Effect of Particles Size and Density on Fracture Toughness of Polypropylene Particulate Composite

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Abstract. The addition of mineral fillers to polypropylene (PP) can profoundly change the mechanical properties of polymer system. The properties of the particles themselves (size, shape, and material properties) can have significant effect on the global behaviour of composite, particularly on its toughness and stiffness. The adhesion between the particles and the matrix essentially contributes to the ability of the matrix to transfer macro-load and plays a deciding role in evaluation of the driving force of micro-cracks. This contribution is focused on effects of particles size and their density on fracture toughness of polyprophylen particulate composite. The effect was studied from the experimental as well as from the theoretical point of view. The change of fracture toughness was estimated with utilisation of linear elastic fracture mechanics approach. The particle-reinforced composite was modelled as a three-phase material with homogeneously distributed coated particles and numerically simulated using the finite element program ANSYS.

Introduction

Polymeric particulate composites with thermoplastics, especially polypropylene (PP) matrix and mineral fillers, are of great practical importance due to the possibility of modifying mechanical properties and reducing the price/volume ratio of resulting material [1,2]. Characteristic structure feature of thermoplastics is very long molecules with repeating structure groups. The macromolecules haven't chemical bonds. Therefore their interaction is weak and consists of van der Waals interactions and H-bridging [3]. The particular filler designates stiffness and toughness of composites. Changes of mechanical properties caused by fillers have two aspects. On the macro-level it is the change of matrix volume part from low-modulus to high-modulus filler particles [4] and on the micro-level it is the blunting of micro-cracks due to their interaction with particles.
The matrix molecules near the surface of the fillers may have different macroconformations, appear as different thermodynamic phase, or even have a different chemical composition. These regions are called interphases [1,5]. Obviously, the adhesive must 'wet' the particles to be joined in order that a strong bond might result. Particle surfaces are often pre-treated or activated, to improve their adhesion [6].

Table 1 Filler specification

Type of particles	Designation	Origin	Particle size [μm]
precipitated	Pharmaceutical grade	Czech company	d50 = 14.58
microground	Calcitec M/30	Sacilese	d50 = 9.89
microground	Calcitec M/ALFA	Sacilese	d50 = 3.26
microground	Microcarb WMIT	Reverteminerals	d50 = 0.90

Both filler properties and interface properties have a great effect on the modules of the composites [7,8,9]. The higher the specific surface of the filler, the greater the efficiency factor, regardless of chemical nature of the filler and the matrix. The tensile yield stress σ_Y of particle-filled rigid-ductile isotactic poly(propylene) decreases with both volume fraction and diameter. This behaviour can be explained by assuming zero adhesion between matrix molecules and spherical filler particles where the total load is carried by the matrix. Good adhesion between filler particles and matrix does not necessarily mean improved impact strength, however [10-14]. The effect of the composite structure on their mechanical properties is studied here from the experimental as well as from the theoretical point of view. Experimentally the influence of the filler particles size on the fracture toughness of the composite has been investigated. Further, heterophasic system composed of an PP matrix, interphase and $CaCO_3$ particles has been numerically modelled using the finite element program ANSYS. A model explaining the possible change of the fracture toughness values due to the existence of particles is estimated with utilisation of Linear Elastic Fracture Mechanics (LEFM) approach.

Experimental study

Commercially available polypropylene (MOSTEN, PH4* powder, gas phase process, MFI = 4 g/10min and isotacticity index I.I.=98,2 %) supplied by Czech company Chemopetrol Litvínov was used as a matrix material. As fillers we used calcium carbonate ($CaCO_3$) with difference average diameter (d50) and volume content 5% and 10%. The $CaCO_3$ particles were coated with surface agent improving their dispersion (see Table 1). PH4* power and 0,3%wt. of Irganox B 225 were mixed with precipitated $CaCO_3$ and homogenized in homogenizer (Kenwood professional) for 5 minutes. At the second step this blend was granulated in double screw (APV MP 19-255C). The blends were than compression-moulded into plaques (130x130x4 mm) according ISO standard (ISO 293).

Table 2 Fracture toughness of PPH composite filled by $CaCO_3$

Material	K_{Id} [MPa.m$^{1/2}$]	standard deviation [MPa.m$^{1/2}$]
PPH	3.62	0.08
PPH + 5vol.%$CaCO_3$ (14.58μm)	3.34	0.13
PPH + 10vol.%$CaCO_3$ (14.58μm)	3.24	0.05
PPH + 5vol.%$CaCO_3$ (9.89μm)	3.33	0.09
PPH + 10vol.%$CaCO_3$ (9.89μm)	3.22	0.07
PPH + 5vol.%$CaCO_3$ (3.26μm)	3.69	0.08
PPH + 10vol.%$CaCO_3$ (3.26μm)	3.64	0.04
PPH + 5vol.%$CaCO_3$ (0.90μm)	3.80	0.04
PPH + 10vol.%$CaCO_3$ (0.90μm)	3.72	0.03

The experimental study was carried out with the main goal to analyse the influence of particle sizes on the fracture toughness of the composite.
To this aim the following steps have been performed and used:

- The instrumented notched Charpy impact tests (ISO 179-Part 2) using instrumented pendulum PSW/MFL (150 J). The measurement run under the following conditions: (i) span support (s) 40 mm, (ii) speed 1m/s and temperature 23°C.

- SEM for estimation the size and distribution of particles, and for observation the fracture surfaces after impact test. For this purposes we used scanning electron microscope (SEM) TESCAN VEGA TS 5136LM. SEM Tescan is low-voltage SEM that enables to observe specimen without covering of layer.
- Dynamic mechanic thermal analysis (DMTA - Dynamic Thermomechanical Spectrometer DMA DX04T) for estimate the complex modulus E^* i.e. the values of E' and E'' or the values of E and tanδ.

Experimental results

The dynamic fracture toughness (K_{Id}) was estimated according standard procedures, see e.g. [15]. Results obtained are presented in Table 2 and Fig. 1 for two different values of filler particle density.

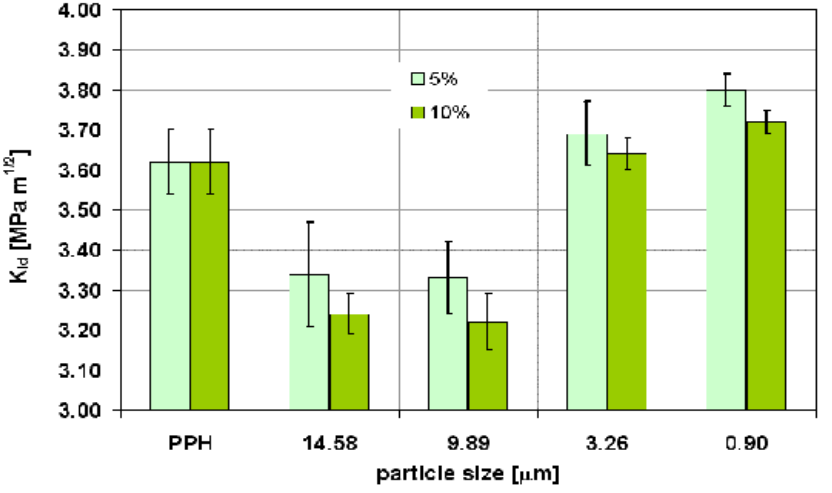
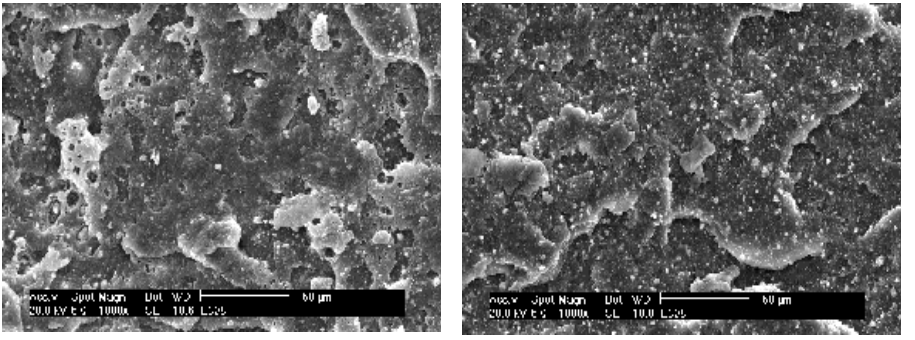


Fig. 1 Fracture toughness versus particle size

SEM was used at first for estimation the size and distribution of particles, at the second step for observation the fracture surfaces after impact test. We used dynamic mechanic thermal analysis (DMTA) for studying the changes in morphology due to adding of $CaCO_3$ particles [16].



Without treatment With 1% stearic acid treatment

Fig. 2 SEM picture of fracture surface after impact test

The influence of treatment on mechanical behavior of the composite was studied. Generally the treatment of the fillers contributes to its better dispersion in PP matrix, see Fig.2. This is one of basic presumptions to achieve higher toughness in relation to matrix.

Table 3 The increase of modulus of composite E_{comp} as a consequence of adding of treated $CaCO_3$ particles to the matrix

Material	E_{comp} [MPa]
PPH	1 810
PPH + 5 %vol $CaCO_3$	2 230
PPH + 10%vol $CaCO_3$	2 500

In one case (d50 = 0.9 μm) the change of the modulus of the composite, E_{comp}, as a consequence of treated particles adding to the matrix has been studied as well for two values of filler particles density, see Table 3.

Numerical simulations

To discuss the basic conclusions following from experiments two basic types of numerical simulations have been performed. The intension of the first part is to relate the information concerning the deformation behaviour from micro- to macro- scales. The model on this level results in relation between micro-properties of the composite (i.e. geometrical and material characteristics of the particles including the properties of the interphase and the matrix) and macro-behaviour of the composite (represented e.g. by global values of Young´s modulus). The second part of the numerical modelling deals with interaction of micro-cracks initiated and propagated in the matrix with particles. In both cases the composite is modelled as a three phase continuum consisting of matrix, interphase and particles. The aim of numerical simulations is, correspondingly to the experiments performed, to assess the influence of particles size and density on macro-characteristic properties of the composite. The aim of the research in this field is to find balance between size and volume fraction of the particles and the thickness and material properties of the interphase and to find a compromise between values of global macro-properties and the fracture toughness.

Numerical model

The deformation behaviour of the three phase composite with homogeneously distributed coated particles was numerically simulated on a microscopic scale using the finite element program ANSYS, see [7] for details.

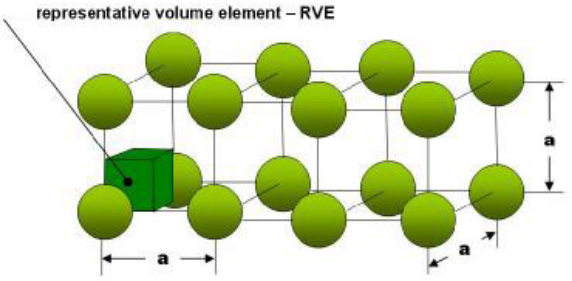


Fig. 3 Homogenous distribution of the spherical particles inside polymer matrix

By assuming the spherical particles to be packed in symmetry and in the cubic array as in Fig. 3, only one-eighth of the particle embedded in the cube is needed for analysis.

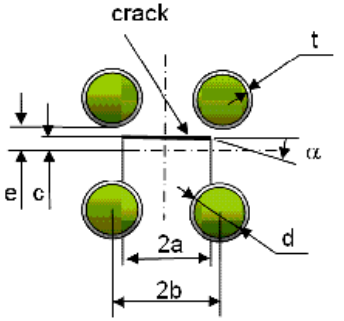


Fig. 4 Geometry of the model used for micro crack behavior estimation in the PP-$CaCO_3$ polymer composite. α is the angle of deflection.

The geometry of the representative unit cell (representative volume element – RVE) for the three phase material model is shown in Fig. 3. The material properties characterizing the composite corresponding to calcium carbonate ($CaCO_3$) - filled polyprophylene (PP) at room temperature are used. The calculations have been performed for different particle dimensions d50 = 0.9, 3.26, 9.89 and 14.58 μm and wide interval of particulate filler volume fraction (between 0.016 – 0.163). The thickness of the interphase is supposed to be independent on the particles size, see [8], and its value was chosen t = 150 nm. As a special case the configuration corresponding to perfect adhesion between particles and matrix (corresponding to zero thickness of the interphase) was considered as well. The internal stress and strain distributions have been determined for two values of Young´s modulus of the interphase 0.05 and 0.4 GPa. It is assumed that Young's modulus of the interphase is constant through its thickness.

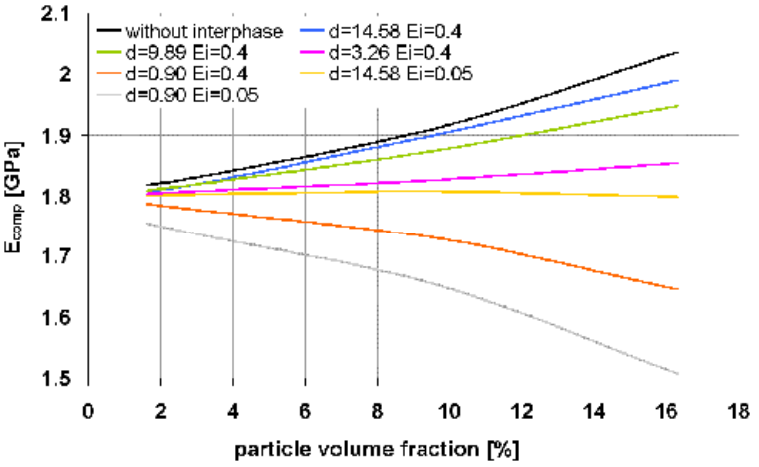


Fig. 5 The dependence of the macroscopic modulus of the composite E_{comp} on particles density for two different values of the Young modulus of the interface E_i (0.05 and 0.4) and four values of the particles size.

Further, micro-crack behavior in the three phase composite with homogenously distributed particles was numerically simulated on a microscopic scale, see [17]. Only particles located close to the crack tip significantly influence microcrack behavior. Assuming again that particles are

homogenously and regularly distributed in the matrix, the structure is strictly periodical and a unit cell with four particles can be regarded as representative for the composite structure, see Fig. 4.

Selected numerical results

Only basic typical results of the performed numerical simulations are presented here. The meaning of the results is discussed later in the text.
The change of the macroscopic modulus of the composite due to different particles density is shown in Fig. 5 for two values of Young´s modulus of the interphase 0.05 and 0.4 GPa and four values of the particles size (0.9, 3.26, 9.89, 14.58 μm).

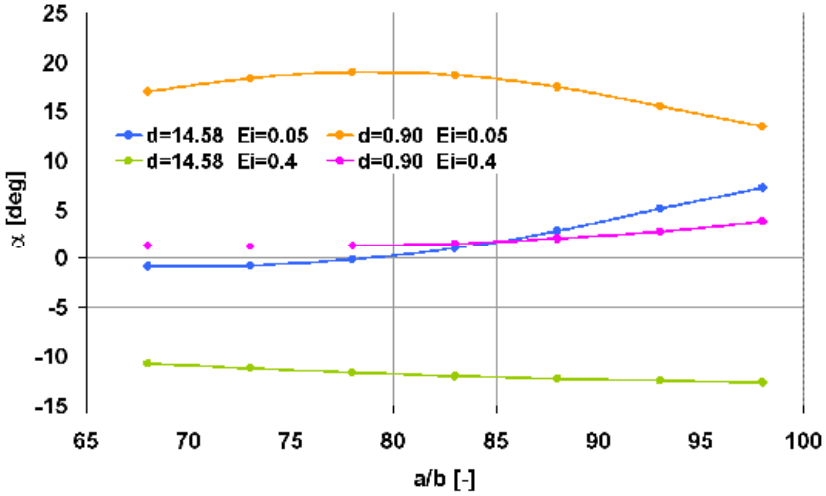


Fig. 6 Dependence of crack propagation direction α on the ratio a/b (see Fig. 4) for two limiting sizes of particles and two different values of Young modulus of the interphase E_i. Volume fraction is 16.3%.

Assuming that particles are regularly distributed in the matrix, the interaction of a micro-crack (length of the crack 2*a* is comparable with distance between particles 2*b*) with particles is studied for two limiting particle sizes 0.9 μm and 14.58 μm, see Fig. 6. Note that positive values of the angle of deflection α mean that the crack avoids the particle and the negative values mean that the crack is attracted by the particle, see also Fig. 4.

Discussion and conclusions

The presence of $CaCO_3$ particles in PP matrix significantly influences basic properties of the composite [15]. Depending on the size of fillers the presence of rigid particles in a polymer matrix leads to the change of fracture toughness of the composite, see Fig. 1. The results of experiment performed show increasing toughness with decreasing particle size (for particles size less than 3.26 μm).
Several phenomena influence the fracture toughness of the polymer composite: aggregation of the particles, particle shape and size, distribution of the particles and also material properties of the interphase.
The interphase resides in a region between the constituents of the composite with the size ranging from a few to a few thousand nanometres. Although the region has a microscopic scale, the adhesion between particles and matrix essentially contributes to the ability of the matrix to transfer

macro-load and moreover plays a deciding role in the evaluation of the driving force of micro-cracks, see e.g. [7,17]. Properties of the interphase differ from those of the particles and the matrix. There are influenced by the cure reaction between constituents and by treatment of fillers themselves. In the present case the 1% stearic acid has been used. The treatment of the filler contributes to its better dispersion in PP matrix, see Fig. 2, where SEM picture of fracture surface without and with treatment is shown.
It is assumed in the paper that the interaction between micro-cracks and particles basically influences fracture behavior of the composite. In the case of perfect adhesion (modeled here as an uncoated particle) the angle of deflection α is always positive, meaning that the micro-crack avoids regions with rigid particles and grows only in the net matrix. If Young modulus of the interphase decreases and is less than those of particles the effect of the rigid particles is partially shielded by a softer interphase. For smaller values of the interphase Young modulus ($E_i < 0.1$ GPa) stiff particles are completely shielded by softer interface, and the calculated angle of deflection α is always negative and in this case the micro-crack is attracted by the particles, see Fig. 6. When the crack tip touches interphase, the interphase is damaged due to high stresses and the particle can be fully debonded. As a consequence, the crack is blunted, the stress singular field is changed to a regular one and the crack stays arrested near the particle, see Fig. 7. The blunting of micro-cracks in connection with debonding can contribute to increase in fracture toughness of the composite.

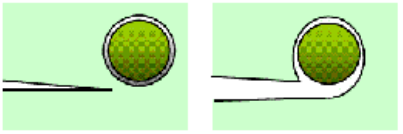


Fig. 7 a) micro crack approaching particle covered by interphase, b) the particle is fully debonded and the micro-crack is blunted.

If the particle size decreases the micro-cracks are more attracted to the particles and this phenomenon leads to increase of the fracture toughness. This result is in agreement with experimental observations, see Fig. 1.
The aim of the research in this field is to find balance between size and volume fraction of the particles and the thickness and material properties of the interphase and to find a compromise between level of E_{comp} and the fracture toughness. The influence of particle size and properties of the interphase on Young modulus (E_{comp}) of the composite is visible from Fig. 5 for different volume density of particles and Table 3. Generally the presence of rigid particles leads to relatively strong increase of Young modulus (E_{comp}) of the composite in dependence on volume fraction of the particles. Contrary to it the presence of soft interphase contributes to decrease of Young modulus and resulting tensile properties are given by both these phenomena. This is documented for small particles size (0.9μm) where the influence of the soft interphase is prevailing, see Fig. 5. From this point of view the experimental results presented in Table 3 show that the stiffness increase in this case is connected preferentially with morphology changes of matrix caused by particles presence.

The results of the contribution can be briefly summarized as follows:

- The treatment $CaCO_3$ fillers with 1wt.% of stearic acid leads to its better dispersion in PP matrix
- The PP + treated $CaCO_3$ composite exhibits higher toughness in comparison to the neat PP for particle size less than 3.26 μm
- The fracture mode of the system in study is not changed it remains brittle.
- Results following from the numerical model allow estimate the relation between properties of microstructure versus macroscopic behaviour of the composite.

- The existence of the interphase around the particles leads generally to decrease of macro modulus of the composite.
- The toughening of a particle reinforced composite was investigated using the three-phase finite element model. It was found that one of the basic mechanisms of toughening consists in the shielding of the rigid particles by a soft interphase followed by debonding. In agreement with performed experiments this effect is size and material dependent.

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References

[1] Pukánszky B.: *European Polymer Journal* **41** (2005) 645-662.

[2] Elias H.-G.: *An Introduction to Plastics*. 2ndEd.Weinheim, Wiley-VCH GmbH&Co., Weinheim, 2003, ISBN 3-527-29602-6.

[3] Karger, J.-Kocsis: *Structure and Morphology: Polypropylene Structure, blends and composites. Volume 1 Structure and Morpholog*y. Chapman & Hall, London 1995, ISBN 0 412 58430 1.

[4] Raab M., Křesálek V., Sova M.: *Plasty a kaučuk* **36** (1999) 132.

[5] Scheirs J.: *Compositional and Failure Analysis of Polymers*.1st Ed. England, by John Wiley&Sons, Ltd.,2000, ISBN 0 471 625728.

[6] Pukánszky B., Fekete E.: *Adhesion and Surface Modification.* Advanced in Polymer Science, Vol.139, Springer-Verlag Berlin 1999

[7] Knesl Z., Hutař P., Náhlík L., Nezbedová E., Vlach B.: *Role of particle size and filler matrix adhesion on stress state in thermoplastic composites.* Computational Modelling and Experiments of the Composite Materials with Micro- and Nano- Structure. 2007, Liptovský Mikuláš, Slovak Republic.

[8] Pukánszky B.: *The Journal of Adhesion* **78** (2002) 861-875.

[9] Zebarjad S.M.: *Journal of Materials Processing Technology*: **155-156** (2004) 1459-1464, Proceedings of the International Conference on Advances.

[10] Jancar J.: *Polymer Engineering and Science* **June** (1990) 707-720

[11] Goldman A.Y.: *Polymer toughened with calcium carbonate mineral filler.* Material Research Innovation, 1st Springer-Verlag GMbH, June 2000, ISSN:1432-8917

[12] Thio Y.S.: *Polymer* **43** (2002) 3661-3674

[13] Zuiderduin W.C.J., Westzaan C., Huétink I., Gaymans R.J.: *Polymer* **44** (2003) 261-275.

[14] Zhang Ling: *Journal of Polymer Science*, *Part B*: *Polymer Physics*, **42** (2004) 1656-1662.

[15] Nezbedova E., Kalfus J., Divisova L.: *Influence of Partical Size on the Toughening of Polypropylene*. 11. International Konference Polymeric Materiále 2004, Halle/Saale 29.9.-1.10. 2004.

[16] Kucera J. and Nezbedova E.: *Polym. Adv. Technol*. **18** (2007) 112-116.

[17] Knesl Z., Hutar P., Nahlik L.: *Effect of the interface on fracture toughness of partije reinforced composites.* 15th International Conference on Composite/Nano Engineering, Hainan Island, China 2007.