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Microparticles as Additives for Increasing the Mechanical Stiffness of Polypropylene

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Abstract: Composite materials of polypropylene and mineral microparticles have been generated by compounding and tested in terms of mechanical stiffness. In a first step silica, boehmite and functionalized clay microparticle powder have been mixed with the polymer in a twin-screw compounder. The elastic modulus was highest for mixtures with a microparticle concentration of 5 to 10%w/w. An increase of 25% of the elastic modulus was achieved by simple melt extrusion. In a second step, a maleic anhydride-grafted polypropylene (PP-g-MA) was used as a matrix. When measured by nanoindentation, the pure PP-g-MA matrix showed an elastic modulus twice as high as pure PP, probably because of a partial reticulation. During extrusion, amino-silane functionalized clay microparticles were added to the PP-g-MA matrix and reacted with it by building covalent amide group bonds. The resulting compound material showed an elastic modulus of more than four times the stiffness of pure PP.

Keywords: Composite · Functionalization · Microparticles · Polymer · Polypropylene

1. Introduction

Polypropylene (PP) is a common thermoplastic low-cost material that is used for a variety of industrial applications such as packaging and automotive parts. However, pure polypropylene has a relatively low elastic modulus and cannot be used for components supporting high mechanical stresses. The mechanically more resistant polypropylene composite compounds contain glass fibers (PP-GF) but have the major drawback that injection of parts with small wall thickness (<1 mm) is difficult. The use of micrometer size additives with high mechanical stiffness seems promising. Iturrondobeitia and coworkers^[1,2] studied polylactic acid/Clay (PLA/Clay) nanocomposites generated by melt extrusion. They presented the influence of processing parameters, the mechanical properties and thermal stability as well as a mechanical predictive model. Carrasco *et al.*^[3] reported the influence of additive concentration on the material crystallinity and morphology of PLA/clay composites. Several studies have been conducted on PP/clay composites.^[4–6] Dong^[4] mixed PP of different molecular weight with maleic anhydride grafted PP and clay particles of different types. He linked the resulting mechanical properties with divers theoretical models.

This paper presents the development of composites of polypropylene and three different types of silica oxide and alumina based microparticles. Two approaches were conducted; co-extrusion of particle powder with pure PP and alternatively

a reaction followed by an extrusion of maleic anhydride grafted PP and functionalized clay particles as proposed by Dong *et al.*^[5]

2. Experimental Section

2.1 Polymer and Microparticles

The polypropylene is a DuPure R50 homopolymer from Duroc Petrochemicals with a melt flow rate of 1.2 g/min, an elastic modulus of 1.6 GPa and a density of 0.91 g/cm³. A functionalized polypropylene blend grafted with 8 %w/w maleic anhydride was received from Sigma Aldrich.

Silica particles were purchased from Deurex (S3012M Micronized) with 90% of the particles smaller than 12 micrometer. Boehmite (Disperal® 40) with 80% Al₂O₃ content and a particle size d_{50} = 35 micrometer was acquired from Sasol. Surface-modified clay microparticles (size ≤ 20 micrometer) functionalized with aminopropyl-triethoxysilane (0.5–5%w/w) and octadecylamine (15–35%w/w) were obtained from Sigma Aldrich. This montmorillonite powder is mainly based on aluminum silicates.

2.2 Compounding

All polymer microparticle composites were extruded with a co-rotative twin-screw extruder (Coperion ZSK 18MI) equipped with two 724 mm (18 mm diameter) stainless martensitic steel screws and nine independent heaters. The optimal extrusion temperature has been determined through DSC analysis to exclude possible decompositions or phase changes. The heaters of the compounding section were set to 200 °C, the screw speed to 400 t/min and the production speed to 5 kg/h. The solidified compound leaves the compounder as a long continuous filament. The filaments were cut into pieces of 10 mm length, embedded in polycarbonate and then polished for nanomechanical analysis. Polypropylene compounds were generated with all three particle types by realizing at first a 20%w/w master batch followed by co-extrusion with pure PP to realize 2.5, 5 and 10% w/w mixtures.

In a second experiment 99.6 g of maleic-anhydride-grafted polypropylene (PP-g-MA) and 54.65 g of clay microparticles were mixed with 1.8 L toluene. The mixture was heated to 125 °C during 3 h (alternatively 24h). The solvent was then evaporated ($T_{\text{bath}} = 40$ °C; $P = 50$ mbar) and the compound was dried ($T_{\text{bath}} = 45$ °C; $P = 23$ mbar) in a rotavap, finishing by heating overnight in a stove ($T = 80$ °C; $P = \sim 125$ mbar) to give 104.2 g of clay-modified PP-g-MA. The final blends were extruded (parameters 170 °C, 400 t/min and 5kg/h) to improve the mixture homogeneity.

2.3 Mechanical Analysis via Nanoindentation

The mechanical properties were characterized with a CSM (Anton-Paar) Ultra Nanoindenter equipped with a Berkovich tip. Many publications give a comprehensive explanation of this technology.^[7–9] Nanoindentation is a nanoscopic test where a tip penetrates the sample with a defined load and speed while recording the force-depth curve. This test is divided into three parts. First, the loading phase, then a holding phase during which the force is constant, to prevent the influence of creep on the measurement. The last part is the unloading during which the force is released and the elastic recovery of the material is measured. The initial slope S of this unloading part is used to

calculate the reduced elastic modulus E_r

$$S = \frac{2}{\sqrt{\pi}} \cdot E_r \cdot \sqrt{A_c} \quad (1)$$

where A_c is the contact area of the tip and the sample; a parameter that is determined through a tip shape calibration. The reduced modulus E_r is further used for the calculation of the elastic modulus of the sample

$$\frac{1}{E_r} = \frac{1-\nu_{sample}^2}{E_{sample}} + \frac{1-\nu_{tip}^2}{E_{tip}} \quad (2)$$

where the elastic modulus of the diamond tip is $E_{tip} = 1140$ GPa and the Poisson's ratio is $\nu_{tip} = 0.07$. The Poisson's ratio of the sample was set to $\nu_{sample} = 0.3$, a standard setting when the exact value is unknown. For each sample a set of 30 indents has been programmed. The nanoindentation tests were run up to a maximum load of 200 μ N with a constant loading and unloading rate of 200 μ N/min and a 10 s holding period. Prior to the mechanical tests, the homogeneous dispersion of the microparticles has been checked by optical microscopy to exclude that particle agglomerations close to the surface affect the nanoindentation results.

3. Results

3.1 Compounding of Microparticles with Pure Polypropylene

For all composite materials an increase of mechanical stiffness has been observed. However, this increase was not proportional to the additive content but has shown a saturation or a maximum around 5 to 10%w/w. Fig. 1 shows the elastic modulus for pure polypropylene ($E = 2 \pm 0.3$ GPa) and those microparticle compounds for which the highest elastic modulus has been measured. The highest increase of stiffness was observed for the PP & 10% boehmite blend with $E = 2.5 \pm 0.4$ GPa. For the PP & 5% Si and the PP & 10% clay blend this increase was 18% and 19% respectively.

The mixing with the aminopropyl-triethoxysilane (0.5–5% w/w) and octadecylamine (15–35%w/w) surface-modified clay particles lead therefore to a similar stiffness increase like the mixing with unmodified particles.

3.2 Compounding of Clay Microparticles with Maleic Anhydride-grafted Polypropylene

The elastic modulus of the maleic anhydride grafted PP has shown with $E = 4.8 \pm 1$ GPa a significantly higher stiffness than pure PP ($E = 2 \pm 0.3$ GPa). The additional mixing with functionalized clay microparticles has shown with $E = 9.7 \pm 1.6$ GPa for 3 h reaction time and $E = 8.4 \pm 1.6$ GPa for 24 h reaction time a further significant stiffness increase (Fig. 2). Surprisingly, the shorter reaction time has shown a greater effect on the elastic modulus.

4. Discussion and Conclusions

This paper presents the results of a set of twin-screw compounded polypropylene-microparticle composites. Nanoindentation was an adequate choice for mechanical analysis since this method can be applied for testing the filaments at the extruder outlet without further processing.

The results of this work show that a purely mechanical mixing of microparticles with a chemically saturated polypropylene matrix leads to a maximum stiffness increase by 25% to $E = 2.5$ GPa. Compared to the stiffness of commercial PP compounds with 20% glass fibers (for example Campus® CESTRAN PP-GF20

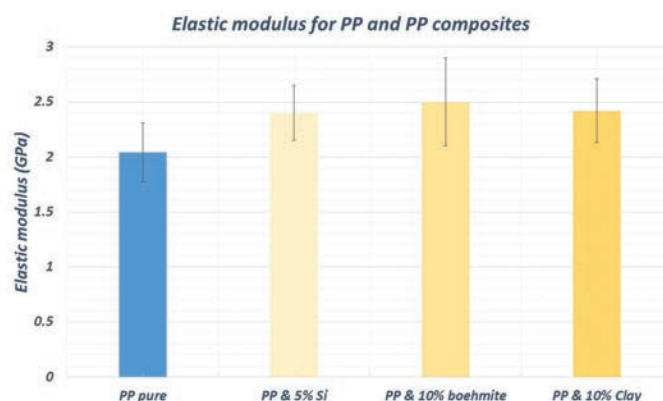


Fig. 1. Elastic modulus as obtained by nanoindentation of pure PP and one selected microcomposite compound for each microparticle type. Stiffness increase was highest (+25%) for the PP-boehmite blend.

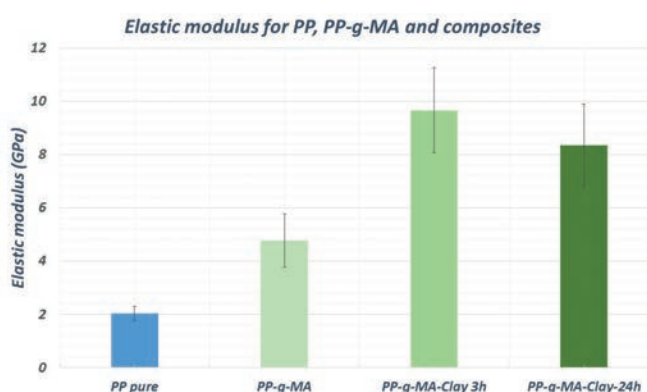


Fig. 2 Elastic modulus as obtained by nanoindentation of pure PP, maleic anhydride grafted PP (PP-g-MA) and two PP-g-MA microcomposites with clay microparticles applying 3 h and 24 h reaction time.

with $E = 5.4$ GPa) this value is significantly lower. Furthermore, the additional functional groups of the clay particles did not lead to a greater stiffness increase with respect to the chemically more inert silica and boehmite particles.

The composite based on PP-g-MA and functionalized clay microparticles show with $E = 9.7$ GPa a 100% increase of the elastic modulus with respect to pure PP-g-MA. The high elastic modulus of pure PP-g-MA with respect to pure PP could be due to a reaction of maleic anhydride molecules with each other or with neighbored propylene molecules what would lead to a partial matrix reticulation. Such a possibility was first reported by Gaylord^[10] who introduced the possible implication of poly(maleic anhydride) in the grafting of maleic anhydride on various polymer substrates. However, the significant stiffness increase of the clay reinforced PP-g-MA can definitely be associated to new chemical bonds between the amino-functionalized clay particles and maleic anhydride, the most probable reaction being a covalent bonding through amide groups. The used PP-g-MA blend only possess 8%w/w of maleic anhydride. The initial mixture was with 35%w/w of clay more concentrated in terms of microparticles with respect to the aforementioned mechanical mixing compounds. This high concentration has been chosen to increase the probability that clay and PP-g-MA bonds are created through amide groups. The high elastic modulus increase may therefore be due to a relatively small portion of covalently bound clay particles.

The results of two different preparation protocols have been presented, one using 3 h and one with 24 h reaction time of the PP-g-MA and the clay particles. Surprisingly, the samples with 3 h reaction time have shown a higher mechanical stiffness what could indicate a higher number of amide bonds. However, further

work is ongoing to determine the exact amount to clay particles covalently bounded to PP, to evaluate the total mass of clay particles entrapped in the PP matrix and to analyze if the shorter reaction time can indeed show an optimum effect.

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