FABRICATION OF PP/AL2O3 SURFACE NANOCOMPOSITE VIA NOVEL FRICTION STIR PROCESSING APPROACH

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ABSTRACT
In the present study, a novel friction stir processing method was utilized to produce surface PP/Al_2O_3 nanocomposite. This approach is a new variant of friction stir processing technology. A new tooling system has been devised which include rotating pin, stationary shoulder and a close-loop heating section. The volume percentage of nano Al_2O_3 particles ranged from 5% to 15% in polypropylene matrix. From microscopic observations, it was clear that the distribution of reinforcing particles was uniform in polypropylene matrix. Moreover, tensile and micro-hardness tests have been utilized to investigate the mechanical properties of prepared samples in different volume percentages. It has been observed that the samples with high percentage of nano Al_2O_3 powder show higher micro-hardness number as well as higher ultimate tensile strength. Furthermore, it was found that distribution of reinforcement particles has magnificent effect on mechanical properties of fabricated surface composites.

KEYWORDS: *Nanocomposite, PP/Al_2O_3, Friction stir processing, Mechanical Properties*

I. INTRODUCTION

Polymers have extensive applications in aeronautics, automobiles, constructions, oil and gas industries, and so on. Polypropylene (PP) is one of these materials that widely used in automotive industry and electronic applications due to its good performance, high strength to weight ratio and excellent processing properties as well as low cast. However, its application is somewhat limited due to its weak abrasive properties, relatively poor impact resistance at room or low temperatures and low hardness [1-5]. The use of inorganic fillers has been a common practice in the plastics industry to improve the mechanical properties of thermoplastics, such as heat distortion temperature, hardness, toughness, stiffness, and mould shrinkage. Therefore, so much attention has been paid to improve the mechanical properties of PP thermoplastic in the last few decades [5]. The effects of filler on the mechanical and physical properties of the composites strongly depend on its shape, particle size, aggregate size, surface characteristics and degree of dispersion. In general, the mechanical properties of composites filled with micron-sized filler particles are inferior to those filled with nano particles of same filler [6,7]. Nano particles are entities with diameters in the range of 1–100 nm. When nano particles are embedded in polymer, the resulted composite material is known as polymer nanocomposite. Recently, the methods utilized for preparation of nanocomposites and properties of manufactured nanocomposite are much under attention [8]. Among reinforcement utilized to modify mechanical properties, alumina (Al_2O_3) has received large interest because of its excellent dielectric properties, good thermal conductivity, high strength, and resistance to strong acid and bases even at elevated temperatures [9].

In last few years, much attention has been paid to a new surface modification technique named friction stir processing (FSP) [10-13]. FSP is a solid-state processing technique, which was developed based on friction stir welding (FSW) [13]. The main aim of this process is to obtain a fine–grained microstructure and it has been advanced as a grain refinement technique. Moreover, it is a very attractive process for fabricating surface composites [14]. As mentioned above friction stir processing of metallic materials is a solid-state technique and temperature of material does not reach to its melting point. However, friction stir processing of polymeric materials is not a solid-state process because polymers consist of molecules of different lengths and the materials do not have single melting point, but melting ranges. Thus, as FSP applied to polymeric materials, some shorter chains reach their melting point while longer chains do not. Therefore, bits of solid material are suspended in enough molten material to render the mixture easy to move and form. Another problem that occured during friction stir processing is to promote uniform cooling rate throughout the processing zone. If outer layer of a plastic sheet cools much quicker than inner, a hard shell is formed. As the inner layers then cool, the material contracts and pulls away from the shell. So, large voids will be formed which remarkably reduce the mechanical properties of fabricated composite. For this reason friction stir processing of these materials requires additional cares.

In this study, an attempt has been made to investigate the mechanical properties of nano-alumina filled PP via a new variant of friction stir processing technique and three volume percentages of nano-powder in polymeric matrix has been compared in mentioned properties. The method used in the present work utilizes friction stir processing concept in which a heating system is added to process for promote a uniform cooling rate which significantly affects the mechanical and microstructural properties of these materials. The designed tool is consists of a shoe, a rotating pin and a heater, which located at the back of pin. It provides the mixing and joining of plastic parts together in the presence of heat. The shoulder is stationary relative to pin, whereas in FSW and FSP of metals the shoulder rotates with the pin. The tooling system is shown in figure 1. Tensile and microhardness tests were carried out to evaluate mechanical properties of fabricated nanocomposites. Furthermore, in order to make a judgment about the dispersion state of alumina particles in the system, produced samples has been studied by light and electron microscopy.

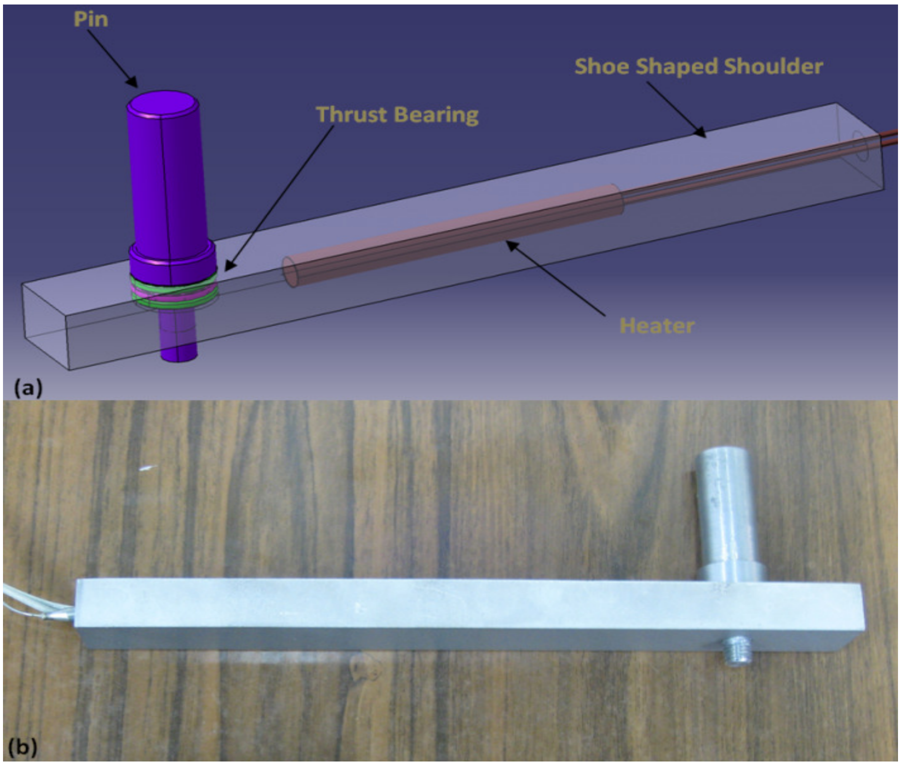

Figure 1. Picture of designed tool for FSW of polymers: a) Schematic illustration b) Photograph of tool

II. EXPERIMENTAL WORKS

Polypropylene sheets utilized were commercial grade and supplied from Germany Company. The Al_2O_3 powder used in this work has particle size <90 nanometer, which packaged by Nano Pars Lima Chemical Company in Iran. In order to produce PP/Al_2O_3 nanocomposite, alumina particles were contrived in a groove with various dimensions in the middle of samples. Then the Al_2O_3 particles were compressed into the groove. It is important to note that various groove dimensions result in different volume fraction of alumina powder in nanocomposites. Volume fraction of particles was estimated by dividing the amount of particles in the slot and area over which it was distributed in the matrix [15]. The final stage is plunging of tool with pin inside the plate for producing nanocomposite. In contrast to conventional friction stir processing technique, in this novel approach there isn't any requirement to close material upper surface with a FSP-shaped tool (this tool is similar to FSP tool but there isn't any pin on it) which prevents outpouring of particles, because the tooling system has a shoe shape shoulder that provide this purpose. In the other words, with utilizing this tooling system one of the friction stir processing steps could be eliminated. This mechanism in turn saves the production time and lessens the costs. The photograph of tooling system is shown in figure 1.

The tool used is consists of a shoulder which is look like a shoe, a rotating pin and a heater which located at the back of pin. Additionally, a specially designed fixture was utilized to assure that the tool works in its best performance and keep shoulder stationary relative to pin (Figure 2). Furthermore, the shoulder surface was coated with PTFE. The main role of pin is to produce frictional heat for softening the workpiece and stirring material within the joint. The tool's shoulder is similar to a shoe, which is utilized to contain the displaced material and hold it on the sheet, while it is cooled. A heater, equipped with a closed-loop thermo-controller, is primarily responsible for providing a uniform cooling rate.

Figure 2. producing of Al_2O_3/PP nanocomposite via novel friction stir processing technique

Samples' thickness, width and length were 10mm, 100mm and 300mm, respectively. The tool pin was made of H13 hot worked steel but shoulder's material was made of 7075 aluminum alloy due to its high thermal conductivity and stability in elevated temperatures. Pin diameter and length were 9 and 6 mm respectively and threaded with standard pitch. The shoulder's width and length were 28 and 250 mm, respectively. A thrust bearing separated the pin from the shoulder and its main purpose was to hold the shoulder stationary relative to pin. Transverse speed of tool, pin rotational speed and shoulder temperature were 1000 rpm, 50 mm/min and 190˚c, respectively. To ensure that shoulder applies enough pressure on work pieces, a tool-offset depth is required during plunge step of the process. The optimum value of 0.5 mm was achieved for plunge depth through experimental tests. It is worth noting that a dwell time is necessary to start the process. Contact of the pin with the workpiece creates frictional heating and softens the workpiece material; contacting the shoe shaped shoulder to the workpiece increases the workpiece heating, expands the zone of softened material. In general, this step is necessary to heat the material in order to create a pool of semi-molten polymer.

In present study, Al_2O_3/PP nanocomposites were produced in three different Al_2O_3 percentages, PP-5% Al_2O_3, PP-10% Al_2O_3 and PP-15% Al_2O_3 by making 3 grooves with 1*2.8, 2*2.8 and 3*2.8mm dimensions, respectively. Tensile tests were performed by Zwick/Roll (model TIFR010THA50) device with autograph capability and samples were extracted from each welded part in accordance with ASTM D 638 standard. The three specimens were obtained for evaluating properties of each sample. These tests were conducted at a crosshead speed of 50 mm/min. In addition, the micro-hardness properties of the produced composites were measured on the cross section of processed zone and perpendicular to the processing direction with Struers-Duramin device. For this purpose, an indenter with a 100 g load for 15 s on a standard Vickers micro-hardness tester had been utilized. The standard Vickers micro-hardness (H) was determined by the equation [16]:

$$\mathbf{H=KP/d^2} \qquad (1)$$

Where **P** is the applied load, **k** is a geometric factor equal to 1.85 and **d** is the mean diagonal length of the imprint after removing the indenter. At least five imprints were made under each load. For making judgment about particles distribution in polypropylene plates, an OLYMPUS, SZ61 Stereo microscope was utilized. For microscopic evaluations, samples were cut through a LEICA RM2135 microtome device.

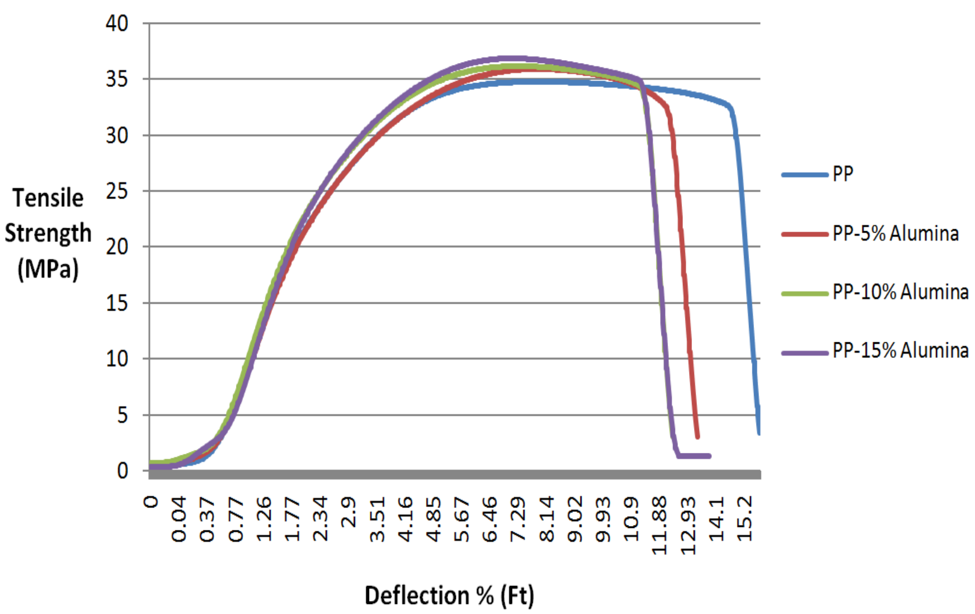

Figure 3. Diagrams of tensile tests of samples with different alumina contents

Table 1. Data obtained from tensile test of fabricated nanocomposites in different volume percentage

Sample	PP	PP+5%Al_2O_3	PP+10%Al_2O_3	PP+15%Al_2O_3
Young's modulus (MPa)	1491	1378	1430	1493
Ultimate Strength (MPa)	34.7	35.8	36.2	36.9
Deflection %(Ft)	14.7	13.3	12.5	12.4

III. RESULTS AND DISCUSSION

Tensile test results of samples are shown in figure 3. Also table 1 illustrated the date which has been obtained through tensile test. Young's modulus, ultimate tensile strength and percentage of deflection are shown in this table. In all processing conditions, the plunge depth was same and 0.5 mm. In other words, designed tool is operated with about 0.5 mm of the tool on contact with the workpiece; any additional workpiece contact will produce significant amount of flash around the shoe. As the penetration depth of tool shoulder increases, more pressure applied to the material exists at the surface of sheets. Since these surface materials are completely melted, increasing pressure will results in outpouring of them from weld nugget, consequently leads to thickness reduction. Therefore, tensile strength decreases due to stress concentration in this area. If the penetration depth is selected lower than 0.5 mm, the shoulder will ride on a cushion of material that will smear across the joint line, which in turn lead to low quality joints. From Figure.3 and Table 1, it is clear that increasing volume fraction of Al_2O_3 nanopowder leads to an enhancement in ultimate tensile strength of samples. Comparing tensile propeties of samples with 15% alumina with pure polypropylene, it can be inferred that ultimate tensile strength of fabricated nanocomposite shows about 10% enhancement. This can be explained as follows: As Al_2O_3 powder incorporated to polymer matrix, the polymer chains had not enough space and time to orientate which results in a material with shorter molecular chains and consequently reduction of mechanical strength is occurred. On the other hand, addition of a reinforcement material such as alumina powder to the matrix of a polymer can increase tensile properties due to nucleating effect of this particles. As polypropylene cools, in crystallization step existense of nucleating particles like alumina will cause to a reduction in sperulite size and therfore an enhancement in tensile strength. From above mentined points it is clear that in fabricated composites via this method the second mechanism has dominant effect on mechanical properties. However, this second phase generally reduce the alongation because of poor interface bonding between polymeric matrix and reinforcement. So, there is a general trend of decreasing elongation as volume fraction of alumina powder increases.

The obtained micro-hardness values of produced PP/Al_2O_3 nanocomposites are reported in figure 4 in terms of Al_2O_3 contents. According to the results, a 54% increase was observed in the case of micro-hardness values of the nanocomposites with 10% nano alumina powder. The high values of micro-hardness obtained by this method could be attributed to the good dispersion and higher level of nano alumina particles, which is known as hard materials in polymeric matrix. Figure 5 that shows microstructure of PP+10%Al_2O_3 nanocomposite that was taken through Stereo microscope are a proof to above-mentioned statement. Furthermore, it is obvious that in samples with alumina percentage above 10% agglomeration of nano powder is responsible for a little reduction in micro-hardness value

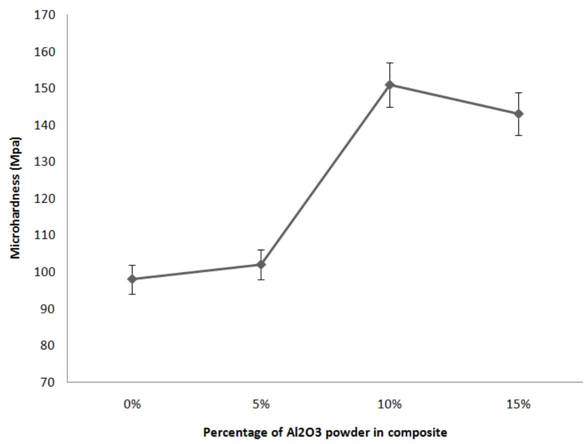

Figure 4. Micro-hardness of fabricated composites in different nano-alumina contents

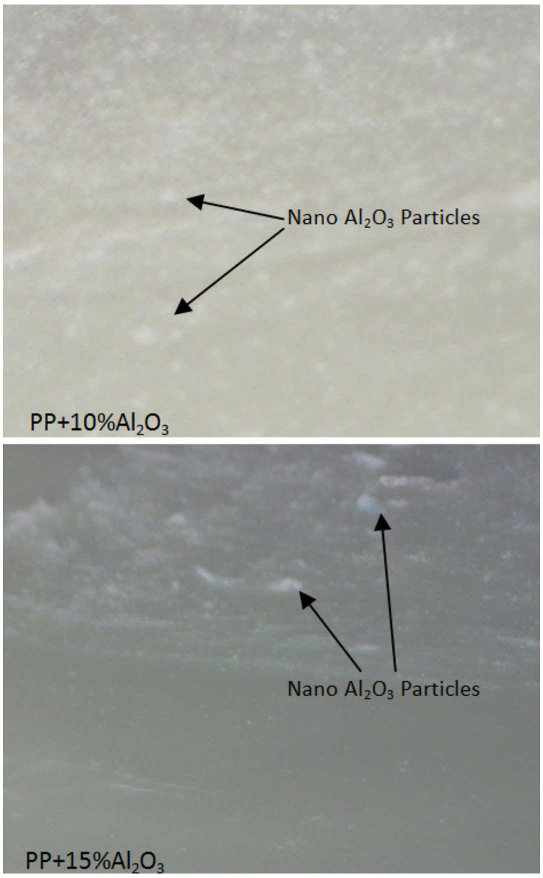

Figure 5. Microscopic observation of fabricated nanocomposites

Figure 6 is demonstrated the SEM images of fabricated nanocomposites in different volume percentage. The images have been taken in two different magnifications (300 and 1 µm scales). Good distribution of particles in polymeric matrix is one the main criteria during fabricating of nanocomposites by various technique. Figure 6. A. is shown the nanocomposite with 5% of Al_2O_3 volume percentage. From this figure it is obvious that particles are distributed uniformly in PP matrix. Although, in some regions there are some bonding between alumina and polypropylene, this in turn demonstrated nanocomposite formation in its best form. In some processing techniques that utilized to produce polymeric nanocomposite, formation of small voids around reinforcement particles is a drawback to achieve high mechanical properties. However, according to SEM images, there is not any void inside processing zone, which is a major reason to improved tensile and micro-hardness properties. It is worth to mention that in nanocomposite with high volume percentage of alumina powder agglomeration phenomenon was occurred that resulted in a reduction in mechanical properties. This can be clearly seen in figure 6. F.

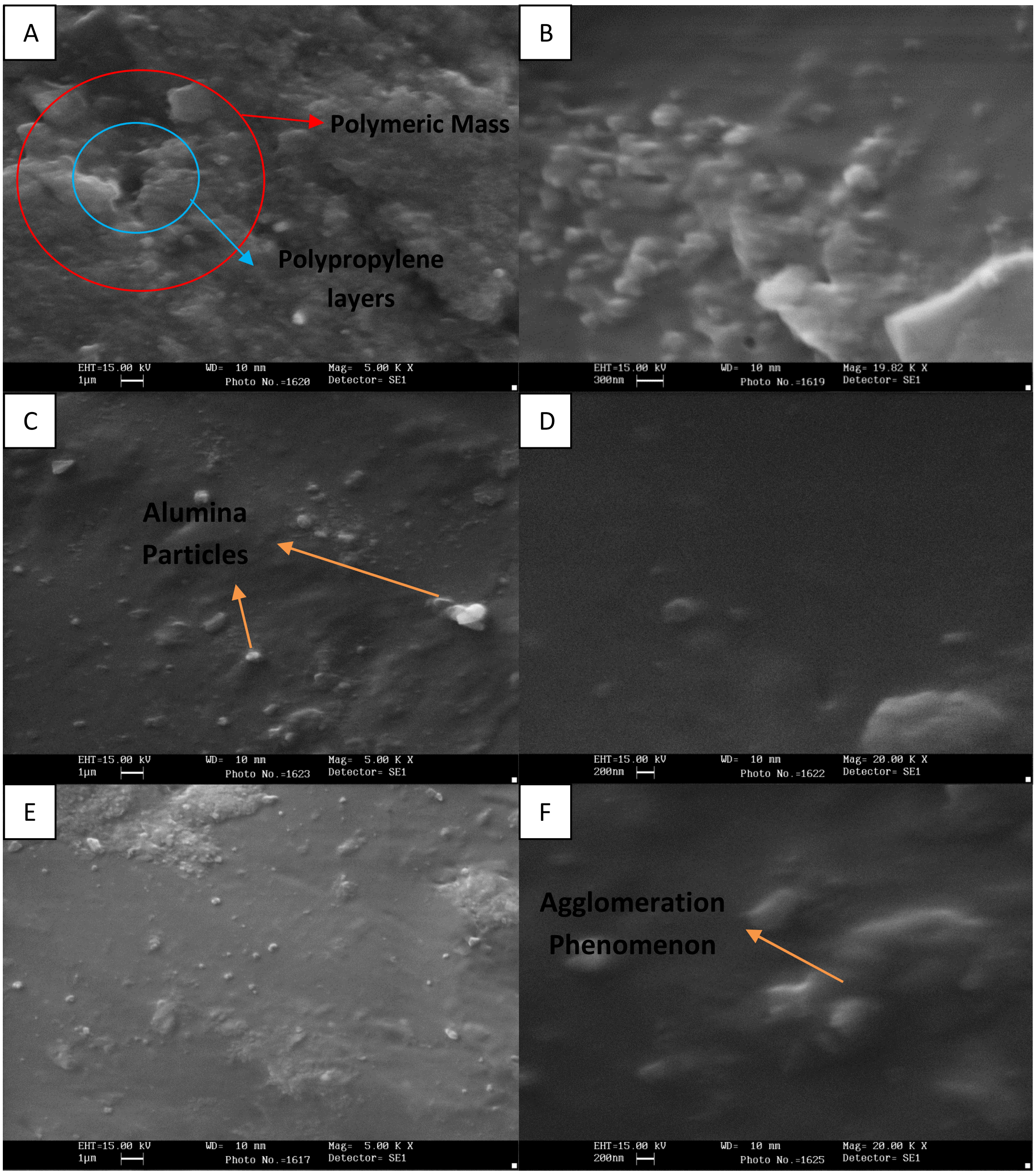

Figure 6. Scanning electron microscopy of fabricated nanocomposites a) PP- 5% Al_2O_3 with 1µm scale b) PP-5%Al_2O_3 with 300 ηm scale c) PP- 10% Al_2O_3 with 1µm scale d) PP-10%Al_2O_3 with 300 ηm scale e) PP- 15% Al_2O_3 with 1µm scale f) PP-15% Al_2O_3 with 300 ηm scale

IV. CONCLUSIONS

Taking all above-mentioned discussion into consideration the following conclusion can be drawn about issue: In this study a novel friction stir based method is developed for producing polymeric nanocomposites. Furthermore, it is a very effective method for surface modification of polymers and makes an improvement in mechanical properties of these materials such as tensile strength and hardness value. Comparing with conventional friction stir processing method, designed tooling system leads to a great reduction in manufacturing time because this system eliminate second step of FSP (movement of FSP like tool to close upper surface of samples) and shoe shaped shoulder prevent outpouring of powder during process. A 54% increase in micro-hardness value and 10% enhancement in ultimate tensile strength were observed for the sample with 10% Nano Al_2O_3 content. Good distribution of reinforcement alumina particles is responsible for this enhancement. In fabricated nanocomposites with higher volume percentage agglomeration phenomenon is occurred with leads to a reduction in mechanical properties.

References

[1]. Zhen. J & Ding. YZ & Du. JQ, (2001) *Plast. Proc. Appl,* vol. 23, no. 1, pp. 5-8.
[2]. Zheng. Yp & Wang. B, (2002) "Studies of TiO_2/epox nano composites". *Compos. Mater.*vol. 9, no. 4, pp. 3-11.
[3]. Liang. JZ, (2002) "Toughening and reinforcing in rigid inorganic particle filled polypropylene": a review. *Appl. Polym. Sci.*vol. 83, pp. 1547-1555.
[4]. J.Z. Liang, (2007) " Evaluation of dispersion of nano-$CaCO_3$ particles in polypropylene matrix based on fractal method", *Compsites. Part A,* vol. 38, no. 6, pp. 1502-1506
[5]. Morel. R, (1985) "Handbook of properties of technical and engineering ceramics", part 1: an introduction for the engineer and designer. England, Her Majesty's Stationary Office
[6]. Sumita. M & Shizuma. T & Miyasaka. K & Ishikawa. K, (1983) *Macromol. Sci. Phys.* ;B22:601.
[7]. Sumita. M & Tuskurmo. T & Miyasaka. K & Ishakawa. K, (1983) *Mater. Sci.* ;18:1758.
[8]. Chi. MC & Jingshen. W & Jian. XL & Ying. KC, (2002) "Polypropylene/calcium carbonate nanocomposites", *Polymer, vol.* 43, no.10, pp. 2981-2992.
[9]. H.J. Liu & H. Fuji & K. Nogi, (2004) *Mater. Sci. Technol.* 20 pp. 399-402.
[10]. K. Ohishi & T.R. Mcnelley, (2005) *Metal. Trans.* A 35 A pp. 2951-2961.
[11]. J.Q. Su & T.W. Nelson & C.J. Sterling, (2005) *Scripta Mater.* 52 pp. 135-140.
[12]. D.C. Hofmann & K.S. Vecchio, (2005) *Mater. Sci. Eng.* A 402 pp. 234-241.
[13]. R.S. Mishra & Z.Y. Ma (2003*) Mater. Sci. Eng.* A341 307-310.
[14]. A. Shafiei-Zarghani & S.F. Kashani-Bozorg & A. Zarei-Hanzaki (2009) *Mater. Sci. Eng.* A 500 pp. 84-91
[15]. Uma. Ramadorai & Joseph. W Newkirk & Rajiv S. Mishra (2005) "Modification of aluminium alloys to create In-Situ surface composites", *Proceedings of 19th international conference on surface modification technologies, August 1-3, , St. Paul, Minnesota, USA*
[16]. H. Dong & T. Bell (1999) *Surf. Coat. Technol.* 111pp. 29–40.

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