

Mechanical and Morphological Study of Synthesized PMMA/CaCO₃ Nano composites

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Abstract: In this study, Nano-composites have been synthesized in which PMMA is the matrix material and calcium carbonate nanoparticles as the filler by In-situ polymerization reaction. Nano-CaCO₃ added during polymerization and the quantity of nano-CaCO₃ varied as 0.2, 0.4 and 0.6 wt. % of monomer quantity. The Nano-composites were prepared at three distinct stirring speeds 600, 800, 1000 rpm in order to observe the property with respect to stirring speeds. XRD gram depicts that the presence of nano-CaCO₃ has given crystalline nature to Nano-composites. The effects of different concentrations of nano-CaCO₃ loading on PMMA morphology were studied by using scanning electron microscope (SEM). The mechanical property is increasing with the stirring speed and concentration. Relative to neat PMMA a 62% increase in impact strength were observed in PMMA based Nano-composites using 0.6 wt.% nano-CaCO₃.

Keywords: Impact strength, Nano composites, SEM, XRD

1. INTRODUCTION

Nanocomposites are the materials which have attracted a great research interest in the past decades. They have exhibited improved mechanical properties, such as high strength, toughness and hardness [Alexandros et al 2011]. The final properties of nanocomposites depend upon the methods of mixing of filler material and matrix material, because interface interaction, particles distribution and concentration depend upon method of compounding. In-situ method is generally adopted for synthesis of various inorganic/ Poly (Methyl Methacrylate) (PMMA) nanocomposites, because the type of nanoparticles and the nature of polymer can vary to meet the requirements [Alexandros et al 2011]. Poly (methyl methacrylate) (PMMA) is transparent, hard, stiff, low water absorption and outstanding outdoor weathering properties [Wang et al 2006]. In plastic industry Calcium carbonate (CaCO₃) is used as mineral fillers. It is widely available, easy to reduce to a specific particle size, compatible with a many of polymer resins and economical also. As an additive in plastic compounds, CaCO₃ results in decrease surface energy and provides opacity and surface gloss which finally improves the surface finish. In addition, when the filler particle size is carefully controlled, CaCO₃ helps increase impact strength, tensile strength and flexural modulus (stiffness). So, incorporation of CaCO₃ nanoparticles in the PMMA polymer enhances the mechanical properties due to which these PMMA/ CaCO₃ nanocomposites have wide industrial applications. Much work has focused on



PMMA as the matrix material in polymer matrix composites. PMMA/CaCO₃ nanocomposites were synthesized by several scientists' and researchers for the thermal and mechanical properties. The PMMA/TiO₂ nanocomposites synthesized by in-situ polymerization and found increase in Vickers's micro hardness, strength and modulus by incorporation of 1.25 wt. % TiO₂ in PMMA [Chand et al 2012]. PMMA/silica nanocomposites found increase in tensile strength in comparison to pure PMMA by adding 5 to 10 % wt. fillers [Yang et al 2003]. The work made by another researcher which was with PMMA/ modified CaCO₃ nanoparticles, the results reported in the paper shown both increase in impact strength and tensile strength with respect to pure PMMA by adding up to 1.0 wt.% fillers [Xiaoyu et al 2011]. In conventional polymer composites, micron-size CaCO₃ is used as a filler material that is difficult to disperse in the polymer matrix, which leads to coarsely blended composites and hence agglomeration, poor physical and mechanical properties [Bhanvase et al 2009]. To overcome these problems, a new method has been presented for the synthesis of PMMA/ CaCO₃ nanocomposites by in-situ polymerisation reaction. In this study, nanoparticles of CaCO₃ were added at different stirring speeds during reaction. It has been observed that nano-CaCO₃ is comparatively well dispersed into the matrix at higher speed, due to which mechanical properties shown improvement that may be useful for commercial applications.

2. EXPERIMENTAL SECTION

2.1 SYNTHESIS OF PMMA/CACO3 NANOCOMPOSITES

In this work nanocomposites have synthesized at three different speeds and at every level of speed the concentration of nano-CaCO₃ varied from 0.2, 0.4 and 0.6 wt. % of pure MMA. So, nine different composites have been synthesized along with one pure PMMA for the comparisons of properties. Figure 1 shows experimental setup. Firstly 650 ml of MMA is taken into 1000ml beaker. When the temperature of the water bath reached to 80 then beaker is clamped. Then a fixed quantity of free radical initiator BPO is added and mixed thoroughly by glass rod to initiate the reaction. The speed of the stirrer is adjusted to 600 rpm by speed regulator after that 0.2 wt. % of CaCO₃ nanoparticles added. After that the solution was left for 90 min. under continuous stirring and a constant heat of 80 is provided to complete the reaction. After completion of reaction add content of beaker approx. 250 ml methanol (Non solvent) taken in a 1000ml beaker with mild agitation with glass rod. In the second and third series of experiments, speed of the stirrer changed to 800 rpm and 1000 rpm respectively and same procedure have been repeated to get the all composites. In each case, standard ASTM samples were prepared to carry out the mechanical tests.

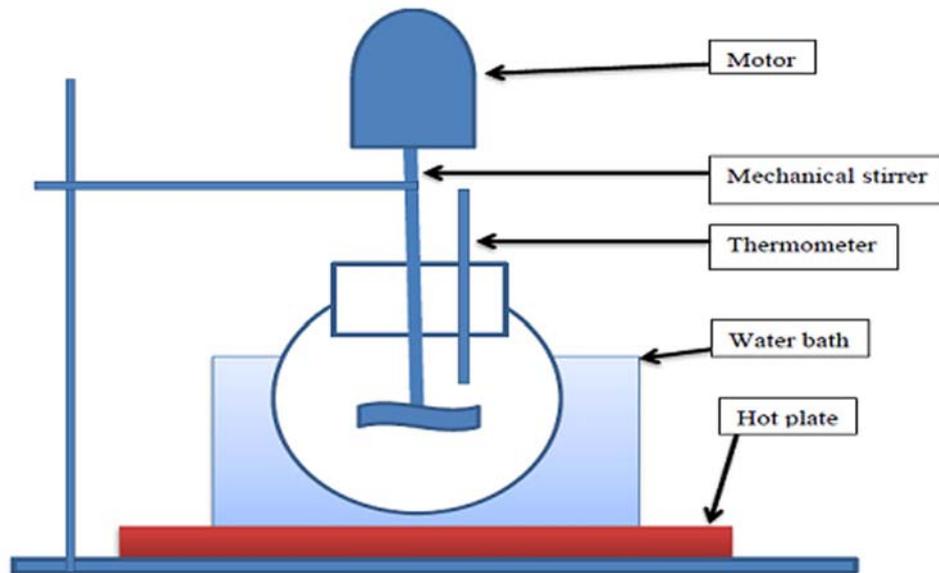


Fig. 1 Experimental Setup

3. RESULTS AND DISCUSSIONS

3.1 X-RAY DIFFRACTION

XRD of neat PMMA: XRD pattern of pure PMMA sample is shown in figure 2. The pattern shows the absence of Bragg's reflections indicating the amorphous nature of PMMA [Kodge et al 2012]. The pattern for pure PMMA also shows broad but low-intensity peaks at 320 and 430 . These broad peaks also indicate the amorphous nature of PMMA sheet. [Kumar et al 2010; Tomar et al 2011].

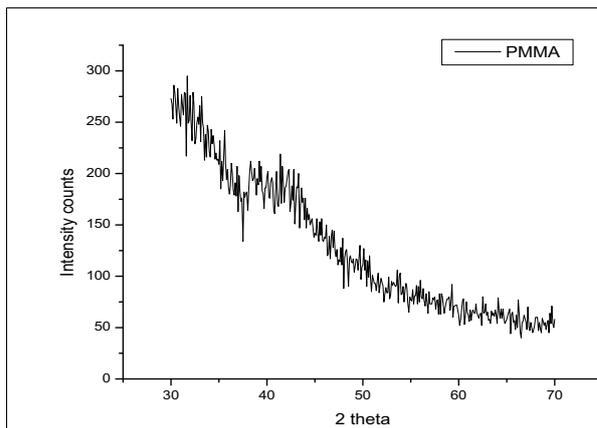


Figure 2 XRD of calcium carbonate nanopowder

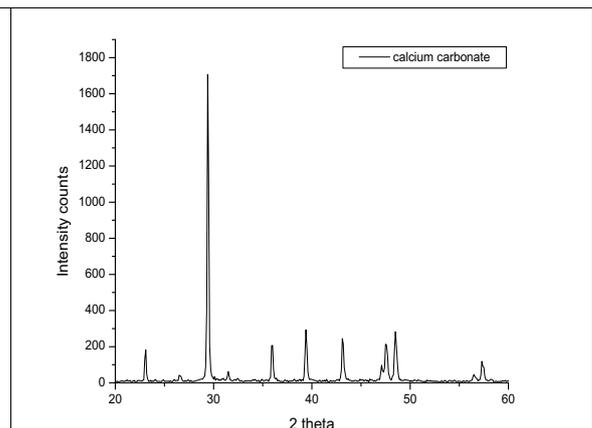


Figure 3 XRD of calcium carbonate nanopowder

XRD of CaCO_3 nanoparticles: The figure 3 is showing the XRD pattern of CaCO_3 nanoparticles with is similar to the pattern obtained in the previous work [Dadkhah et al 2012; Mishra et al 2005].

XRD of composites: Figure 4 and 5 shows the indexed XRD pattern of calcium carbonate dispersed PMMA nanocomposites sample. The pattern shows the presence of some nano-calcium carbonate reflections. The nano- CaCO_3 peaks in the composite pattern confirm the formation of calcium carbonate dispersed PMMA composite and development of crystallinity in the polymer matrix. Development of crystallinity in PMMA matrix is due to the complexation of nano- CaCO_3 nanomaterial with PMMA matrix [Kodge et al 2012].

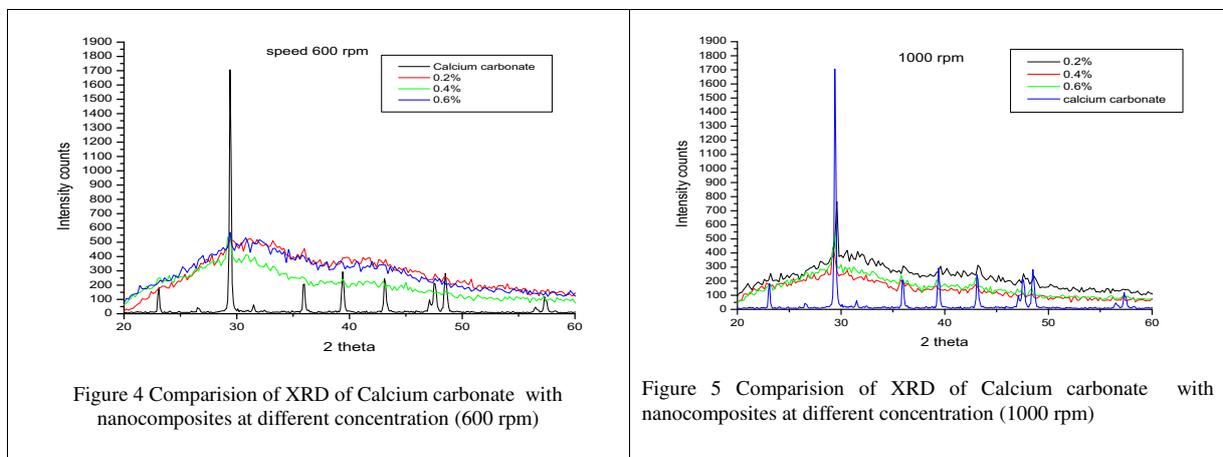


Figure 4 Comparison of XRD of Calcium carbonate with nanocomposites at different concentration (600 rpm)

Figure 5 Comparison of XRD of Calcium carbonate with nanocomposites at different concentration (1000 rpm)

3.2 SCANNING ELECTRON MICROSCOPY OF COMPOSITES

The properties associated with polymer matrix composites are the functions of the filler size, shape, dispersion and the matrix and filler interactions. In our work the filler shape and size is same throughout the experiments. The main purpose of SEM is to check the degree of dispersion and filler matrix interaction. Figure 6 (a)-(i) SEM micrograph of composites at different speed and at different concentration. Figure 6 (a)-(c) is at constant 600 rpm but the concentration is increasing from 0.2 to 0.6%. Figure 6 (a) and (b) is showing good dispersion into the matrix but in figure 6 (c) some agglomeration is visible along with some fair dispersion location. Figure 6 (d)-(f) is at 800 rpm and 0.2 to 0.4% concentration. Again the dispersion is good as expected. Figure 6 (g)-(i) is at the best dispersion level among all three because this group of nanocomposites is synthesized at the highest speed. Figure 6 (a), (d) and (g) is showing the effect of speed on the dispersion of the nanoparticles. From all the figures it can be infer that as the speed is increasing the dispersion is improving. Similarly the same phenomenon can be seen in the figure (b) (e) (h) &(c) (f) (i).

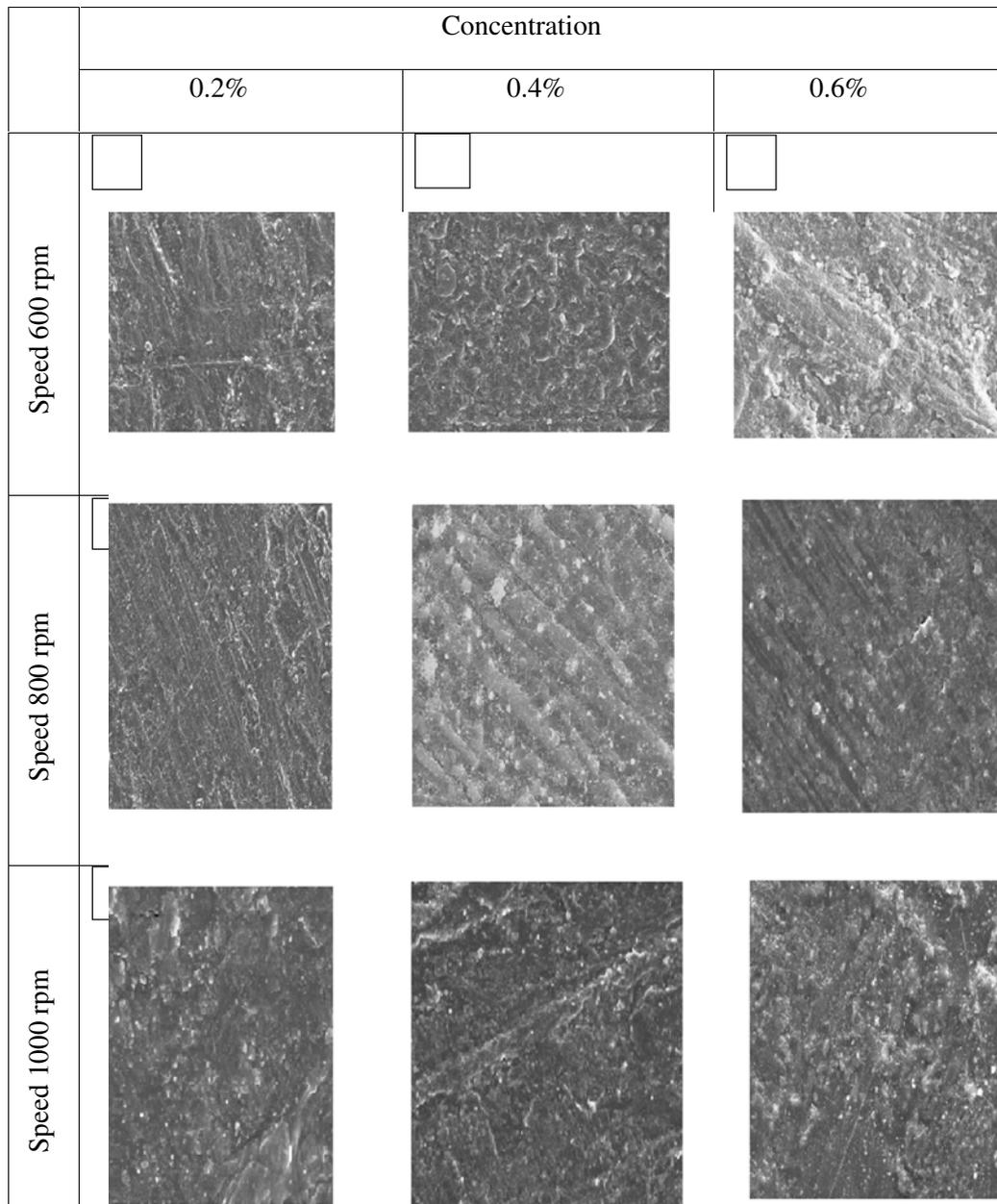


Figure 6 SEM micrographs (a) 0.2% conc. and 600 rpm (b) 0.4% conc. and 600 rpm (c) 0.6% conc. and 600 rpm (d) 0.2% conc. and 800 rpm (e) 0.4% conc. and 800 rpm (f) 0.6% conc. and 800 rpm (g) 0.2% conc. and 1000 rpm (h) 0.4% conc. and 1000 rpm (i) 0.6% conc. and 1000 rpm

3.3 IZOD IMPACT STRENGTH

The figure 7 shows that pure PMMA exhibits impact strength of 2.86 kJ/m². When the filler concentration is increased to a level of 0.2% the strength reaches to 3.33 kJ/m², 2.80 kJ/m² and 3.33 kJ/m² at 600 rpm, 800 rpm and 1000 rpm respectively. A further increment in filler concentration up to 0.4% the impact strength improves to 3.48, and 3.64 kJ/m² at 600 and 800 rpm and respectively. Similarly, at 0.6% filler concentration level again increments in the impact strength have been recorded to 3.488 and 3.6432 kJ/m² at 600 and 800 rpm respectively.

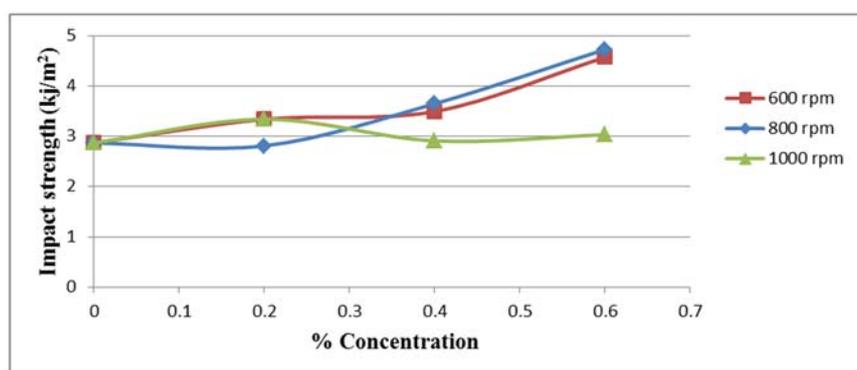


Figure 7 Variation of impact strength against concentration with speed.

The figure also exhibits that when filler concentration is increased keeping stirring speed constant impact strength increases for 600 rpm and 800 rpm. The impact strength increased to 4.568 kJ/m² by changing filler concentration to 0.6 % at 600 rpm. Similarly, impact strength increases to 4.724 kJ/m² by changing filler concentration to 0.6 % at 800 rpm. The impact strength of PMMA nanocomposites increases with the increasing CaCO₃ content, because incorporation of rigid inorganic particle is a promising approach to improve both stiffness and toughness of polymer simultaneously as reported [Tomar et al 2011].

The another reason of increased toughness could be ascribed as more reinforcement sites formed among the polymer chains [Wang et al 2011]. It suggests the importance of incorporating the nano-CaCO₃ particles to improve the mechanical properties of PMMA nanocomposites. The concentration and speed has increased the impact strength because of better dispersion at higher speeds. But for 1000 rpm the impact strength has not increased as 600 and 800 rpm. One of the reasons is that the sheets are prepared at high temperature so they caused the formation of small pin-holes in the composites. During the test of impact strength, such pinholes become the weak sites and easy to break under an abrupt impact causing decrease in impact strength [Wang et al 2011].

When the surface of the calcium carbonate nanoparticles was modified and the poly (methyl methacrylate)(PMMA)/CaCO₃ nanocomposites were prepared by in situ polymerization the impact strength increased to 70 % with respect to pure PMMA by adding 1 wt. % fillers. [Xiaoyu et al 2011].

In our work the increase in impact strength is 62.7% at 800 rpm and 0.6% concentration which is comparable with the previous work.

4. CONCLUSIONS

PMMA/CaCO₃ nanocomposites at different concentrations and stirring speeds have been synthesised by in-situ polymerisation of MMA. Due to presence of PMMA in nanocomposites, the intensity of nano-CaCO₃ was found to be depressed in XRD gram. This indicates that nano calcium carbonate (CaCO₃) gives the crystalline nature to nanocomposites. SEM of composites shows stirring speed is an important parameter for the dispersion of nanoparticles in the PMMA matrix. The nanocomposites shows improved impact strength as compared to pure PMMA.

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