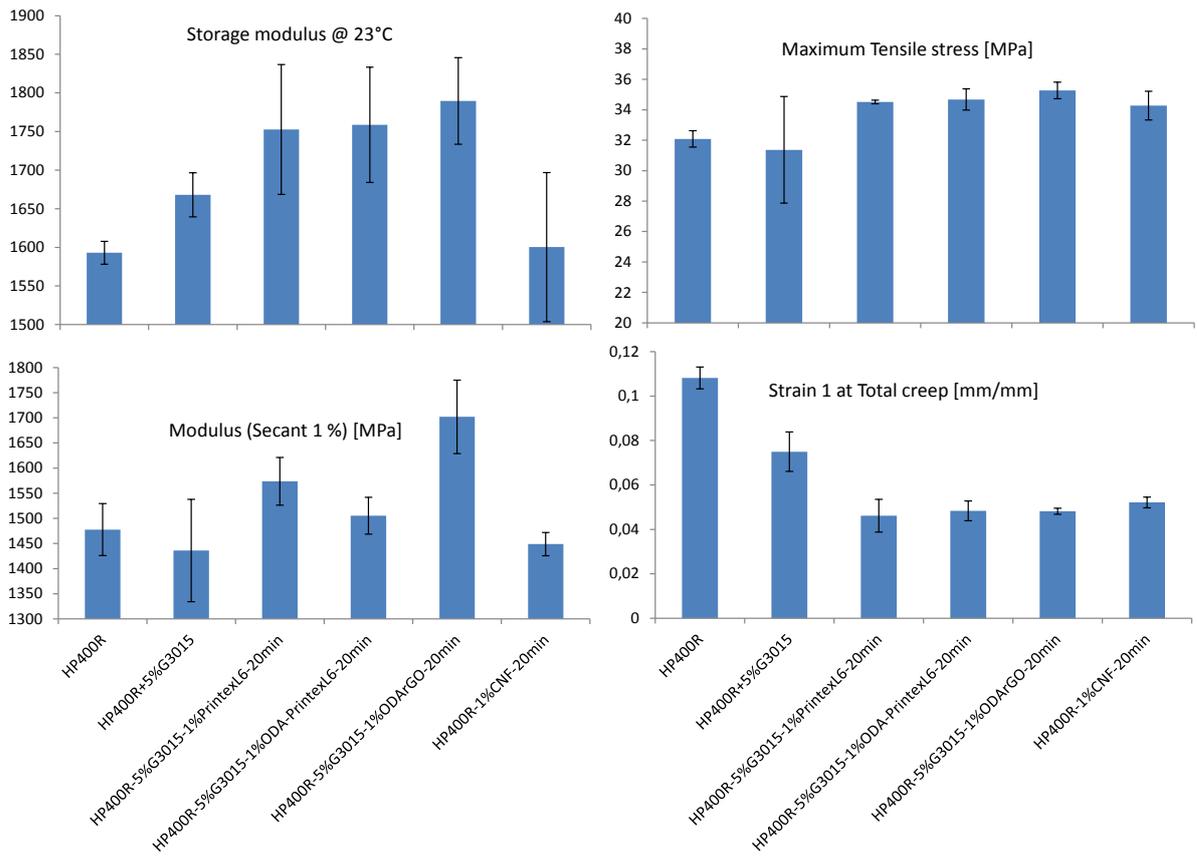


Figure 4 Storage modulus measured by DMA, secant modulus measured by tensile testing, tensile strength and creep strain at 23 MPa and 21°C

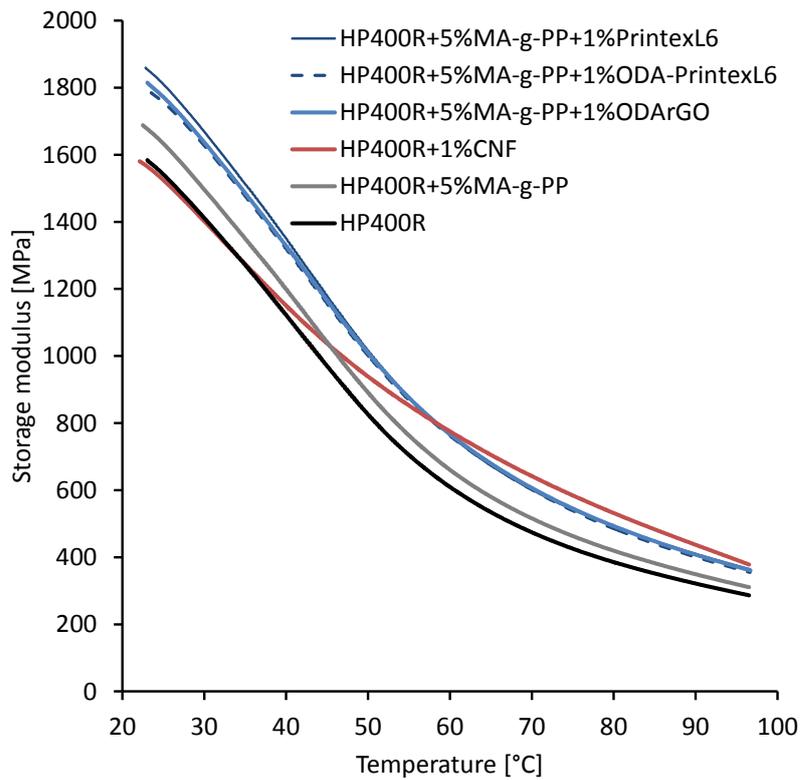


Figure 5 Storage modulus measured by DMA as a function of temperature.

As can be seen in Figure 6 the degree of crystallinity increases due to the addition which acts as nucleation agents as indicated by the crystallisation temperature which increase because of the nanofillers. The nucleating effect of the nanofillers is reported in numerous articles. [1, 2, 4, 6, 13, 14]

It is observed in other research that the nucleation agents lead to smaller crystallites which mainly affect the yield strength. [15] It is difficult to separate the effects from the crystallisation behaviour and the reinforcement of the nanofillers from each other.

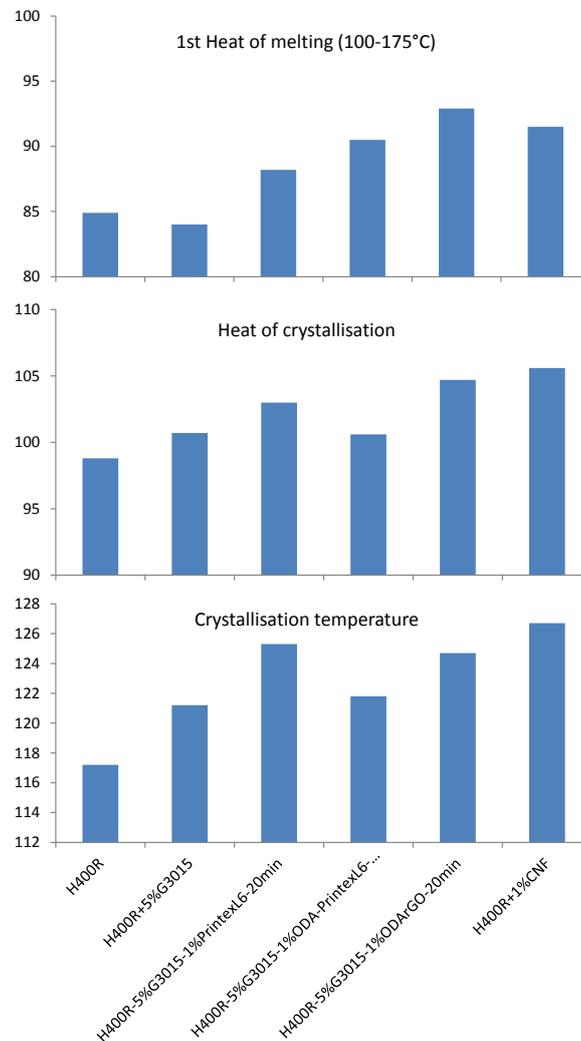


Figure 6 Heat of melting of injection moulded samples, heat of crystallisation and crystallisation temperature measured by DSC.

4. CONCLUSIONS

Addition of carbonaceous nanofillers generally increases the mechanical properties especially the creep resistance and stiffness at elevated temperatures. The nanofillers have an effect on the crystallization of polypropylene and increase the degree of crystallization, which is partly responsible of the reinforcing effect. Generally the best mechanical properties were achieved using octadecylamine functionalized and reduced graphitic oxide despite the lacks of complete exfoliation.

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