

# Effect of Stirring Speed and Filler Concentration on Hardness of PMMA/CaCO<sub>3</sub> Nanocomposites and its Optimization through Taguchi's Analysis

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**ABSTRACT:** Nanocomposites of PMMA reinforced with nano-CaCO<sub>3</sub> have been synthesized by bulk polymerization. The effect of the various input variables i.e. concentration and stirring speed on the hardness have been studied. The different experimental conditions were determined using Taguchi's experimental design. L9 Orthogonal arrays of Taguchi, the signal-to-noise (S/N) ratio and the analysis of variance (ANOVA) are employed to find the optimal input parameter levels and to analyze the effect of these parameters on hardness values. Measurement of Rockwell hardness of PMMA/CaCO<sub>3</sub> nanocomposites indicated that hardness increased up to 28% at 0.6 wt. % CaCO<sub>3</sub> and 1000 rpm in comparison to corresponding pure PMMA. The experimental results and various statistical approaches namely, Taguchi methods, Conceptual S/N ratio and drew similar conclusions i.e. the significant parameters are concentration followed by stirring speed.

**KEYWORDS:** Nanocomposites, In-situ polymerization, Rockwell hardness, Taguchi method, ANOVA analysis.

## I. INTRODUCTION

Nanocomposites are the materials which have attracted a great deal of research interest in the past decades. They have exhibited improved mechanical properties, such as high strength, toughness and hardness [1]. The final properties of nanocomposites depend upon the methods of compounding of filler material and matrix material. The interaction, distribution and concentration of constituents depends upon method of compounding.

In-situ method is generally used for synthesis of various Poly (methyl methacrylate) (PMMA) / inorganic nanocomposites, because the type of nanoparticles and the nature of polymer can vary a wide range to meet the requirements [1].

Poly (methyl methacrylate) (PMMA) is transparent, hard, stiff, low water absorption and outstanding outdoor weathering properties [2]. Calcium carbonate (CaCO<sub>3</sub>) is one of the most popular mineral fillers used in the plastics industry. It is widely available around the world, easy to grind or reduce to a specific particle size, compatible with a wide range of polymer resins and economical. As an additive in plastic compounds, CaCO<sub>3</sub> helps decrease surface energy and provides opacity and surface gloss, which improves surface finish. In addition, when the particle size is carefully controlled, CaCO<sub>3</sub> helps increase impact strength and flexural modulus (stiffness) and tensile strength [3]. So, incorporation of CaCO<sub>3</sub> nanoparticles in the PMMA polymer enhances the mechanical properties due to which these PMMA/ CaCO<sub>3</sub> nanocomposites have wide industrial applications.

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A substantial amount of work has focused on PMMA as the matrix material. PMMA/CaCO<sub>3</sub> nanocomposites were synthesised by several researchers for the thermal and mechanical properties. Navin et al [4] synthesised the PMMA/TiO<sub>2</sub> nanocomposites by in-situ polymerisation and found increase in Vickers's micro hardness, strength and modulus by incorporation of 1.25 wt. % TiO<sub>2</sub> in PMMA.

In conventional polymer composites, micron-size CaCO<sub>3</sub> 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 [6].

To overcome these problems, a new method has been presented for the synthesis of PMMA/ CaCO<sub>3</sub> nanocomposites by in-situ polymerisation reaction. In present study, nanoparticles were added at different stirring speeds during reaction. It was observed that nano-CaCO<sub>3</sub> is comparatively well dispersed into the matrix at higher speed, due to which hardness shown improvement that may be useful for commercial applications. The settings of polymerisation process parameters were determined by using Taguchi's experimental design method. Orthogonal arrays of Taguchi, the signal-to-noise (S/N) ratio and the analysis of variance (ANOVA) are employed to find the optimal levels and to analyse the effect of stirring speed and filler concentration on Rockwell hardness.

## II. MATERIALS AND METHODS OF SYNTHESIS

The methyl methacrylate (MMA) monomer with a purity  $\geq 99\%$  was purchased from Merk, the free radical initiator, benzoyl peroxide (BPO) with a purity  $> 98\%$ , was provided by LobaChemie. For the preparation of nanocomposites, nano-CaCO<sub>3</sub> provided by Sisco research laboratories Pvt. Ltd. was used. All other chemical were used without further purification.

In this work nanocomposites have synthesised at three different speeds and at every level of speed the concentration of nano-CaCO<sub>3</sub> varied from 0.2% to 0.6 wt. % of pure MMA. So nine different composites have been synthesised along with one pure PMMA for the comparisons of properties.

Fig. 1 shows experimental setup, firstly 650 ml of MMA is taken into 1000 ml beaker. When the temperature of the water bath reached to 80°C 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. Then speed of the stirrer is adjusted to 600 rpm by speed regulator. Now 0.2 wt. % of CaCO<sub>3</sub> nano powder is added. After that the solution was left for 90 min. under continuous stirring and a constant heat of 80 °C 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.

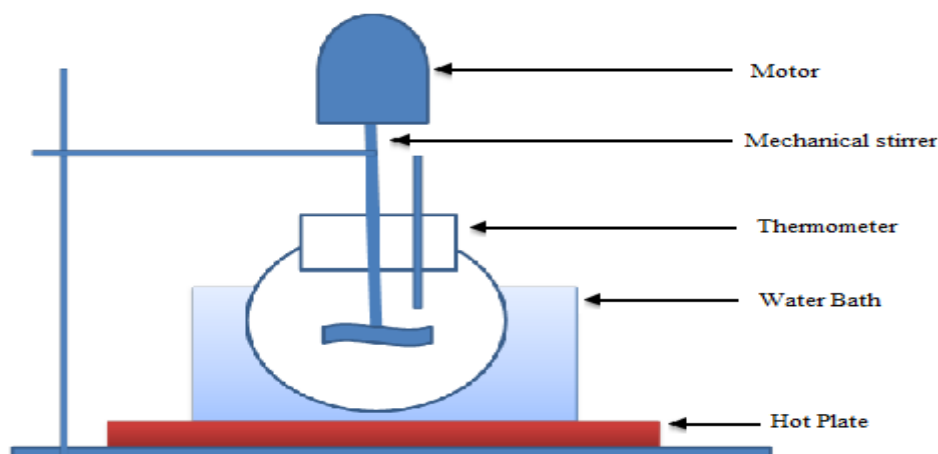


Fig. 1 Experimental setup

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## III. RESULTS AND DISCUSSION

### ROCKWELL HARDNESS

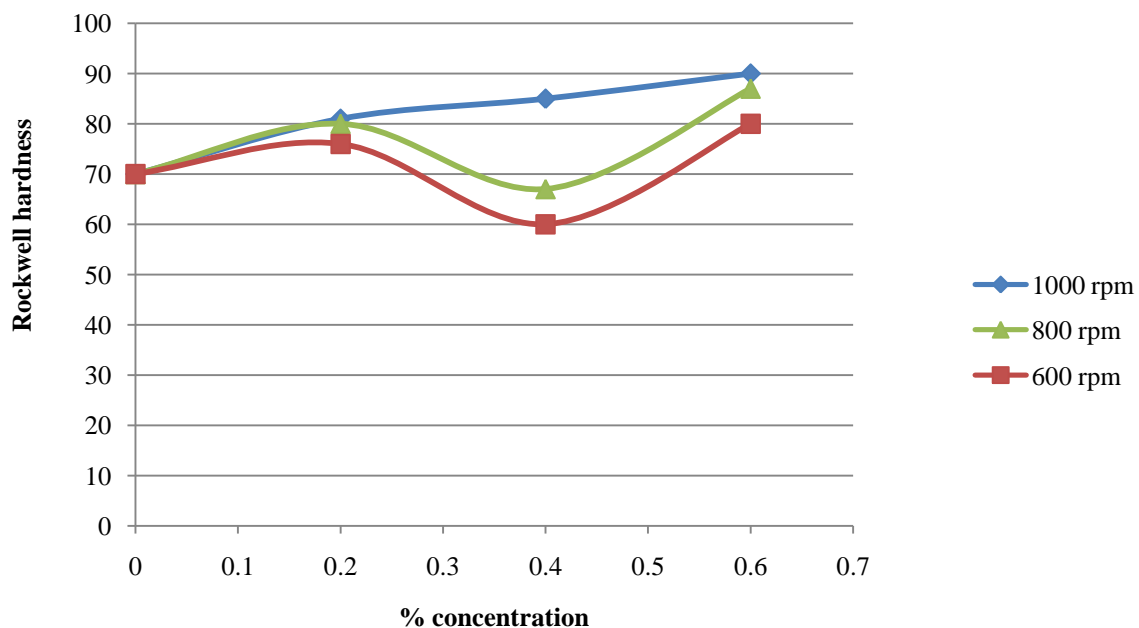


Fig. 2 Variation of Rockwell hardness against concentration with speed.

The fig.2 Variation of Rockwell hardness against concentration with speed, shows that pure PMMA exhibits hardness of 70. When the filler concentration is increased to a level of 0.2% the Rockwell hardness reaches to 76, 80 and 81 at 600 rpm, 800 rpm and 1000 rpm respectively.

At 0.6% filler concentration level the increments in the hardness are 80, 87 and 90 at 600 rpm, 800 rpm and 1000 rpm respectively.

The figure also exhibits that when filler concentration is increased keeping stirring speed constant hardness increases. The hardness changes from 76 to 80 by changing filler concentration from 0.2 to 0.6 % at 600 rpm. Similarly, hardness increases to 80 to 87 and 81 to 90 by changing filler concentration from 0.2 to 0.6 % at 800 and 1000 rpm respectively. The hardness of the all nanocomposites synthesised at different speed and concentration via in-situ polymerization shows an increase over PMMA. Fig. 2 Variation of Rockwell hardness against concentration with speed, showing that with the increase of speed the hardness of the resulting nanocomposites increases. It also indicates that, with an increase of nano-CaCO<sub>3</sub> content in the nanocomposites, the hardness also increases [5]. The enhancement of hardness is because of the good dispersion of nano-particles into the polymer matrix. The work done by Bharat et al.[6] which was with a PMMA/ CaCO<sub>3</sub> nanocomposites shows 100 % increased pencil hardness with respect to pure PMMA by adding 4 wt. % fillers. In the same way the result obtained by Navin et al [4] which was with a PMMA/TiO<sub>2</sub> nanocomposites shows 6.1% increased Vickers's hardness with respect to pure PMMA by adding 1.25 % wt. fillers. In our work the increase in Rockwell hardness is 28.57% at 1000 rpm and 0.6% concentration level.

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## STATISTICAL ANALYSIS OF RESULTS

### TAGUCHI ANALYSIS

Taguchi methods used widely in engineering analysis and to study the effect of multiple variables simultaneously involving a series of steps which must follow a certain sequence for the experiment to yield an improved understanding of process performance [7].

In this work nine experiments were conducted at different concentrations and speeds. Taguchi L9 orthogonal array was used, which has nine rows corresponding to the number of tests, with two columns at three levels. For the purpose of observing the degree of influence of the process parameters on hardness, two factors, each at three levels, are taken into account, as shown in Table 1. Table 2 Taguchi L9, showing the hardness values corresponding to each experiment.

Table 1 Process parameters

Variables	Code	Level 1	Level 2	Level 3
Concentration	A	0.2	0.4	0.6
Speed (rpm)	B	600	800	1000

Table 2 Taguchi L9

Experiment No.	A	B	Hardness
1	0.2	600	76
2	0.2	800	80
3	0.2	1000	81
4	0.4	600	60
5	0.4	800	67
6	0.4	1000	85
7	0.6	600	80
8	0.6	800	87
9	0.6	1000	90

Table 3 Taguchi Analysis: Hardness versus Concentration, Speed

Experiment	Concentration	Speed	Hardness	S/N ratio
1	0.2	600	76	37.6173
2	0.2	800	80	38.0618
3	0.2	1000	81	38.1697
4	0.4	600	60	35.5630
5	0.4	800	67	36.5215
6	0.4	1000	85	38.5884
7	0.6	600	80	38.0618
8	0.6	800	87	38.7904
9	0.6	1000	90	39.0849

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Table 4 Response Table for Signal to Noise Ratios

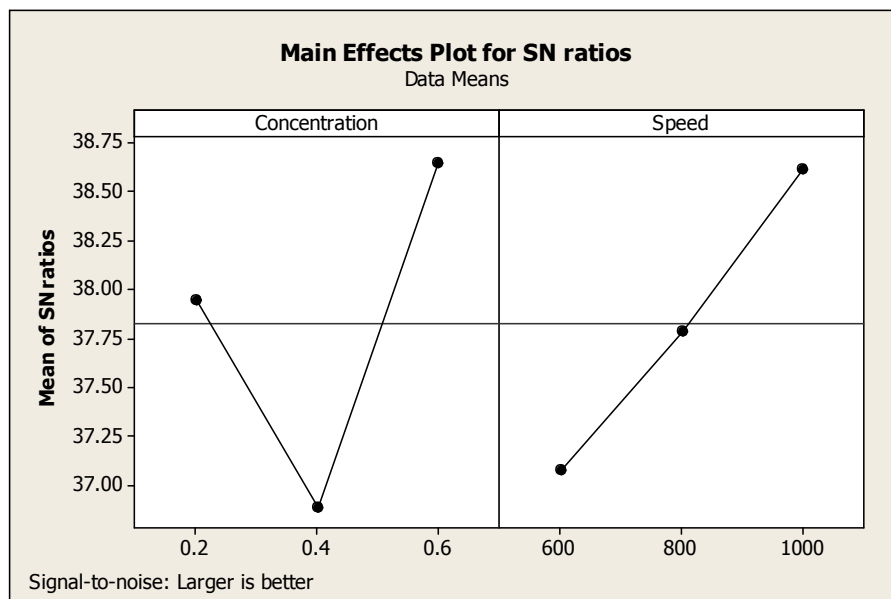
Larger is better

Level	Concentration	Speed
1	37.95	37.08
2	36.89	37.79
3 <sup>a</sup>	38.65 <sup>a</sup>	38.61 <sup>a</sup>
Delta	1.75	1.53
Rank	1	2

Optimum level <sup>a</sup>

The results for various combinations of parameters were obtained by conducting the experiment as per the orthogonal array. The hardness value were analysed using software MINITAB 15. Table 2.Taguchi L9, shows hardness values which is average of three replications. The effect of input parameters such as concentration and stirring speed on hardness has been analysed using signal to noise ratio response shown in table 3. Taguchi Analysis: Hardness versus Concentration, Speed. Table 4. Response Table for Signal to Noise Ratios, shows the ranking of process parameters using signal to noise ratios obtained for different levels for hardness.

Fig. 3Effect of process parameters on Hardness, shows the effect of the process parameters on hardness values.A greater S/N value corresponds to a better performance. Therefore, the optimal level for the hardness is the level with the greatest S/N value. Based on the analysis of the S/N ratio, the optimal input factors for the hardness obtained at 0.6 % concentration (level 3) and 1000 (level 3).



**Figure 3** Effect of process parameters on Hardness

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### ANOVA ANALYSIS

Table 5 Two-way ANOVA: Hardness versus Speed, Concentration

Source	DF	SS	MS	F	P	% contribution
Speed	2	267.556	133.778	4.06	0.109	36.25
Concentration	2	338.889	169.444	5.14	0.078	45.90
Error	4	131.778	32.944			17.85
Total	8	738.222				100

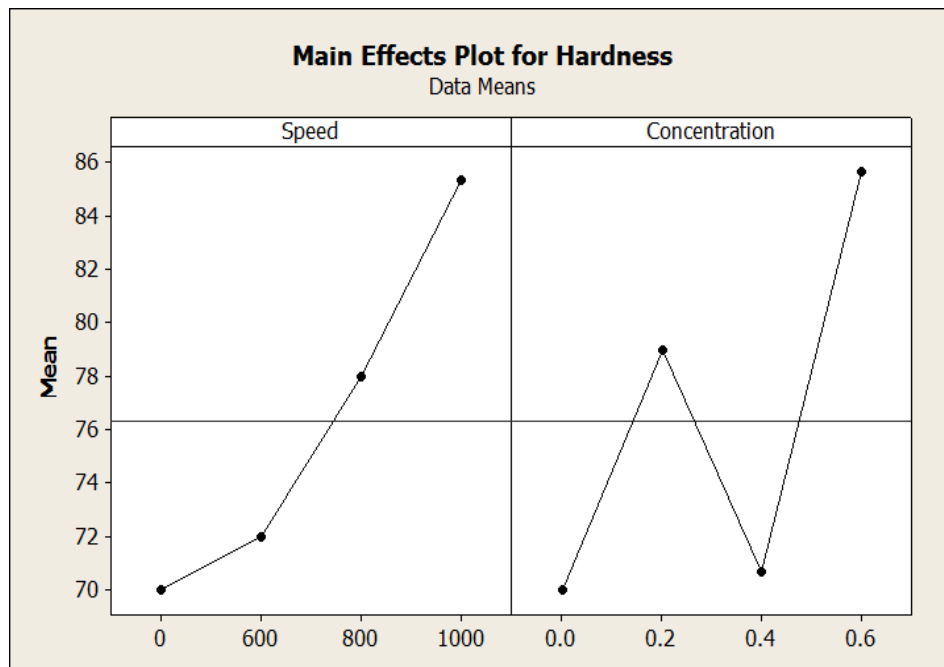


Figure 4 Main effect plot for Rockwell hardness

The Rockwell hardness of the all nanocomposites synthesised at different speed and concentration via in-situ polymerization shows an increase over pure PMMA as shown in fig. 4 Main effect plot for Rockwell hardness.

Table 5. Two-way ANOVA: Hardness versus Speed, Concentration, shows the two way ANOVA table for Rockwell hardness against speed and concentration generated by MINITAB 15. From the table 5. Two-way ANOVA: Hardness

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versus Speed, Concentration, it can be infer that contribution of concentration 45.90% while contribution of speed is 36.25% it means that effect of concentration is more on Rockwell hardness as compared to speed. Their contribution of error is 17.85 %. More the error lesser will be the simultaneous effect of input parameter on output parameter [8].

## IV. CONCLUSION

In the present experimental work we have successfully synthesized PMMA/CaCO<sub>3</sub> nanocomposites at different concentration and different stirring speeds by in-situ polymerisation. In addition to this following conclusions are drawn from the analysis.

1. The hardness of composites have increased by the incorporation of nano-CaCO<sub>3</sub> powder.
2. The experimental results show that (i) concentration and (ii) speed are the important parameters for the enhancement of Rockwell hardness.
3. Taguchi methods, Conceptual S/N ratio and ANOVA approaches for data analysis drew similar conclusions
4. For hardness, the significant parameters are concentration followed by stirring speed. The maximum increase in hardness is 28.57% at 1000 rpm and 0.6% concentration level.
5. In case of Rockwell hardness, the role of concentration and stirring speed are 45.90% and 36.25% respectively as analysed by ANOVA.
6. The optimum conditions for maximum hardness is calculated at 0.6 % concentration and 1000 rpm by Taguchi's optimization method.

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