PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 3, 03CNN20(4pp) (2012)

Effect of Nano-Al_3Mg_2 Addition on the Microstructure of PEEK Nanocomposite Bulk Samples Consolidated from Mechanically Milled Powders

Ashkan Zolriasatein*, Ali Shokuhfar, Mehdi Alzamani

Advanced Materials and Nanotechnology Research Lab, Faculty of Mechanical Engineering, K. N. Toosi University of Technology, Tehran, Iran

(Received 22 June; published online13 August 2012)

In this investigation, the effect of the novel nano-Al_3Mg_2 particles addition on the microstructure of polyetheretherketone (PEEK) polymer matrix nanocomposite was studied. Bulk nanocomposite samples were fabricated by consolidation of ball milled composite powders through hot pressing method. The structural evolutions of mechanically milled powders as well as consolidated nanocomposites were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with an energy dispersive X-ray analyzer (EDX). The results showed that, although increasing the amount of ß-Al_3Mg_2 nanoparticles up to 5 vol. % results in no chemical interaction, a low degree of PEEK crystallization, reduction in powder particle size, homogeneous distribution and well bonding of nanoparticles in the PEEK matrix but the tendency for agglomeration and porosity formation increases in comparison with 3 vol% of ß-Al_3Mg_2.

Keywords: Nanocomposite; Mechanical milling; Hot pressing; Microstructure.

PACS numbers: 81.20.Ev, 82.35.Np

1. INTERODUCTION

Polyetheretherketone (PEEK) is among the high performance semi-crystalline thermoplastics with remarkable physical and mechanical properties namely high strength, modulus, toughness, and wear resistivity. Furthermore, PEEK exhibits significant thermal stability and chemical resistivity which makes it appropriate for industrial and biological applications [1], in addition to its high melting temperature of 350 °C and glass transition temperature of about 143 °C [2].

In recent years, various inorganic nanoparticles, e.g., Si_3N_4 [3] modified and unmodified surface SiO_2 [4-6], Al_2O_3 [7] SiC [8] were used as a nano filler in PEEK resin or powder in order to achieve significant enhancement in physical and mechanical properties of nanocomposites. Nano fillers have much higher surface area to volume ratio in comparison with micro fillers, which results in more extended interfaces between filler and matrix.

Complex metallic Alloys (CMAs) are a new category of intermetallics which are characterized by their giant unit cells comprising tens up to thousands of atoms, high structural complexity and large lattice parameters [9,10]. CMAs can be novel candidates for reinforcing metal matrix and polymer matrix composites. Scudino et al. [11] propound an idea for applying CMA materials as a new reinforcement in aluminum matrix composites (AMCs). There is a little work on the effects of these novel reinforcements on the structural and mechanical behavior of metal matrix nanocomposites (MMNCs) and specifically using CMA nanoparticles in the field of PMNCs is completely new. ß-Al_3Mg_2 has a complex structure with lattice parameter of 2.8 nm containing approximately 1168 atoms arrange in a cluster substructure [12,13]. This unique structure leads to exclusive physical and mechanical behaviors. ß-Al_3Mg_2 with the low density of 2.25 g.cm^{-3}, the low surface energy and the high strength [14,15] represents satisfying technological potential as reinforcing agent in polymer matrix nanocomposites.

Agglomeration tendency of nanoparticles particularly in a polymeric matrix is one of the inevitable drawbacks to nanocomposites which impair composite properties. Different technical methods were used for achieving a homogeneous dispersion and distribution of the nano-fillers in the matrix such as solution intercalation [16] and latex precompounding [17, 18]. These routes are mostly based on solving or melting the polymeric matrix and dispersion of the filler in the liquid, but PEEK has poor solubility in solvents and has good resistance to most organic solvents [19]. Furthermore PEEK has relatively high melting temperature (340°C) and it is difficult to fabricate its composites in the molten or solution states. Hence, solid state processing such as ball milling techniques is an appropriate route for improving the dispersion state of nano filler in the PEEK matrix. Recently, researchers have been co-milled SiO2 [20,21] nanoparticles with PEEK powder through ball milling technique to progress and modify the microstructure and the mechanical properties of PEEK matrix nanocomposites.

In our previous works [22, 23] synthesizing of aluminum matrix nanocomposites reinforced with ß-Al_3Mg_2 nanoparticles has been done through the ball milling technique and the results have been proved that mechanical behavior is improved continuously by adding nanoparticles due to the uniform distribution of nanoparticles which can been achieved thorough a mechanical milling process. The low melting temperature of ß-Al_3Mg_2 (about 452°C) can be considered as a demerit for high temperature applications such as aluminum matrix composites, but for polymer matrix and particularly PEEK matrix composite these lightweight fillers can be appropriate selections.

The main purpose of the present study is to synthesis novel PEEK/ß-Al_3Mg_2 nanocomposite by planetary ball milling and hot pressing and then characterization of the effects on the microstructure.

* a.zolriasatein@dena.kntu.ac.ir

2. EXPERIMENTAL

PEEK powders with an average particle size of 2 µm and spherical morphology were used as the matrix material as shown in Fig. 1a. ß-Al_3Mg_2 nanoparticles with average particle size of 25 nm were used as reinforcement agent. ß-Al_3Mg_2 nanoparticles were produced by 100 h mechanical milling of the crushed and pulverized pre-alloyed Al-37.6wt.%Mg intermetallic ingot. A bright-field TEM micrograph of the ß-Al_3Mg_2 nanoparticles with corresponding selected area electron diffraction pattern is presented in Fig. 1b. As it can be seen, the size of the nanoparticles is in the range of 15 to 30 nm. Fig. 2 shows X-ray diffraction pattern of the nanoparticles representing nanostructured model of ß-Al_3Mg_2 intermetallic.

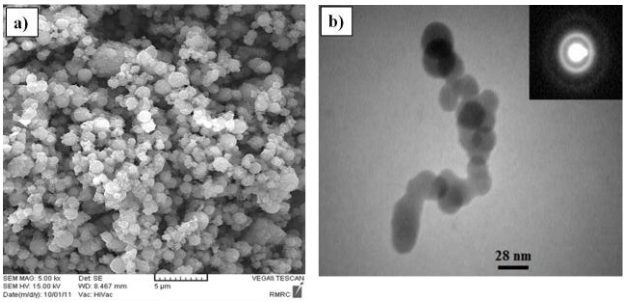

Fig. 1 – a) SEM micrograph of the PEEK powder used as matrix of nanocomposite powder mixtures. b) TEM micrograph of the ß-Al_3Mg_2 nanoparticles used as nano-filler produced by 100 h milling of pre-alloyed intermetallic ingot.

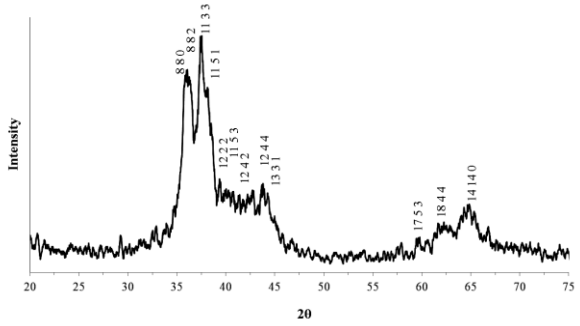

Fig. 2 – X-ray diffraction pattern of the ß-Al_3Mg_2 nanoparticles used as nano-filler

The mixtures of PEEK powder with different amounts (0, 1, 3 and 5 vol. %) of pre-alloyed ß-Al_3Mg_2 nanoparticles were milled in planetary ball mill (Fritsch pulverisette-6) for 15 h. About 10 g of each mixture was charged in a stainless steel vial containing eight 30mm balls. The milling vial was sealed and filled with Argon gas before milling. The ball to powder ratio used for milling was 26:1 and a rotating speed of 300 rpm had been employed. Consolidation of milling products and pure PEEK powders was done by a laboratory hot pressing at 350 °C and 20 MPa for 10 min in a cylindrical mould. Afterwards, mould was cooled to under glass transition temperature of PEEK in air. The molded samples were about 10 mm in diameter and 20 ± 0.5 mm in height.

XRD patterns of nanoparticles, as-received, milled and molded pure PEEK and nanocomposites were recorded on Philips XPert PANalytical PW 3040/60 in order to qualitatively investigate the phases and the structure evaluations. XRD data were obtained by using CuKα radiation of wavelength 1.54 A, operating at 40 kV and 30 mA. Microstructure characterizations of initial powders, ball milled mixtures and polished cross-section of consolidated samples were carried out using scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) Vega II Tescan analysis and transmission electron microscopy (TEM) ZEISS.

3. RESULTS AND DISCUSSION

X-ray diffraction was performed in order to study phase and structural evaluations during milling and hot pressing of PEEK powder and PEEK matrix nanocomposite powders. As shown in Fig.3a the as-received PEEK has an amorphous structure and after milling for 15 h the crystallinity decreases which corresponds to reduction of peak intensity (Fig.3b). Since semi-crystalline PEEK suffers from strong shear deformation during mechanical milling, the change in width and height of peak with milling could be related to change toward lower crystallinity of semi-crystalline PEEK. In fact a higher degree of amorphization can form in semi-crystalline PEEK with mechanical milling. Similar studies have been reported that the milling process leads to decreasing of crystalline order [24, 25].

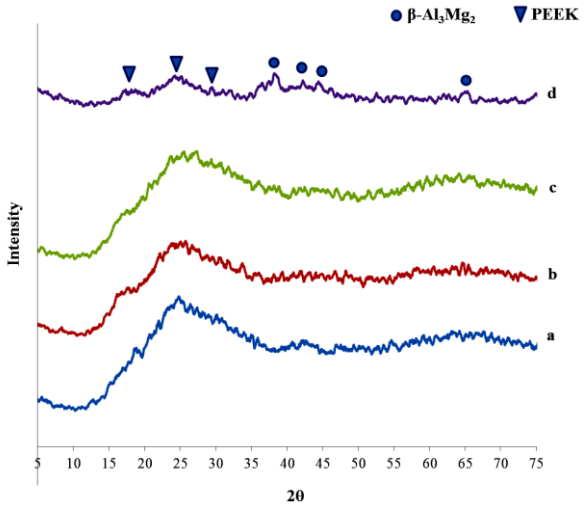

Fig. 3 – X-ray diffraction patterns of the a) as-received and b) millied PEEK powder for 15 h, c) as-milled and d) hot pressed PEEK nanocomposites powder filled with 5 vol. % ß-Al_3Mg_2

With the addition of 5 vol.% of ß-Al_3Mg_2 nanoparticles, no detectable extra peak was created or disappeared in comparison with those of the pure milled PEEK, which can obviously be seen in Fig.3c .The ß-Al_3Mg_2 diffractions are too low to be resolved in XRD. There are only four low intensity diffraction peaks of ß-Al_3Mg_2 and there is no extra peak created or disappeared in comparison with those of the pure PEEK and it reveals that there is no apparent interaction that would result in appreciable new interfacial phases, as well as the nanofillers did not change the crystal structure of PEEK.

According to Fig. 3d, after hot pressing of nanocomposite powder, crystallization occurred in PEEK matrix

since some small peak of PEEK crystallites such as (110), (200) and (211) forms in diffraction. It was reported that the crystal structure of the PEEK polymer is orthorhombic structure, and there are four main diffraction peaks appeared in the XRD patterns at about 18.7°, 20.8°, 22.9° and 28.9° corresponding to diffraction planes of (110), (111), (200) and (211) [7]. For the nanocomposites with 5 vol.% fraction of nanoparticles, a lower degree of crystallization is probable to occur, since the PEEK matrix filled with abundant nanofillers may decrease the mobility of the polymer chain segments during the period of crystallization [19].

Fig.4. shows SEM micrographs of the as-received (Fig.4a) and mechanically milled (Fig.4b) PEEK powders after 15 h of milling times. SEM micrograph of as-received PEEK powder illustrates the spherical particles and as it is expectable, after mechanical milling the PEEK powders severely deformed and the morphology of particles has been changed into flake shape. The particle size fell in the range of 15 and 50 μm due to the agglomeration of the deformed PEEK powders. An agglomerated particle which consists of several deformed PEEK powder is separated in Fig.8b and magnified image is shown in Fig.4c.

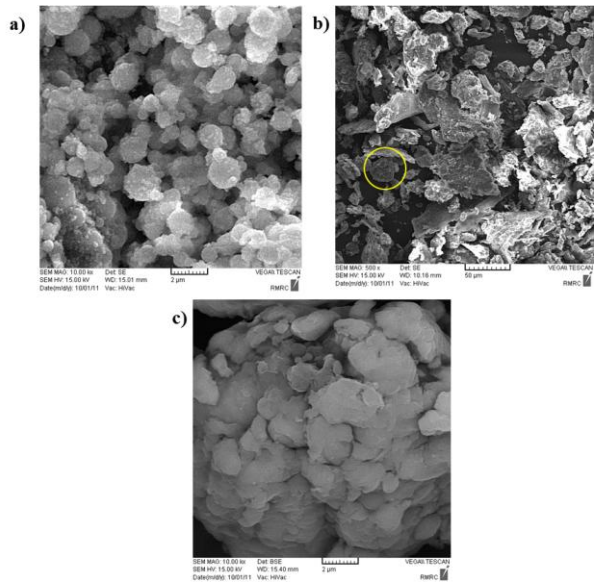

Fig. 4 – SEM images of the a) as-received and b) milled PEEK powders for 15 h. c) Magnification of selected area in (b).

At early stages, spherical particles, the ductile PEEK particles, undergo deformation due to severe load applied by ball collision and milling apparatus. As a result, the powders begin to flatten and results in formation of laminated particles. By increasing milling time to the maximum of 15 h, laminated particles agglomerated and consequently, the ductile polymer particles start to weld because of high pressure and locally high temperature and leads to formation of semispherical shape with larger mean particle size[20,26].

The SEM microstructure of PEEK matrix nanocomposite milled for 15 h with different amount of ß-Al_3Mg_2 nanoparticle is presented in Fig. 5. By increasing the amount of nanofiller, from 3 to 5 vol.% the mean particle size decreases and smaller nanocomposite particle are formed during mechanical milling.

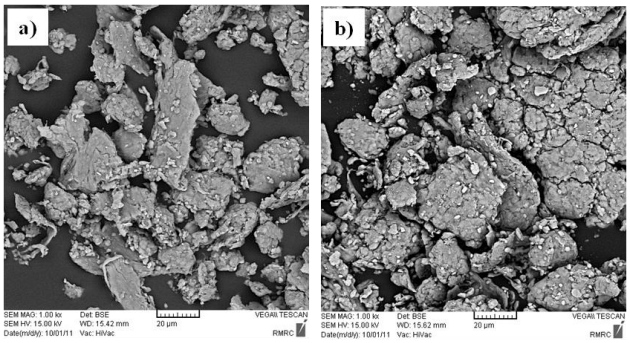

Fig. 5 – SEM micrographs of the PEEK matrix nanocomposite powder mixture filled with a) 3 vol.%, and b) 5 vol.% ß-Al_3Mg_2 nanoparticle after milling for 15 h.

Nanoparticle smears the surface of PEEK particles, in this circumstance, matrix particles are surrounded by nanoparticles and these phenomena leads to prevent the occurrence of cold welding, therefore the nanocomposite particles size decreases.

Fig. 6 represents the SEM microstructures and the corresponding X-ray mappings for Mg and Al concentrations of the consolidated PEEK matrix nanocomposites containing various amounts (3 and 5 vol.%) of nanoparticles. Mg and Al concentrations are the evidence for presence of ß-Al_3Mg_2 nanoprticles in PEEK matrix.

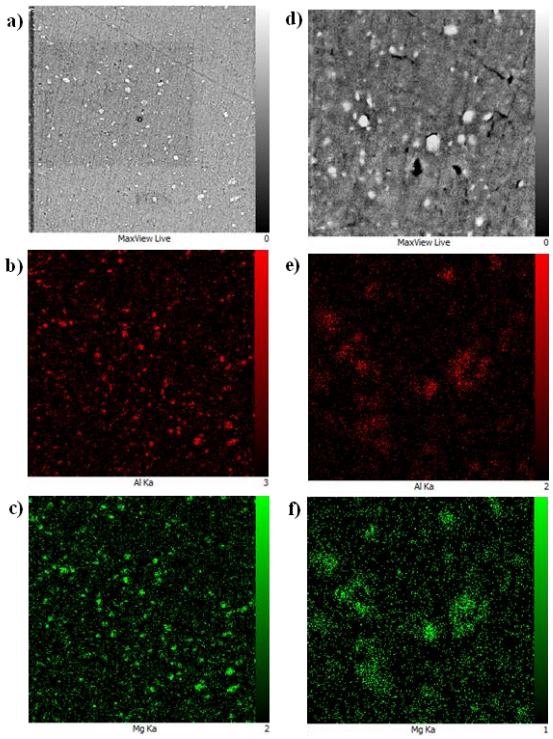

Fig. 6 – EDX map analyses of Al and Mg elements from the polished surfaces of consolidated samples of PEEK nanocomposites containing (a-c) 3 vol.% ß-Al3Mg2 and (d-f) 5 vol.% ß-Al3Mg2 nanocomposites.

X-ray mappings show the formation of uniformly distributed ß-Al_3Mg_2 nanoparticles in the matrix for both low and high amounts of nanofillers, but there are some micro-sized agglomerates. It can also be concluded from Fig.6 that there is a tendency to clustering of filler for higher amount of nanoparticle (5 vol.%) (Fig. 6 d-f). On

the other hand, more porosity is formed in the samples containing higher amounts of reinforcement. Since the nanocomposite powder mixtures are hot pressed at constant pressure, therefore it can be concluded that nanoparticles decrease the densification and compressibility of powders mixture by strengthening of the nanocomposite and augmentation of the powder surface area.

SEM micrograph of the polished surface of milled and hot pressed PEEK/3 vol.% ß-Al_3Mg_2 and PEEK/5 vol.% ß-Al_3Mg_2 nanocomposites are shown in Fig. 7. As indicated from backscattered electron image (BSE) which is sensitive to atomic number (Z), nanoparticles (indicated by arrows) embedded in PEEK matrix and well-bonded to the matrix. Agglomerated nanoparticles seems brighter correlates with greater average Z in the nanocomposite microstructure and PEEK matrix with lower average Z seems as dark areas.

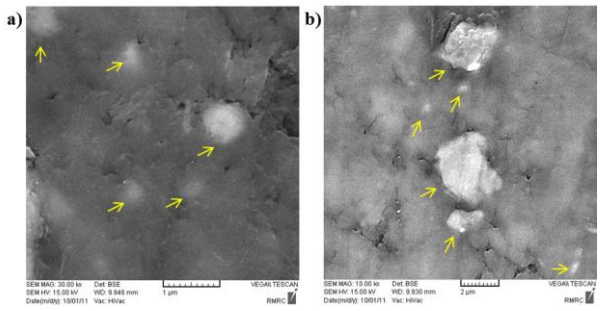

Fig. 7 – BSE SEM microstructure of the polished surfaces of PEEK/ß-Al_3Mg_2 nanocomposites filled with a) 1 vol.%, and b) 5 vol.%, hot pressed at 350 °C under pressure of 20 MPa

4. CONCLUSION

Based on microstructural characterization of milled powder as well as consolidated samples it can be concluded that:

1. Mechanical milling can lead to severe deformation and morphological change as well as increasing the degree of amorphization in semi-crystalline PEEK structure. Larger particles, which consist of flakey agglomerated particles formed due to cold welding of deformed particles.
2. The Addition of ß-Al_3Mg_2 nano-filler to the PEEK powder results in no chemical interaction during but the presence of nanofiller can lead to a low degree of PEEK crystallization.
3. Increasing the amount of ß-Al_3Mg_2 nanoparticles up to 5 vol. % can lead to the reduction in nanocomposite particle size by preventing PEEK particle cold welding.
4. PEEK/3 vol.% ß-Al_3Mg_2 nanocomposite bulk sample has a homogenous distribution and well bonding of nanoparticles in the PEEK matrix. The tendency for agglomeration and porosity formation increases as the volume ratio of nanoparticles (5 vol. %) increases.

ACKNOWLEDGEMENT

The authors would like to thank the supports from K. N. Toosi University of Technology and Iran Nanotechnology Initiative Council (INIC).

REFERENCES

1. X.-M. Chen, S.-H. Song, L.-Q. Weng, S.-J. Liu, K. Wang, *Mater. Sci. Eng. A* **528**, 8299 (2011).
2. G. Pan, Q. Guo,W. Zhang, A. Tian, *Wear* **266**, 1208 2009).
3. Q. Wang, J. Xu, W. Shen, W. Liu, *Wear* **196**, 82 (1996).
4. Q.Wang, Q. Xue, W. Shen, *Tribol. Int*. **30**, 193 (1997).
5. M.C. Kuo, J.S. Kuo, M.H. Yang, J.C. Huang, *Mater. Chem. Phys.* **123**, 471 (2010).
6. Y.H. Lai, M.C. Kuo, J.C. Huang, M. Chena, *Mater. Sci. Eng. A* **458**, 158 (2007).
7. R.K. Goyal, A.N. Tiwari, U.P. Mulik, Y.S. Negi, *Compos. Sci. Technol.* **67**, 1802 (2007).
8. Q. Wang, J. Xu, W. Shen, Q. Xue, *Wear* **209**, 316 (1997).
9. K. Urban, and M. Feuerbacher, *J. Non-Cryst. Solids*, **334-335**, 436 (2004).
10. E.B. lin-Ferré, Basics of thermodynamics and phase transitions in complex intermetallics (World Scientific: 2008).
11. S. Scudino, G. Liu, M. Sakaliyska, et al., *J. Acta Mater.* **57**, 4529 (2009).
12. J.L. Murray, *Phase diagrams of binary magnesium alloys* (Ohio: ASM International; 1988).
13. W. Sikora, J. Malinowski, A. Kuna, L. Pytlik, J. *Phys.: Conf. Ser.* **104**, 012023 (2008).
14. M.L. Chwa1ek, S.Balanetskyy, C.Thomas, S. Roitsch, M. Feuerbacher, *Intermetallics* **15**, 1678 (2007).
15. N. Diomidis, N.Goçkan, P. Ponthiaux, F. Wenger, J.P. Celis, *Intermetallics* **17**, 930 (2009).
16. D. Ratna, S. Divekar, A.B. Samui, B.C. Chakraborty, A.K. Banthia, *Polymer* **47**, 4068 (2006).
17. S. Siengchin, J. Karger-Kocsis, R. Thomann, *J. Appl. Polym. Sci.* **105,** 2963 (2007).
18. S. Siengchin, J. Karger-Kocsis, A.A. Apostolov, R. Thomann, *J. Appl. Polym. Sci.* **106**, 248 (2007).
19. M.C. Kuo, C.M. Tsai, J.C. Huang, M. Chen, *Mater. Chem. Phys.* **90**, 185(2005).
20. M. Hedayati, M. Salehi, R. Bagheri, M. Panjepour, A. Maghzian, *Powder Technol.* **207**, 296 (2011).
21. G. Zhang, A.K. Schlarb, S. Tria, O. Elkedim, *Compos. Sci. Technol.* **68**, 3073 (2008).
22. A. Zolriasatein, A. Shokuhfar, M. Ghadimi, et al., *Physics, Chemistry and Application of Nanostructures* (Singapore: World Scientific: 2011).
23. R. A. Khosroshahi, A. Zolriasatein, M. Emamy, N. Nemati, *Adv. Mat. Res.* **445**, 827 (2012).
24. M. Liang, C. Lu, Y. Huang, C. Zhang, *J. Appl. Polym. Sci.* **106**, 3895 (2007).
25. J. Font, J. Muntasell, E. Cesari, *Mater. Res. Bull.* **36**, 1665 (2001).
26. C. Suryanarayana, *Prog. Mater. Sci.* **46**, 1 (2001).