Preparation and mechanical properties of intercalated PP/OMMT nanocomposites

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Abstract. The preparation of polymer nanocomposites by melt compounding polypropylene (PP) with organically modified montmorillonite using maleic anhydride modified PP as compatibilizer is described. Compositions with organomontmorillonite content 0, 5, 10 wt.% were prepared and tested. Data on the influence of organomontmorillonite content on the tensile stress–strain curves, elastic modulus, strength, and ultimate elongation of the nanocomposites are obtained. The concentration dependences of elastic properties of materials with differently oriented plate like nanoparticles analyses taking into account hierarchical structure features of nanocomposites is considered. Theoretical analysis results are compared with experimental data. The presence of unexfoliated particles in the form of multilayer packages must be taken into account. The results of an investigation of hardness, impact strength, and thermal properties of polymer nanocomposites are presented. Tension creep tests were performed to predict nanocomposites long term deformation behaviour.

1. Introduction

It is known that ultra-thin layers of smectite clays have been used as fillers in many polymer systems. The addition of such one dimensional nanoscale fillers to polymers results in nanostructured composites with impressive material properties compared to micron scale fillers. This may be in large part due to the small size of the filler, the large surface area of nanoscale fillers and their extremely high aspect ratio. In case when such layered filler particles are finely dispersed in a polymer matrix, the polymer properties can be modified to a dramatic extent even for very moderate amounts of filler (less than 15 wt.%). Many of the materials properties are concurrently enhanced (strength, stiffness, gas permeability and flammability, etc.).

This study is a continuation of the investigations aimed to create polymer nanocomposites containing organically modified montmorillonite (OMMT) as filler. Previously [1, 2], nanocomposites based on OMMT and styrene-acrylate copolymer were prepared and investigated. This time, we report our experimental results on investigations of PP/OMMT nanocomposites. Our investigations aimed to fabricate PP nanocomposites and investigate their properties for engineering applications, and also vitally important is to understand the structure/property relations of nanocomposites

Modeling elastic properties of nanocomposites taking into account hierarchical structure features of nanocomposites is considered. Theoretical analysis results are compared with experimental data.
2. Experimental

The nanocomposites were prepared by melt compounding PP (SABIC 571P) with OMMT powders (DELLITE 72T). Maleic anhydride modified PP copolymer – MAPP (LICOMONT AR504) is used as a compatibilizer in composites. 3 wt.% of MAPP was added to succeed constitutes homogeneous blending in Banbury compounder. The filler properties are summarized in Table 1. Altogether, five variants of specimens were prepared, with a content of OMMT from 0 to 10 wt.%. Specimens were investigated using several experimental methods. In that way prepared materials were compression moulded and injection moulded into films, plates, bricks, dumbbells shaped specimens that were further tested using several experimental methods determining mechanical (tensile, long term creep, microhardness, and impact), and thermal (destruction temperature) properties.

Table 1. Filler properties.

| Mineral          | Montmorillonite   |
|------------------|-------------------|
| Loss at ignition, % | 37-41             |
| \(d_{001}\), nm  | 2.9               |
| Particle size after dispersion, nm | 500            |
| Organic modifier | Dimethyl dihydrogynated tallow ammonium |
| Bulk density, g/cm\(^3\) | 0.45            |

Uniaxial tensile tests were performed on dog-bone shaped samples on Zwick BDO-FB 020T test unit at ambient conditions. Charpy impact strength with notch was determined on a Zwick 24 material testing machine with pendulum capacity 2 J according to EN ISO 179. Vicker microhardness was tested on Vickers M-17 1021 using 200g load. Long term creep tests in tension were performed at 25\(^\circ\)C and 2.5MPa on the experimental creep equipment. Thermal properties as, for example, temperature of destruction were detected on Mettler gravimeter TGA-50. Samples of about 10 mg were heated up from 25 to 600 \(^\circ\)C in the atmosphere of nitrogen. Heating rate was 10 \(^\circ\)C/min. The X-ray diffraction measurements were carried out on a Dron-3 diffractometer at a temperature of 20\(^\circ\)C. The CuK\(_\alpha\)-monochromatic radiation with a wave length of \(\lambda = 0.154\) nm in the range of diffraction angles 2\(\theta\) from 2 to 15 deg was used. The scanning rate was 1 deg/min.

X-ray diffraction of the nanocomposites clearly indicates the intercalation of PP macromolecules into the MMT gallery space increasing interlayer distance \(d\) from 2.9 nm to about 3.7 nm. It means that no true exfoliation occurs and MMT platelets remain in the stack form, though well swelled with polymer. It should be noted that OMMT concentration doesn’t influence the value of \(d\) of the stacks that remains almost the unchanged.

Introduction rather small amount of OMMT strongly influenced the mechanical properties of the material. Tensile test results show significant change of nanocomposites tensile properties comparing to pure polymer. Experimental data show that appropriate tensile parameters of the polymer can be improved after incorporation of OMMT. Initial PP deforms with inherent yielding area that corresponds to necking and its subsequent development - yielding flow and strain hardening till failure occurs. PP nanocomposites behave in a similar way; however even 1 wt.% OMMT incorporation into the polymer generates reduction of yielding flow and strain hardening. It should be mentioned, that addition of MAPP to the polypropylene plasticize it a little. Yield stress of PP nanocomposites does not change considerable in comparison to neat PP. It should be noted also that ultimate tensile strain considerably decreases with increasing concentration of OMMT.
Addition of relatively small quantities of OMMT, considerably improves the elastic modulus value. Figure 1 shows the concentration dependence of the experimentally obtained and theoretically calculated nanocomposites elastic modulus ratio $E/E_m$. At 10 wt.% content of OMMT, i.e., at only ~4 vol.%, the elastic modulus of the nanocomposites increase 1.7 times compared with that of the unfilled polymer. In [1,2], it was shown that the inverse slope of the curve related to the retarded growth rate of elastic modulus with increasing filler concentration can be caused by the decreased degree of exfoliation of layered particles.

Theoretically calculated nanocomposites elastic modulus ratio $E/E_m$ values are displayed as lines for nanocomposites containing randomly oriented plate like filler particles -stacks with number of layers $N=1, 2, 4, 6, 8$ and $10$. First, the elastic constants of transversely isotropic structural elements with coplanarly placed filler particles are obtained, and then they are averaged over all spatial directions by using the orientational averaging method. More analysis details are discussed in [1]. The calculations contributed to average layers number in the stack equal to $N= 6-10$.

Results of long-term (up to one year) creep tests show that unfilled PP exhibits considerable creep. The introduction of the OMMT allows us to reduce the long-term creep of PP substantially. After 1 year creep of nanocomposite with 5 and 10 wt.% drops 1.25 and 1.55 times, correspondingly. Results of long-term (up to one year) creep tests show that unfilled PP exhibits considerable creep; the total strains for PP at the end of testing exceed the instantaneous ones in loading by ~ 3 times. The introduction of the OMMT allows us to reduce the long-term creep of material substantially. The reinforcing makes it possible to suppress the creep effect in the nanocomposites. Such possibilities of purposeful suppression of the creep of polymer material can be useful in designing structures subjected to a long-term action of mechanical loads.
Polymer incorporation in the OMMT interlayer, resulting in the nanoscopic interfacial regions with altered macromolecular chain mobility, also essentially increases up to 30°C the thermal destruction temperature of the PP nanocomposites (figure 3). During the heat treatment, the carbonized layer formed on the platelet surface serving as an efficient barrier on the way of distribution of decomposition volatile products and thermal energy front [3]. Nanocomposites microhardness, shown in figure 4, also improves up to 40% due to incorporation of rigid, stiff and hard clay nanoparticles.

Figure 2. Long term creep compliance $D(t)$ and $D(lgt)$ for PP/MAPP (1), PP (2) and nanocomposites with OMMT content 5 (3) and 10 (4) wt.% of OMMT.
Figure 3. Destruction temperature of PP and PP/MAPP/OMMT nanocomposites as a function of the weight content $W_f$ of OMMT.

Figure 4. Vickers microhardness $HV$ of PP and PP/MAPP/OMMT nanocomposites as a function of the weight content $W_f$ of OMMT.

Figure 5. Impact strength $A$ of PP and PP/MAPP/OMMT nanocomposites as a function of the weight content $W_f$ of OMMT.
As was shown earlier, polypropylene nanocomposites provide a significant increase in elastic, creep and thermal properties, while, in figure 5 is shown a little decrease in notched Charpy impact properties. It is generally recognized that filled polymer has significant decrease in impact toughness properties because of poor dispersion, weak interaction and strong aggregation of fillers; however, polymer nanocomposites differs from the traditionally filled composites, frequently showing only small decrease or even no change in impact strength.

3. Conclusions
Investigations of nanocomposites based on polypropylene and organically modified montmorillonite showed that addition of relatively small content of filler, even in the case of non-complete layer stack exfoliation, significantly improves sequent properties: elastic modulus, creep elongation, microhardness and thermal destruction temperature.

The diffraction analysis of PP nanocomposites shows the presence of layered structure that refers to expanded OMMT stacks. At a 10 wt.% content of OMMT the elastic modulus of the nanocomposites increases 1.7 times compared with that of the unfilled polymer. Modeling elastic properties of nanocomposites taking into account hierarchical structure features of nanocomposites is considered. Theoretically calculated elastic moduli are compared with experimental data. It was found that for nanocomposites the presence of unexfoliated particles in the form of multilayer stacks must be taken into account. It should be noted also that ultimate tensile strains considerably decrease with increasing concentration of OMMT.

Addition of only 10 wt.% of OMMT significantly effect the thermal, the microhardness and the impact properties of the material. Thermal destruction temperature increases about 30°C, microhardness enhances about 30% and impact toughness decreases about 15%.

It is considered, that high aspect ratio of the platelets, large contact area with the matrix could be responsible for tensile property enhancement. Polymer introduction in the MMT interlayer, resulting in large volume of nanoscopic interfacial regions, also could essentially imply the properties of polymer nanocomposites [3,4].

References
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