Structure, thermal and mechanical properties of polypropylene composites with nano- and micro-diamonds

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Abstract: The influence of diamond powders on properties of isotactic polypropylene (PP) was investigated. PP composites containing 0.2—5 wt % of the powders with particles of average size between 100 nm and 1 μm were prepared, and their structure and properties were examined. Dispersion of each filler depended on its grain size and content. The presence of fillers raised the crystallization temperature of PP matrix by up to few Celsius degrees. The modulus of elasticity of composites increased with increasing filler content, by up to 40 % in comparison to neat PP. The tensile impact strength of the composites with 1 μm powders and also the other composites at the filler content as low as 0.2 wt % improved by up to 30 %. The composites did not exhibit any decrease in the yield strength and retained good drawability. The elongation at break exceeded 1000 % in most cases. Examination of the uniaxially drawn specimens revealed that the filler grains separated from the PP matrix during drawing.

Keywords: isotactic polypropylene, composites, diamond powders, mechanical properties.

Struktura oraz termiczne i mechaniczne właściwości kompozytów polipropylenu z nano- i mikro-diamentami

Streszczenie: Badano wpływ proszków diamentowych na właściwości izotaktycznego polipropylenu (PP). Wytworzono kompozyty PP zawierające 0,2—5 % mas. proszków o średnich rozmiarach cząstek w zakresie od 100 nm do 1 μm oraz zbadano ich strukturę i właściwości. W każdym przypadku dyspersja napełniacza zależała od rozmiarów ziaren i ich zawartości w kompozycie. Obecność napełniaczy wywołała podwyższenie, maksymalnie o kilka stopni Celsjusza, temperatury krystalizacji matrycy polipropylenowej. Moduł sprężystości kompozytów zwiększał się wraz ze zwiększeniem zawartości napełniacza (maksymalnie o 40 %). Odporność na zerwanie udarowe kompozytów z proszkami o ziarnach wielkości 1 μm oraz pozostałych kompozytów z zawartością napełniaczy wynoszącą 0,2 % mas., wzrosła, maksymalnie o 30 %. Naprężenie na granicy plastyczności kompozytów nie uległo zmniejszeniu, została też utrzymana dobra ciągliwość. W większości przypadków wydłużenie przy zerwaniu przekroczyło 1000 %. W trakcie badania odkształconych próbek stwierdzono, że podczas jednoosiowego rozciągania zachodziło oddzielanie się ziaren napełniaczy od matrycy polipropylenowej.

Słowa kluczowe: izotaktyczny polipropylen, kompozyty, proszki diamentowe, właściwości mechaniczne.

Advantages of incorporating fillers and nanofillers into polymers are long known. The use of nanometer-sized particles as fillers permits to modify properties at very low loading levels, usually a few percent. Nanofibers and nanoplatelets are frequently used for such a purpose. Well known examples include carbon nanotubes and exfoliated montmorillonite. It has also been found that low amounts of nanopowders added to a polymer, for instance isotactic polypropylene (PP), can improve its tensile strength and ductility [1—6]. For example, 0.1—0.3 wt % of silver nanoparticles, with size in the range of 30—110 nm, increased both the elongation at break and the Izod impact strength of PP, the latter by 30 % [6]. Recently, Dolmatov [7—9] reported enhancement of the mechanical performance of a range of elastomers by addition of detonation nano-diamond particles. The detonation diamonds were also used to modify properties of other polymers [10—16] including poly(lactic acid), polycarbonate, poly(methyl methacrylate), low density polyethylene, styrene-acrylonitrile copolymer, polysulfone and epoxy resins. Usually, an increase of stiffness and hardness was observed. It has to be mentioned that synthetic micron and submicron diamonds are commercially available as particles of various sizes and are used for polishing, grinding, *etc*.

In our work we explored the possibility to modify PP properties with micro- and nanosized diamond powders.

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Composites with 0.2, 2 and 5 wt % of the fillers with various grain sizes ranging from 100 nm to 1 μm were prepared and examined.

EXPERIMENTAL PART

Polypropylene (PP) with trade name Malen-P F 401 [melt flow rate (*MFR*) of 3.0—3.5 g/10 min (230 °C, 2.16 kg), density 0.91 g/cm^3, weight average molar mass ($\overline{M}_w$) of 300 kg/mol and dispersity ($\overline{M}_w/\overline{M}_n$) of 5.3], produced by Orlen SA (Poland) was selected to prepare composites.

Diamond powders with sizes ranging from 100 nm to 1 μm were used as fillers. Powders with irregular, semi-blocky particles, having a number average size (R_{av}) of 100, 150, 250 and 500 nm, denoted as D100, D150, D250 and D500, respectively, and blocky particles with R_{av} of 150 nm (DS150), were purchased from Diamond Innovations (Worthington, OH). 1 μm synthetic and natural diamond particles were supplied by Sigma-Aldrich (St. Louis, MO): natural monocrystalline (DNM1), synthetic monocrystalline (DSM1), and synthetic polycrystalline (DSP1).

Preparation of samples

PP composites with 0.2, 2 and 5 wt % of the fillers were prepared in an internal Brabender mixer operating at 60 rpm for 5 min at the temperature of 195 °C, under a flow of dry gaseous nitrogen. Owing to the density of filler, 3.5 g/cm^3, the filler volume fractions, 0.052, 0.52 or 1.3 vol %, respectively, were markedly lower than the weight fractions. The composites were denoted as, for example, PP/D100-5, where the end number relates to the filler weight fraction. Neat PP was processed under the same conditions to obtain a reference material. For further studies, 1 mm and 0.5 mm thick films were compression molded in a hydraulic press at 190 °C for 3 min and quenched in ice water.

Methods of testing

Cryo-fracture surfaces of the composites were sputtered with gold and studied under scanning electron microscopes (SEM) JEOL LV5500 and JEOL 6010LA (Tokyo, Japan).

To examine thermal properties, specimens of the films were heated in a differential scanning calorimeter (DSC) TA Instruments 2920 (New Castle, DE) to 220 °C, annealed for 3 min, cooled to the ambient temperature at the rate of 10 °C/min and heated at the same rate to 220 °C, under a flow of dry gaseous nitrogen.

The crystal structure of the materials was characterized by wide angle X-ray diffraction (WAXD) in the reflection mode using a wide-angle goniometer coupled to a Philips PW3830 sealed tube X-ray generator (Eindhoven, The Netherlands) operating at 50 kV and 30 mA. The X-ray beam consisted of Cu K$_\alpha$ radiation filtered by a Ni filter and electronically. The slit system enabled collection of the diffracted beam with a divergence angle of less than 0.05°.

At least 3 oar-shaped specimens of each material, conforming to ISO 527-2 standard, with gauge length of 25 mm and gauge width of 5 mm, were cut of 1 mm thick films and uniaxially drawn in an Instron 5582 tensile testing machine (High Wycombe, UK) at the strain rate of 50 %/min, at the room temperature. The modulus of elasticity was measured with an extensometer. To have an insight into the structure of deformed materials, the drawn specimens were cryo-fractured along the plane parallel to the drawing direction and analyzed by SEM.

The tensile impact strength tests were performed on 8—10 specimens of each material using an impact tester CEAST Resil 5.5 (Charlotte, NC). The 0.5 mm thick specimens were used in order to fit the absorbed energy level to the measurement range of the hammer. The specimen shape conformed to ISO 8256 test standard: total length of 80 mm, narrow section length and width of 30 and 10 mm, respectively.

RESULTS AND DISCUSSION

Exemplary SEM micrographs of cryo-fractured composites are collected in Figs. 1 and 2. In the composites with particles with R_{av} up to 500 nm good dispersion of filler particles was achieved at the filler content of 0.2 wt %. The cryo-fractured surfaces of these materials were essentially free of agglomerates larger than 1 μm. The dispersion worsened with increasing filler content although it depended also on the particle size. On the cryo-fracture surfaces of composites with 5 wt % of the fillers, large agglomerates, even with sizes of several tens of micrometers, were occasionally found, as in PP/D100-5 shown in Fig. 1a. Nevertheless, the rest of particles were dispersed uniformly within the matrix, as those in PP/D150-5, presented in Fig. 1b. The number of the agglomerates decreased with increasing particle size. Very few such agglomerates were present in PP/D500-5, in which well dispersed particles dominated, as illustrated in Fig. 1c. The 1 μm powders were well dispersed in PP regardless of the filler content, as evidenced in Fig. 2a and 2b, showing isolated filler particles on cryo-fracture surfaces of PP/DSP1-5 and PP/DSM1-5. Similar results (not shown) were obtained for PP/DNM1-5.

Exemplary DSC cooling thermograms are shown in Fig. 3. During cooling in DSC at the rate of 10 °C/min neat PP crystallized with peak rate temperature (T_c) of about 115 °C. The presence of 0.2 wt % of fillers did not affect markedly T_c of PP matrix. However, an increase in the synthetic fillers contents resulted in a rise of the T_c by a few Celsius degrees, although no more than by 6 °C as it was found for PP/DSP1-5. The melting peak temperature (T_m), recorded during the second heating was 160—162 °C for all the materials, whereas the melting enthalpy

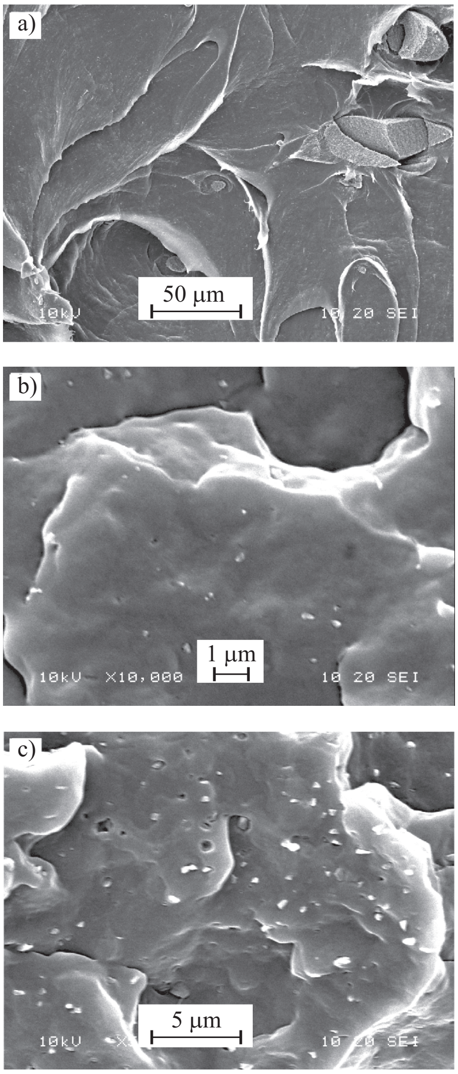

Fig. 1. SEM micrographs of cryo-fractured surfaces of: a) PP/D100-5, b) PP/D150-5, c) PP/D500-5

(ΔH_m) ranged from 88 to 94 J/(g of PP), which corresponds to a crystallinity level of 50—53 wt %, if ΔH_m of PP crystals of 177 J/g was assumed [17]. The increase of T_c was caused most probably by augmentation of heterogeneous nucleation in the composite materials, either on the fillers or on impurities, which are frequently present in synthetic diamond powders [18]. The latter hypothesis is corroborated by the fact that T_c of PP/DNM1 did not increase in comparison to neat PP regardless of the DNM1 content.

Exemplary WAXD diffractograms are shown in Fig. 4. WAXD examination confirmed that neat PP and PP in the composites crystallized in its usual monoclinic alpha form, evidenced by five peaks of (110), (040), (130), (111) and (041) crystallographic planes typical of the alpha phase.

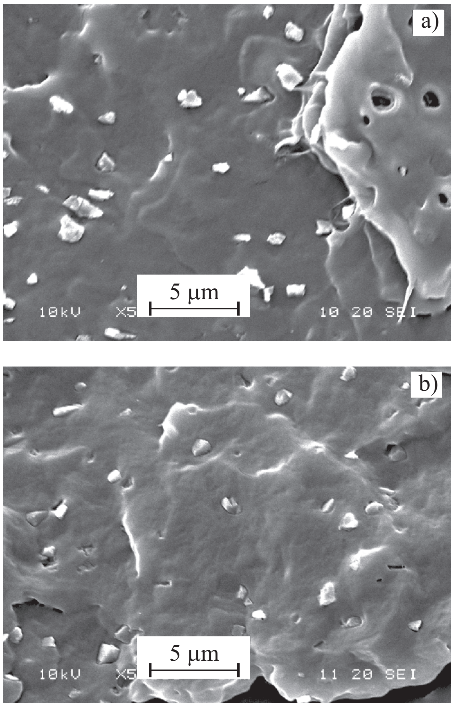

Fig. 2. SEM micrographs of cryo-fractured surfaces of: a) PP/DSP1-5, b) PP/DSM1-5

The values of yield stress (σ_y), stress at break (σ_b), elongation at break (ε_b), elastic modulus (E), and tensile impact strength (U) of the materials studied are reported in Table 1 and Fig. 5. It has to be noted that the data for PP/DS150 are not shown because these composites behaved as PP/D150. The blocky particle shape had no marked effect on the mechanical properties. Also the composites with 1 μm particles, *i.e.* PP/DNM1, PP/DSM1 and PP/DSP1, behaved similarly, and because of this only the data for PP/DSM1 are reported. Neat PP exhibited σ_y of 31.1 MPa, σ_b of 36.9 MPa, and ε_b of 1600 %. E and U of PP were equal to 1.28 GPa and 70 kJ/m^2, respectively. The data in Table 1 evidence that σ_y of the composites was at the same level or even exceeded that of neat PP by a few percents. ε_b of the composites with 0.2 wt % of particles with R_{av} up to 250 nm was close to that of neat PP. Although ε_b decreased with increasing filler content, it re-

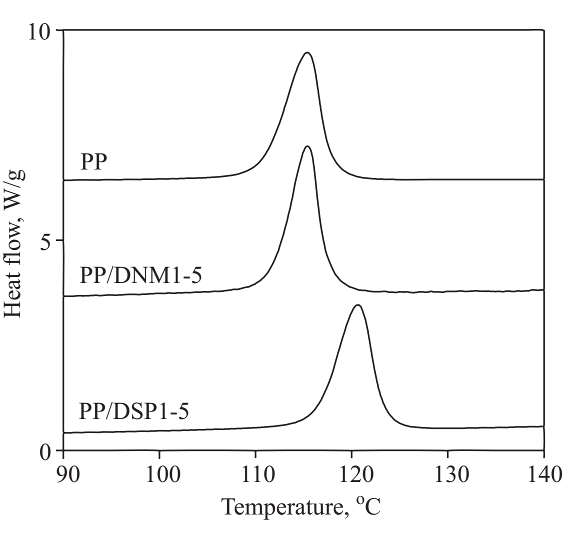

Fig. 3. DSC cooling thermograms of neat PP, PP/DNM1-5 and PP/DSP1-5

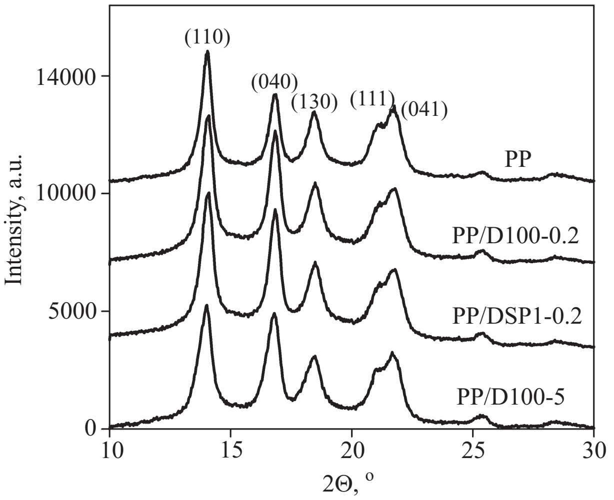

Fig. 4. WAXD diffractograms of neat PP, PP/D100-0.2, PP/DSP1-0.2 and PP/D100-5

T a b l e 1. Mechanical properties (average values) of neat PP and PP composites with diamond powders: yield stress (σ_y), stress at break (σ_b), and elongation at break (ε_b)

Sample code	σ_y, MPa	σ_b, MPa	ε_b, %
PP	31.1	36.9	1600
PP/D100-0.2	32.2	40.4	1570
PP/D100-2	32.4	35.6	1400
PP/D100-5	34.4	33.9	1210
PP/D150-0.2	35.3	39.3	1390
PP/D150-2	35.9	33.3	1090
PP/D150-5	35.0	27.9	420
PP/D250-0.2	30.7	40.2	1620
PP/D250-2	31.7	32.9	1240
PP/D250-5	33.8	26.2	1030
PP/D500-0.2	32.7	32.7	1140
PP/D500-2	32.7	32.8	1170
PP/D500-5	32.2	32.4	1150
PP/DSM1-0.2	31.8	28.9	1020
PP/DSM1-2	33.7	33.7	1140
PP/DSM1-5	33.7	30.1	890

mained above 1000 %, with the only exception of PP/D150-5. ε_b of all the composites with larger particles was close to 1000 % and less depended on the filler content. The decrease in ε_b was usually accompanied by a decrease in σ_b because of smaller extent of strain hardening.

Toughening of polymers with rigid particulate fillers is well recognized; the stress concentration caused by the particles leads to debonding at the filler-matrix interface, which affects the stress state in the matrix and thus promotes its shear yielding, *e.g.* [5, 19]. SEM analysis of internal structure of the composite specimens evidenced intense cavitation, as exemplified in Fig. 6, where PP and PP/DSP1-2 strained to 50 % and cryo-fractured along the plane parallel to the drawing direction are compared. In PP/DSP1-2 numerous voids with filler particles inside are seen. The particles separated from PP during drawing and thus formed voids elongated during further deformation. However, improvement of the drawability requires certain conditions to be fulfilled: a small particle size otherwise the voids would be too large and would initiate cracks, good and homogeneous dispersion, and occurrence of the debonding prior to yield of the matrix [19]. σ_y of the composites studied, at the same level or slightly above that of neat PP, indicates that the diamond particles

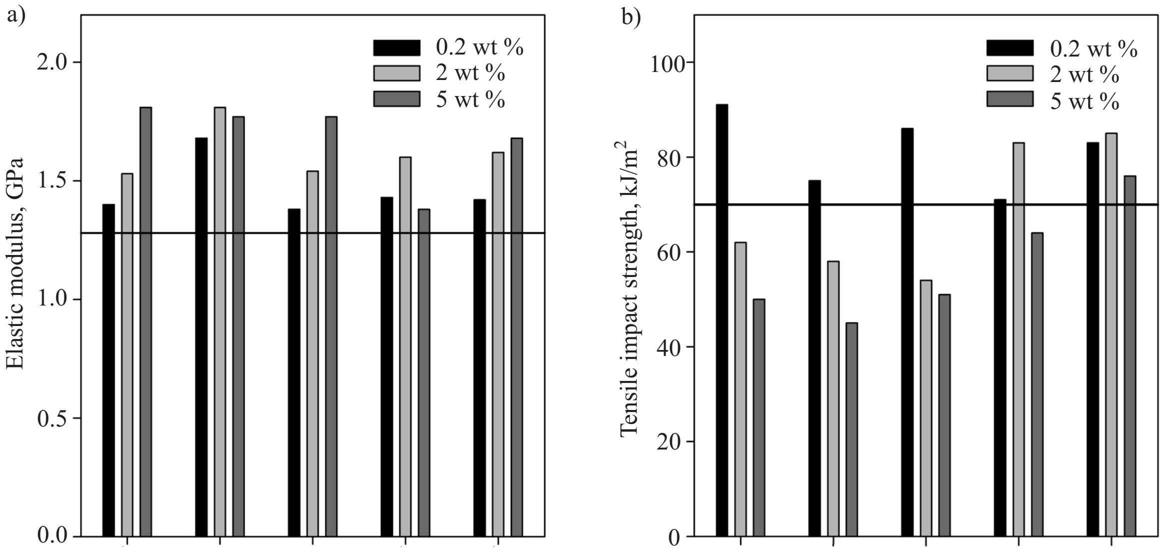

Fig. 5. Influence of diamond filler type and content on mechanical properties of PP composites (horizontal lines indicate the elastic modulus and tensile impact strength of neat PP): a) elastic modulus, b) tensile impact strength

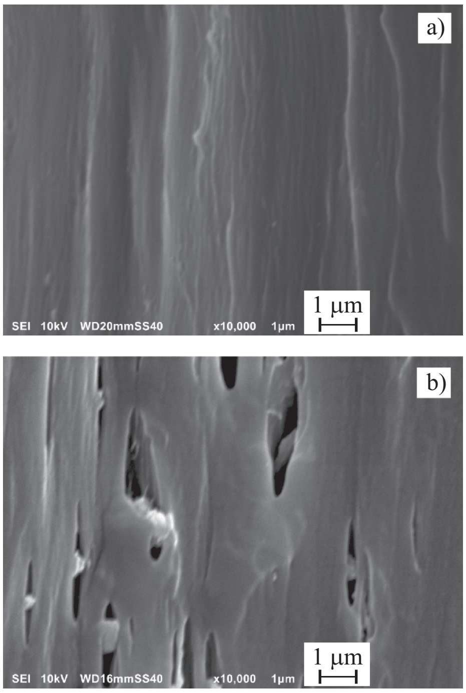

Fig. 6. SEM micrographs of tensile specimens strained to 50 % and cryo-fractured along the plane parallel to the drawing direction (vertical) for: a) neat PP, b) PP/DSP1-2

did not facilitate yielding of PP during tensile drawing. This could be the reason of the lack of improvement in elongation at break. Most probably, the cavitation occurred at the later stages of deformation. In addition, the presence of filler agglomerates in some of the materials was a detrimental factor.

The modulus E of the composites was improved in comparison to neat PP and it enlarged with increasing filler content. The largest increase in E, by up to 40 %, was found for the composites with 5 wt % of particles having R_{av} up to 250 nm. All the composites with 1 μm particles exhibited markedly improved U value. In the case of composites with smaller particles, U exceeded that of neat PP only at the lowest filler content and diminished with increasing filler content. For example, U of PP/D100-0.2 increased by 30 %, whereas U of PP/D100-5 decreased by 30 % in comparison to neat PP.

The drawability and toughness of the composites correlate with dispersion of the fillers. Improvement of U was achieved for the materials with the best dispersion of fillers, that is for those with 1 μm particles and in the other composites at the filler content of 0.2 wt %. It must be emphasized that the loading speed during the impact test is much higher than that during tensile drawing. It is therefore possible that the ability of the filler particles to separate from PP played an important role in the improvement of U, although it did not improve the drawability.

It is well known that properties of composite materials depend on filler content, filler particle size and dispersion. Worsening of the dispersion had a detrimental effect to the drawability and toughness of the composites. Further enhancement of the properties would require improvement of the filler dispersion. It is worth to note that for such a purpose in the case of nanometer size detonation diamonds with the chemical bonding capability, functionalization, for instance by alkyl groups [14, 15], or compatibilization by maleated polymer [11] was employed.

CONCLUSIONS

The composites with diamond powders with particles sizes ranging from 100 nm to 1 μm were prepared and examined. The dispersion of fillers and properties of the composites depended on the filler particle size and content. The best dispersion was achieved in the composites with 1 μm particles, regardless of their content, and also in the other composites with 0.2 wt % content. All the composites exhibited improved E, increasing with the filler content. The materials with well dispersed fillers, that is the composites with 1 μm particles and the composites with 0.2 wt % of smaller particles, exhibited improved toughness, reflected in the increase of U. σ_b and ε_b of the latter were at the same level as for neat PP. The composites with 5 wt % of particles with R_{av} up to 250 nm exhibited the highest E, exceeding by 40 % that of neat PP. T_c of PP matrix in the composites increased by up to 6 °C in comparison to that of neat PP, although the effect depended on the filler grade and content, while T_m and ΔH_m remained unaffected.

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REFERENCES

[1] Bikiaris D.N., Papageorgiou G.Z., Pavlidou E. *et al.*: *Journal of Applied Polymer Science* 2006, *100*, 2684. http://dx.doi.org/10.1002/app.22849

[2] Chan C.M., Wu J.S., Li J.X. *et al.*: *Polymer* **2002**, *43*, 2981. http://dx.doi.org/10.1016/S0032-3861(02)00120-9

[3] Kontou E., Niaounakis M.: *Polymer* **2006**, *47*, 1267. http://dx.doi.org/10.1016/j.polymer.2005.12.039

[4] Wu C.L., Zhang M.Q., Rong M.Z. *et al.*: *Composites Science and Technology* **2002**, *62*, 1327. http://dx.doi.org/10.1016/S0266-3538(02)00079-9

[5] Tjong S.C.: *Materials Science and Engineering: R: Reports* **2006**, *53*, 73. http://dx.doi.org/10.1016/j.mser.2006.06.001

[6] Tjong S.C., Bao S.: *E-Polymers* **2007**, *7*, 1618. http://dx.doi.org/10.1515/epoly.2007.7.1.1618

[7] Dolmatov V.Y.: *Journal of Superhard Materials* **2007**, *29*, 1. http://dx.doi.org/10.3103/S1063457607010017

[8] Dolmatov V.Y.: *Journal of Superhard Materials* **2007**, *29*, 65. http://dx.doi.org/10.3103/S1063457607020013

[9] Dolmatov V.Y.: *Journal of Superhard Materials* **2007**, *29*, 199. http://dx.doi.org/10.3103/S1063457607040016

[10] Attia N.F., Rao J.P., Geckeler K.E.: *Journal of Nanoparticle Research* **2014**, *16*, 2361. http://dx.doi.org/10.1007/s11051-014-2361-y

[11] Jahromi F.H., Katbab A.A.: *Journal of Applied Polymer Science* **2012**, *125*, 1942. http://dx.doi.org/10.1002/app.36299

[12] Karbushev V.V., Semakov A.V., Kulichikhin V.G.: *Polymer Science Series A* **2011**, *53*, 765. http://dx.doi.org/10.1134/S0965545X11090057

[13] Neitzel I., Mochalin V., Knoke I. *et al.*: *Composites Science and Technology* **2011**, *71*, 710. http://dx.doi.org/10.1016/j.compscitech.2011.01.016

[14] Jee A.Y., Lee M.: *Journal of Nanoscience and Nanotechnology* **2011**, *11*, 533. http://dx.doi.org/10.1166/jnn.2011.3290

[15] Jee A.Y., Lee M.: *Current Applied Physics* **2011**, *11*, 1183. http://dx.doi.org/10.1016/j.cap.2011.02.016

[16] Zhao Y.Q., Lau K.T., Kim J.K. *et al.*: *Composites: Part B: Engineering* **2010**, *41*, 646. http://dx.doi.org/10.1016/j.compositesb.2010.09.003

[17] Li J.X., Cheung W.L., Jia D.M.: *Polymer* **1999**, *40*, 1219. http://dx.doi.org/10.1016/S0032-3861(98)00345-0

[18] Singh N., Rashmi, Sarkar A.K.: *Journal of Material Science* **2004**, *39*, 1665. http://dx.doi.org/10.1023/B:JMSC.0000016167.67249.ac

[19] Zuiderduin W.C.J., Westzaan C., Huetink J. *et al.*: *Polymer* **2003**, *44*, 261. http://dx.doi.org/10.1016/S0032-3861(02)00769-3

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