Fracture mechanical investigations of polymeric nanocomposites

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Abstract

Polypropylene nanocomposites were prepared using different layered silicates for reinforcement. These fillers vary in primary particle size, chemical modification and type of layered silicate. Three compatibilizing agents were compared and their influence on materials properties investigated. The influence of the filler content on the behaviour of the nanocomposite was studied.

Furthermore Polyamide 6 nanocomposites with four different layered silicates were examined. These fillers also differ in primary particle size and chemical modification. Additionally, the filler content was varied to investigate the influence of the amount of filler on the material properties.

The morphological properties of these nanocomposites were analyzed with several methods including differential scanning calorimetry (DSC), wide angle x-ray scattering (WAXS), small angle x-ray scattering (SAXS) and transmission electron microscopy (TEM). The main interest was to characterize the materials behaviour, especially the fracture mechanical properties by instrumented Charpy impact test (ICIT).

Introduction

Polymeric nanocomposites are composed of a polymeric matrix and a filling component with at least one nanometer-sized dimension. Many different matrix materials including polyolefins, epoxy, polyesters, polyamides, styrenic polymers, polyurethanes and others have been tested in combination with variing fillers [1]. One widely used nanosized filler for polymers is clay, especially montmorillonite (MMT). Inside of the platy multi-layered structure of MMT the sodium ions can be replaced by alkyl ammonium ions, which improve intercalation and exfoliation during preparation [2].

Next to the variety of matrix-filler combinations, different preparation routes as solution blending, *in situ* polymerization or melt compounding exist [3]. Typically improved properties include tensile and flexural strength, heat deflection temperature (HDT), thermal stability, flame retardance or barrier properties [1]. But at the same time toughness is highly decreased due to a reduction of deformation ability. Usually insufficient exfoliation is assumed as cause for this behaviour of polymers filled with layered silicates. Exfoliation is obtained when the single layeres are completely separated and dispersed. If the platelets are still stacked, intercalated morhology is obtained. Very often a mixture of exfoliated and intercalated layers are found, which is called hybrid [2].

One interesting matrix material is polypropylene (PP) due to its good property–cost ratio. During last years, some different fillers in the range of nanometers including layered silicates, calcium carbonate or silicium dioxide have been checked [4, 5].

Polyamide (PA) is also an important engineering polymer used as fibers, films and bulk material. PA-nanocomposites are already mentioned in the 1970s by Fujiwara and Sakomoto [6] and preparation improved about one decade later by Toyota research team [7,8].

For preparation of polymeric nanocomposites, mostly melt compounding is chosen, since already existing devices can be used. Not only processing route of nanocomposites and matrix material have an impact on nanocomposite properties, but also the filler material and its modification. Dispersion of layered silicate layers within the polymer is improved by chemical compatibilization of the galleries by exchanging inorganic clay cations within the interlayers with organic cations like alkylammonium cations, for example [9]. These larger cations expand the gap between single layered silicate layers and causes a higher distance. Addition of organomaterials including, for example, maleic anhydride (MA) as compatibilizing agent improves formation of especially polypropylene/organoclay nanocomposites further [3].

Materials

For this contribution, nanocomposites based on a polypropylene (PP) matrix and nanocomposites based on a polyamide (PA) matrix were investigated.

The nanocomposites based on PP (PP HD120MO by Borealis GmbH) are reinforced by different layered silicates. These layered silicates are Nanofil® 5 (here abbreviated with N5), Nanofil® 15 (N15), Nanofil® SE3010 (N3010) and Cloisite® 20A (20A) by Southern Clay Products, Inc. These fillers are all montmorillonites. To compare the MMT with a hectorite, Somasif MTE (MTE) by CO-OP Chemical Co. was also used as filler. The amount of filler was constant with 8 wt.-% for all layered silicates. Additionally, the amount of N5 was varied and therefore, polypropylene was filled with 3 wt.-%, 5 wt.-%, 8 wt.-% and 11 wt.-%. Primary particle size of N5 is smaller than that of N15 and N3010 and N5 have different chemical modification. To improve the adhesion between layered silicate and PP, different compatibilizers were used. This compatibilizers are polypropylene grafted with maleinic anhydride (PP-g-MA). PP with 8 wt.-% N15 and three different types of compatibilizer were produced. These compatibilizers are Scona TPPP2112FA (here named S) by Kometra GmbH and Polybond 3200 (P) by Crompton Corp. The third compatibilizer was S additionially modified with Jeffamine (JS).

The nanocomposites based on PA 6 (PA Ultramid B27 E01 by BASF AG) were reinforced with the MMTs Nanofil® 919 (N919), Nanofil® 9 (N9), Nanofil® 5 (N5) and Cloisite 30B (30B) by Southern Clay Products, Inc. The filler content was 3 wt.-%, 6 wt.-%, 9 wt.-% and 12 wt.-% for the Nanofil types and 3 wt.-%, 5 wt.-%, 8 wt.-% and 11 wt.-% for 30B. The difference between filler contents of Nanofil types and 30B is caused by the different modifications of the layered silicates, but the anorganic content is equivalent. A compatibilizer is not needed in this system.

The fillers differ either in primary particle size or in chemical modification of the layered silicates. The primary particle size of N15 (25 µm) is larger than N5 (8 µm) and N919 (37,5 µm) is larger than N9 (8 µm). The chemical modification of N9 and N5 is the only difference between both fillers.

All tested nanocomposites with PA matrix are in conditioned state, that means that the matrix is saturated with water. This was achieved by storing the nanocomposites in a conditioning cabinet at 70 °C and 62 % air moisture until constancy of mass was achieved.

Experimental

The instrumentated Charpy impact test (ICIT) can be used to determine the fracture mechanical properties of polymers.

Investigations described here were performed with three-point-bending specimens, notched ($a = 2$ mm) with a razor blade. The specimen had dimensions of thickness $B = 4$ mm, width

$W = 10$ mm and length $L = 80$ mm. A support span of 40 mm was realized. The pendulum hammer speed for the examination of PP nanocomposites was 1 m/s and for the PA nanocomposites 1.5 m/s. The recorded load–deflection (F–f) diagrams are analyzed by determination of the characteristical load value corresponding to the transition from elastic to elastic-plastic behaviour F_{gy}, the maximum load F_{max} and the associated deflections f_{max} and f_{gy} (Fig. 1). Splitting of the energy, which is assumed by the specimen, into an elastic and a plastic part is possible [10].

Based on the mentioned characteristical measured variables and the load–deflection diagram the parameters fracture toughness K_{Id}, the critical crack-tip-opening displacement δ_{Id} and the J values J_{Id}^{ST} can be determined [10].
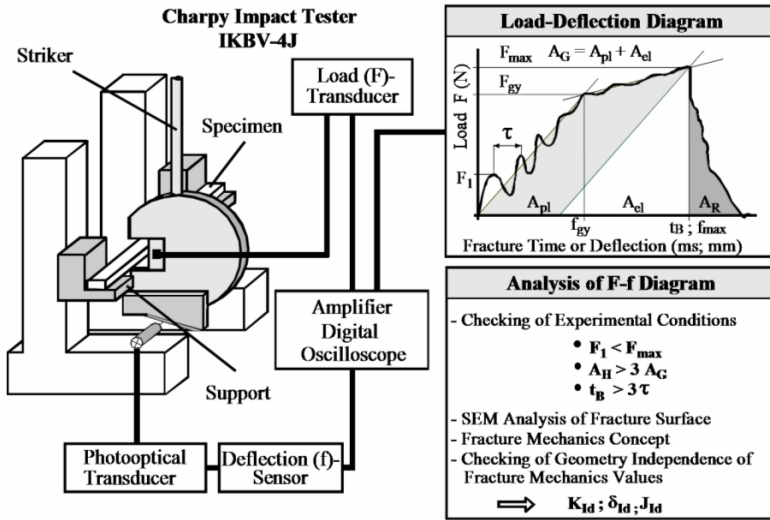

Fig. 1: Fracture mechanics testing device for instrumented Charpy impact test (ICIT)

The aforementioned geometry independent fracture mechanical values K_{Id}, δ_{Id} and J_{Id}^{ST} are calculated with the following equations

$$K_{Qd} = \frac{F_{max}s}{BW^{3/2}} f(\frac{a}{W}) \tag{1}$$

$$\delta_{Qd} = \frac{1}{n}(W - a)\frac{4 f_{max}}{s} \tag{2}$$

$$J_{Qd}^{ST} = \eta_{el} \frac{A_{el}}{B(W - a)} + \eta_{pl} \frac{A_{pl}}{B(W - a)} \frac{W - a_{eff}}{W - a} \tag{3}$$

with

$$\eta_{el} = \frac{2F_{gy}s^2(W - a)}{f_{gy}E_d BW^3} f^2(\frac{a}{W})(1 - v^2) \quad \text{and} \quad \eta_{pl} = 2 - \frac{1 - (\frac{a}{W})(0,892 - 4,476\frac{a}{W})}{1,125 + 0,892\frac{a}{W} - 2,238(\frac{a}{W})^2}.$$

Results

Influence of compatibilizer on crack toughness of nanocomposites based on PP

The influence of different compatibilizers used in polypropylene nanocomposites on fracture mechanical values is shown in Fig. 2a. Furthermore, the percentual change of these values related to the matrix is shown in Fig. 2b. Values of critical stress intensity factor K_{Id} and J-values J_{Id}^{ST} are improved in nanocomposites compared to the pure PP. The critical crack-tip-opening displacement values δ_{Id} are reduced due to the filler except using the compatibilizer JS. That means, that JS improves the critical stress intensity factor and the J values most, compared to the compatibilizers S and P, while it also increases the critical crack opening displacement. So, a modification of the compatibilizer with Jeffamine improves the fracture toughness properties of PP nanocomposites.
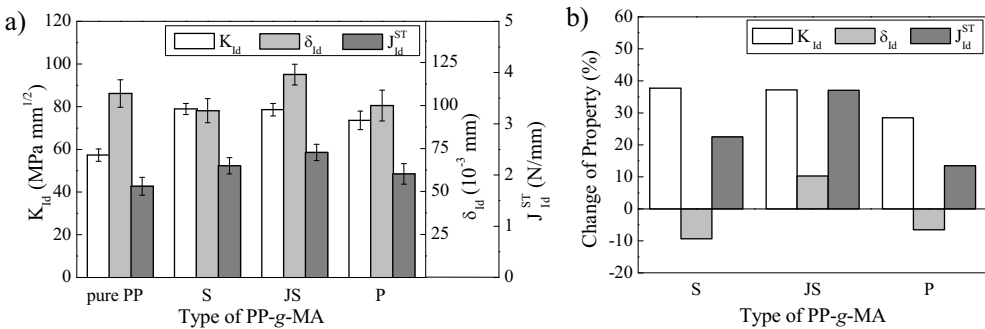

Fig. 2: a) Fracture mechanical values of polypropylene nanocomposites with 8 wt.-% N15 and different compatibilizers (PP-g-MA) and b) the percentual change of the values compared to the matrix properties

A larger distance of platelets of layered silicates, that means better exfoliaton, may improve the material properties of nanocomposites. The above mentioned improvement of the fracture mechanical properties of the nanocomposite compatibilized with JS comes along with a larger layer distance in these nanocomposites, compared to the other PP nanocomposites (Fig. 3a). Smaller diffraction angles correspond to higher layer distances, so the modification with JS causes an increased platelet distance of 1 nm compared to nanocomposites compatibilized with S or P. Combined with the analysis of transmission electron microscopy (TEM) pictures (Fig. 3b), an intercalated structure in the nanocomposites is found, since also single exfoliated platelets can be detected.
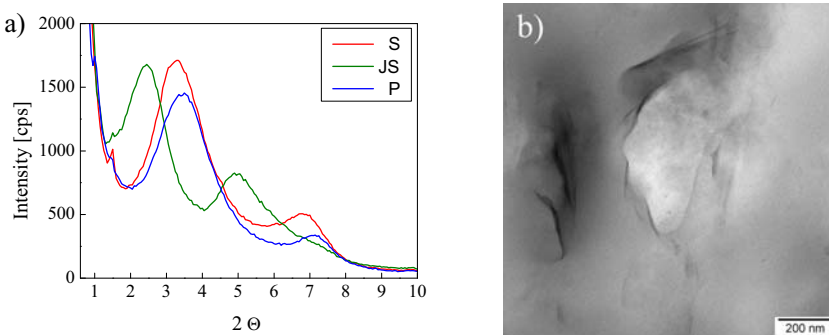

Fig. 3: a) SAXS plot of PP nanocomposited with different compatibilizers and b) TEM image of PP filled with 8 wt.-% N15 and compatibilizer JS

Results from differential scanning microscopy (DSC), which are here not presented, indicated, that MMT is a nucleating agent because the grade of crystallization of PP nanocomposites is increased compared to the matrix. The grade of crystallization is independent of the N5 content, since it is almost constant for all PP nanocomposites filled with N5. Wide angle x-ray scattering (WAXS) results show a partly change of crystal modification of PP nanocomposites from α modification to γ modification compared to the matrix. WAXS plots show a peak of the plane (117) of the γ modification, which cannot be found at the plot of the matrix.

Influence of type of layered silicate on the crack toughness properties of PP

Investigations of the influence of the type of layered silicate on the crack toughness of PP nanocomposites indicated a strong influence. Five different layered silicates were used to prepare nanocomposites. All nanocomposites are based on PP, filled with 8 wt.-% filler and compatibilized with PP-*g*-MA type S. The change of fracture mechanical properties related to the matrix values is shown in Fig. 4. The critical stress intensity factor and the *J* values of all nanocomposites increase compared to the values of the matrix. The critical crack-tip-opening displacement δ_{Id} of the nanocomposites is reduced when using N5, N15 or N3010, but inceased using 20A or MTE. Using MTE as filler results in the highest fracture toughness of the PP nanocomposites investigated here (see Fig. 4), expressed in the strong increase of K_{Id}, δ_{Id} and J_{Id}^{ST}.

The analysis of PP nanocomposites with different primary particle size leads to the result that using a larger primary particle size (N15) in PP nanocomposites improves the crack toughness.

The influence of chemical modification of the layered silicate was investigated by comparing the fillers N5 and N3010, which are modified differently. The change of modification of the layered silicate increases not only K_{Id} and J_{Id}^{ST} compared to the values of the matrix of more than 40 %, but also the critical crack-tip-opening displacement for unstable crack growth has almost the same value as pure PP.
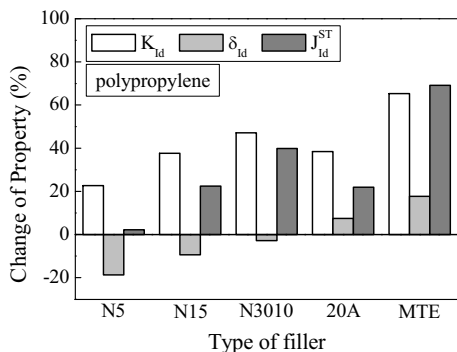

Fig. 4:   Change of fracture mechanical properties of PP nanocomposites filled with different layered silicates compared to the matrix

Influence of filler content on fracture mechanical properties of PP nanocomposites

Characterizing the influence of the layered silicate content on the materials properties, the amount of N5 in PP was varied up to 10 wt.-%. In these nanocomposites the compatibilizer type S was used.

Fracture toughness K_{Id} and *J* values J_{Id}^{ST} increase with increasing filler content (Fig. 5). The force-determined critical stress intensity factor increases with 3 wt.-% filler content strongly and rises again from 8 wt.-% filler content to 10 wt.-% filler content.

Values of crack opening displacement δ_{Id} do not show a significant change up to 3 wt.-% of N5 content. However, they have a minimum at around 8 wt.-% amount of filler. The crack-tip-opening

displacement is a deformation-determined material parameter, so one can assume that the ability to deform decreases with increasing filler content. J values, which are energy-determined, show an almost linear slope with increasing amount of N5.
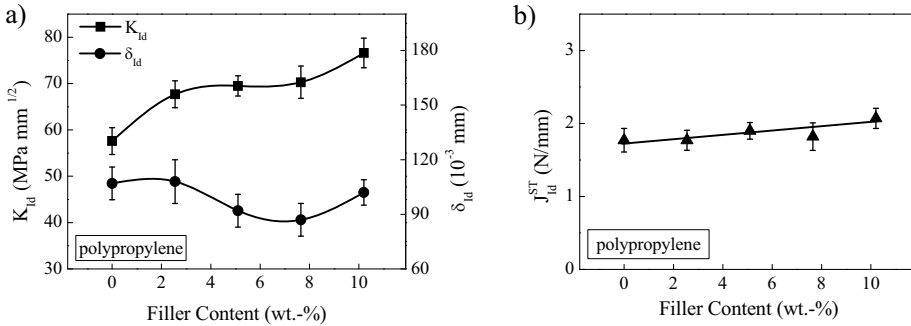

Fig. 5: a) Critical stress intensity factor K_{Id}, critical crack-tip-opening displacement δ_{Id} and b) J values J_{Id}^{ST} of PP nano-composites with increasing filler content.

Influence of modification, primary particle size of layered silicates and filler content on fracture mechanical properties of PA nanocomposites

Investigations of the influence of the modification of layered silicate on the properties of the nano-composite were performed using different MMTs to prepare nanocomposites based on a PA matrix. The fracture toughness K_{Id} and the J values J_{Id}^{ST} of PA filled with different amounts of N919 and N9 show the same behaviour of these nanocomposites (Fig. 6). Since the primary particle size of N919 is larger than the one of N9, but there is no difference of the fracture mechanical properties, one can assume that the particle size has no significant influence on the material properties of these nanocomposites.
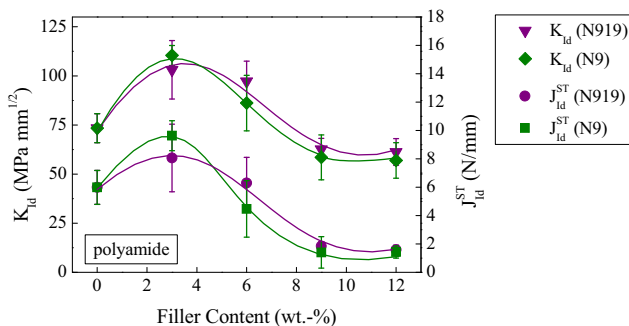

Fig. 6: Fracture toughness and J value of PA nanocomposites filled with N919 and N9

The influence of the modification of the layered silicate is analysed by a comparison of material properties of nanocomposites reinforced with N9 and N5, which are modified differently. In Fig. 7 the fracture mechanical values K_{Id} and J_{Id}^{ST} from ICIT for these nanocomosites are displayed. At lower filler contents both nanocomposites show an increased fracture toughness compared to pure PA. But at higher filler contents, the fracture mechanical properties of the nanocomposites filled

with N5 are much better than the matrix values. Values of nanocomposites filled with N9 are below the matrix level at higher amounts of filler.
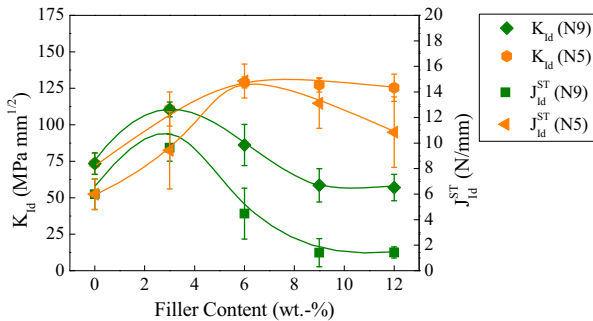

Fig. 7: Critical stress intensity factor K_{Id} and J value J_{Id}^{ST} of PA nanocomposites filled with N9 and N5

Fracture mechanical values of different nanocomposites based on PA in dependence of the filler content are already shown in Fig. 6 and Fig. 7. Up to about 3 wt.-%, fracture mechanical values K_{Id}, δ_{Id} and J_{Id}^{ST} of almost all here tested nanocomposites increase. But at higher contents, the nanocomposites behave differently.

Force-determined critical stress intensity factor K_{Id} decreases at higher filler contents, except of nanocomposites with N5, which stay at the high level. The deformation-determined critical crack-tip-opening displacement δ_{Id} and the J_{Id}^{ST} value of PA with 30B decreases linearly with rising filler content and no improvement can be seen. After an improvement of δ_{Id} and J_{Id}^{ST} at lower amounts of N919 and N9, the values of these nanocomposites decrease below the matrix values. J_{Id}^{ST} and δ_{Id} of PA reinforced with N5 show an increase at all filler contents compared to the matrix.

The J values of these nanocomposites show the same behaviour as the critical crack opening displacement δ_{Id}. Therefore, one can assume that deformation-determined behaviour is dominating.

Summary

Structural and fracture mechanical properties of nanocomposites based on PP and PA were investigated. Critical fracture toughness K_{Id}, critical crack-tip-opening displacement δ_{Id} and J value J_{Id}^{ST} were obtained via instrumented Charpy impact tests.

In PP nanocomposites, a compatibilizer is needed to improve exfoliation and adhesion between platelets and matrix. For this reason, PP nanocomposites with different compatibilizers were prepared to investigate the influence of the compatibilizer. It was found, that the fracture toughness of the PP nanocomposites can be improved by using a compatibilizer additionally modified with Jeffamine (JS).

For investigating the influence of different layered silicate types on the nanocomposites, some MMTs and a Hectorite were used to reinforce the PP. Results showed that the PP nanocomposites filled with Hectorite (MTE) has the strongest increase of fracture mechanical values. The comparison of PP filled with N5 and N15 shows the influence of the primary particle size on the materials properties. So better values were obtained using a larger primary particle size. Additionally, the chemical modification of the layered silicates influences the properties of the materials, as the comparison of PP filled with N5 and N3010 shows.

As expected, the filler content influences most properties of the PP nanocomposites. Critical crack-tip-opening displacement shows a little decrease between 3 wt.-% and 8 wt.-% filler content, com-

pared to the matrix. However, fracture toughness and *J* values increase with rising amount of filler (N5).

In polyamide nanocomposites the primary particle size has no influence on the fracture mechanical properties, as the comparison of PA filled with different amounts of N919 and N9 showed.

Furthermore, a strong influence of the chemical modification of the montmorillonite on the fracture resistance of the PA nanocomposites was found, comparing the properties of materials reinforced with N5 and N9. At lower filler contents, both nanocomposites show similar material behavior, but at higher amounts of fillers, the behaviour aparts. While fracture mechanical properties of PA filled with N9 decrease at higher filler contents, even below the matrix values, the fracture mechanical properties of PA reinforced with N5 stay at the high level.

All these results indicate, that fracture mechanical properties are very important materials properties. So, fracture mechanics in combination with analyses of structural properties contributes essentially to the development of polymeric materials especially nanocomposites.

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