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Enhancement in Mechanical Properties of Polystyrene-ZnO Nanocomposites

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Abstract— In this paper we present the results exhibiting an improvement in the tensile & Flexural properties of polystyrene (PS)–ZnO nanocomposites. PS –ZnO Nanocomposites have been synthesized by bulk polymerization. The effect of the various input variables i.e. concentration and stirring speed on the Tensile Strength and Flexural Strength 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 mechanical properties. Measurement of Tensile Strength of PS/ZnO nanocomposites indicated that Tensile Strength increased up to 73.99% at 0.3 wt. % ZnO and 1200 rpm in comparison to corresponding neat PS. The X-ray diffraction pattern verified the crystal structure of ZnO and FT-IR spectra evidenced the existence of ZnO and polystyrene (PS) in ZnO/polystyrene composite particles. 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— Polystyrene; Nanocomposites; X-ray diffraction; tensile properties;Anova analysis.

I. INTRODUCTION

Recently, nanocomposite materials have received a lot of attention and close scrutiny of scientists and researchers. The driving force behind the fabrication of novel composites is to achieve functional properties for promising applications in many fields of technology such as optoelectronics, electrochemistry, coating technology, automotive and aerospace industries [1]. Nanocomposite materials are multiphase solids where one of the phases has a dimension less than 100 nm. These materials typically consist of an inorganic (host) solid containing an organic component or vice versa, or they may also consist of two or more inorganic/organic phases in some combinational form with the constraint that at least one of the phases is nanosized. During the past few decades there has been immense activity in metallurgy and materials science in the synthesis and characterization of metal matrix, polymer-matrix and ceramic-matrix composites for variety of applications. Out of these the polymer-matrix composites are very important as they are most widely used because of their lightness, ease of fabrication and variety of other properties[2].

Nanostructures of ZnO have attracted significant attention due to their proposed applications in the low voltage and short-wavelength electro-optical devices, transparent ultraviolet protection films, gas sensors, optical limiters and spintronic devices [3-5]. A great deal of research has been focused on the development of ZnO/polymer nanocomposite materials using different polymer systems. Polystyrene (PS) is a transparent thermoplastic material, with lots of prospects for making composite materials with nanostructured ZnO. Introduction of ZnO filler into polymeric matrices can modify the optical, electrical, and mechanical properties [6-8].

Sanjay et al. prepared polystyrene/organomotmorillonite nanocomposites by melt processing with a twin-screw extruder. Their experimental findings revealed a consistent improvement in the mechanical properties of PS/layered silicate nanocomposites. Mechanical tests revealed increases in the tensile, flexural, and impact strengths of 82, 55, and 74%, respectively, for C20A/PS nanocomposites at a 5% clay loading. In 2012 Saraeian et al. discussed the effect of Nanoclay particles on the tensile strength and flame retardency of Polystyrene –Nanoclay composite. They used melt-intercalation method and twin extruder was employed to prepare nanocomposite samples from polystyrene with 4,5 and 6% nanoclay and then nanocomposite granules were injected into a mould using a injection machine. For morphology study of nanocomposites, X-ray diffraction (XRD) and transmission electron microscopy (TEM) tests were conducted. Results revealed that by increasing nanoclay upto 5%, the tensile strength, and modulus of elasticity were increased, while the strength was decreased when 6%, nanoclay was used. In present study, composites of PS-ZnO were prepared by bulk polymerization of styrene in the presence of ZnO nanoparticles and the effect of ZnO on the morphology and mechanical properties of composites were investigated. Analyses were carried out using universal tensile testing machine, X-ray diffraction (XRD) and FT-IR to investigate the dispersion of ZnO and its influence on the mechanical properties of composites.

II. METHODOLOGY

A *Materials*

Styrene, the monomer used in polymerization was purchased from Otto chemicals. Benzoyl peroxide was used as the initiator for styrene polymerization. The filler used in this study was Nano-Zinc oxide (Average particle size: 30nm) purchased from Sisco Research Laboratories (SRL) Pvt. Ltd. Methanol was purchased from CDH Pvt. Ltd and supplied in 500ml bottles. Acetone was purchased from CDH Pvt. Ltd and supplied in 500ml bottles.

B *Synthesis of Polystyrene & PS-ZnO nanocomposites*

Neat polystyrene was synthesized at 80°C with the aid of benzoyl peroxide as the initiator. The polymerization time was approximately 1.5 hours. First of all the hot plate was switched on to maintain the water bath temperature to 80^0c. 500ml of Styrene was taken into a beaker and then 0.8 gm of initiator (BPO) is added. The mixture was agitated at room temperature until the peroxide was completely dissolved. Water bath temperature was maintained 80 ± 5^oC throughout the experiment. Initiators thermally decompose, thereby forming active free radicals that are effective in starting the polymerization process. Polymerization was completed in approximately 90 minutes. When the polymer melt (molten product) sample become sufficiently viscous, 50 ml of methanol is added and then sample was taken out and dried. Synthesis of nanocomposites by in-situ polymerization basically involved the dispersion of ZnO in styrene followed by free-radical polymerization initiated by the addititon of benzoyl peroxide. Styrene monomer containing the desired amount of ZnO was mechanically mixed for 30 minutes at room temperature to achieve relatively easy dispersion of the filler in the low viscosity matrix. Benzoyl peroxide was then added to the mixture to initiate the polymerization which took place at 80°C for 90 minutes. The experiment is performed at atmospheric temperature and pressure. ZnO nanoparticles, having 0.1%, 0.2% and 0.3% concentrations by weight were added in pre washed styrene at three different stirring speeds (800, 1000, and 1200 r.p.m). The composites obtained at the end of polymerization were collected into a plate. Then the products were ground and subsequently compression molded. Ten samples were synthesized in similar fashion out of which one is for neat polystyrene and nine others for composites.

Characterization:-

1. *X-Ray Diffraction (XRD) Analysis*

The nanocomposites were analyzed by using a BRUKER AXS D8 ADVANCE (Germany) based X-Ray diffractometer. Diffractometer equipped with CuK anode radiations (of wavelength equal to 1.54 Å) source operated at a generator tension of 40 kV and a generator current of 40 mA. The diffraction patterns were collected at a diffraction angle 2θ from 20° to 60° at a scanning rate and step size of 2°/min and 0.02°, respectively.

2. Fourier transform infrared (FT-IR) anlysis

Fourier transform infrared (FT-IR) spectra were recorded using Perkin Elmer 1725 instrument over a range of 500 to 4000 cm^{-1}.

Measurement of mechanical properties:-

1. *Tensile testing*

Universal testing machine (PTC/ME/08, INSTRON, Max. 100 KN) with tensile test fixture and different types of self aligning grips were used for holding test specimen in machine. It is fitted with load cell and extensometer to record the test load and extension accurately. Tensile tests were conducted according to ASTM D638. The tensile tests were performed at a crosshead speed of 50 mm/min. Four tensile tests were performed for each sample. Results from multiple tests were averaged for each sample.

2. *Flexural testing*

Universal testing machine (Specifications same as that of tensile testing) having flexural test fixture such as specimen support and loading nose is used. Three point loading system method was adopted for flexural test. Flexural tests were conducted according to ASTM D790 on rectangular specimens. Each value obtained represented the average of four sample.

III RESULTS AND DISCUSSION

A. *Tensile strength & Flexural strength*

The tensile strength of the nanocomposites synthesized at different speed and concentration shows a notable increment as compared to neat PS. This improvement can be attributed to uniform dispersion of nano-filler in polymer matrix as reported by Zhang et al [5]. The uniform dispersion of Nano-PS is also revealed that as the speed increases the dispersion improves. Also the particle size has significant contribution on the tensile strength of the composites related with the interfacial area per unit volume. Particle agglomeration tends to reduce the strength of the material in other words, agglomerates may act as strong stress concentrators [9].The flexural strength values are higher than the corresponding results obtained from the tensile test. The difference occurs due to the nature of the test since flexural test involves both tension and compression. In a tensile test flaws show up at very small strains but in flexural test the compressive stresses at the upper half of the specimens tend to close cracks rather than open them [9].In flexural testing the upper half of specimens is in compression while the lower half is in tension. Thus, cracks cannot easily propagate towards the compression side. The compressive stresses tend to close the cracks rather than opening them leading to ductile behaviour and higher strength.

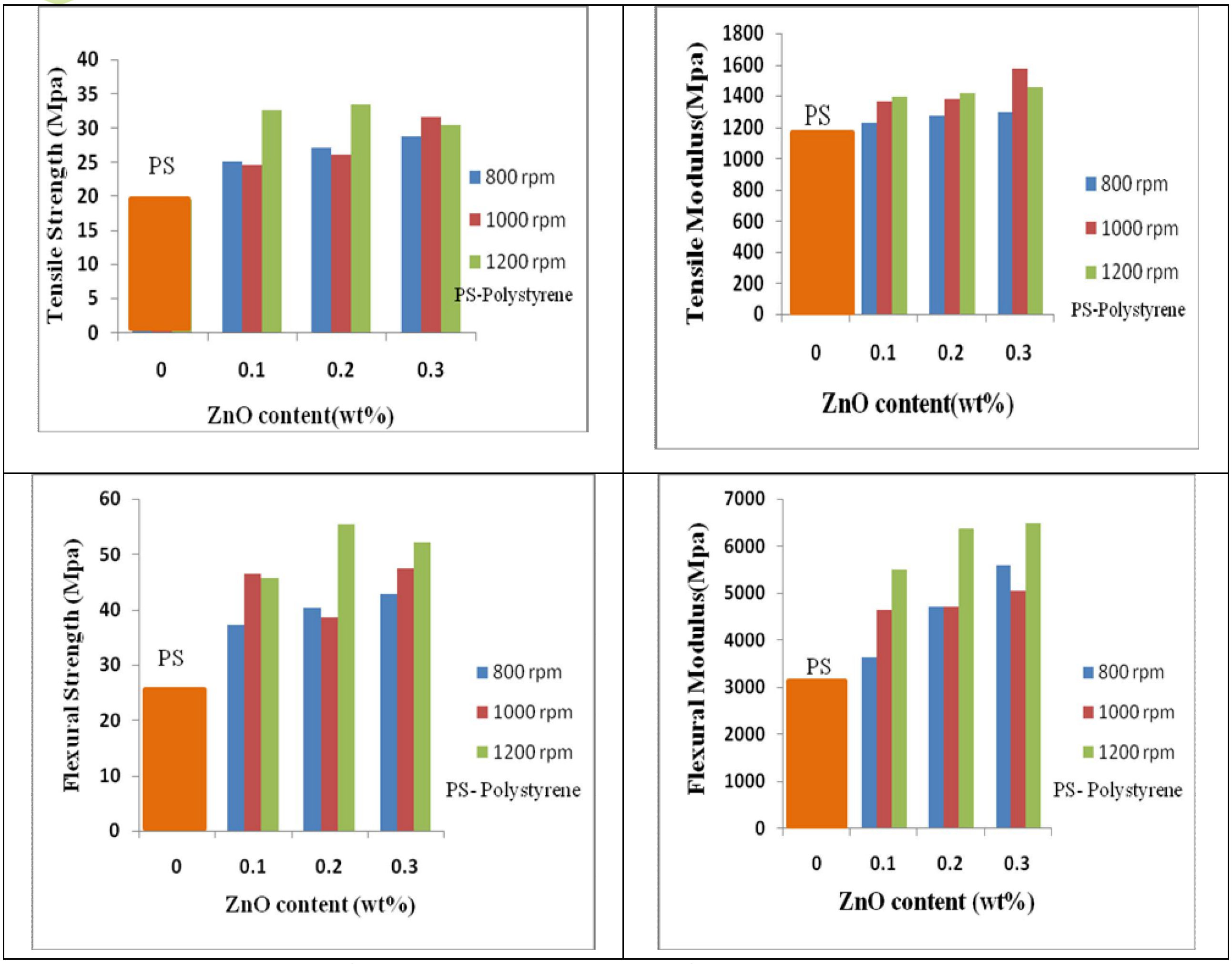


***Fig. 1** Plot of Tensile & Flexural Properties of PS and PS/ZnO nanocomposites.*

B. *FT-IR spectroscopic studies*

The FT-IR spectra of ZnO nanoparticles and PS-ZnO nanocomposite are shown in **Fig. 2.** The FT-IR spectra of PS-ZnO nanocomposite, in the figure print region of PS-ZnO shows absorption peak at 1600, 1491 and 1449 cm^{-1} which is characteristic vibration bands of aromatic C=C contributing from styrene units. The absorption peaks at 2922 cm^{-1} and 2851 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of $-CH_2$ group respectively. The absorption bands ranging from 3600-3100 cm^{-1} are assigned to aromatic C–H stretching vibration. In addition, the bands at 755 and 657 indicate that a monosubstitued ring is present. The main peak of ZnO nanoparticles in the PS-ZnO nanocomposite was observed at 538 cm^{-1}. These results were consistent with previous work reported by Chae et al. **[2].**

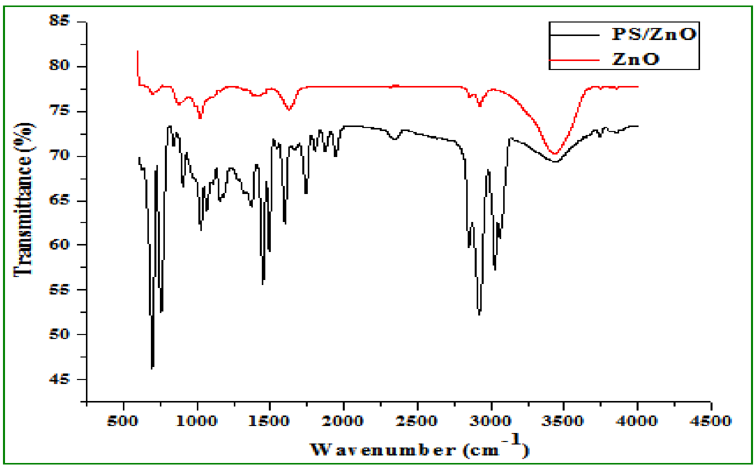


Fig. 2 FT-IR spectra of ZnO and PS/ZnO nanocomposites.

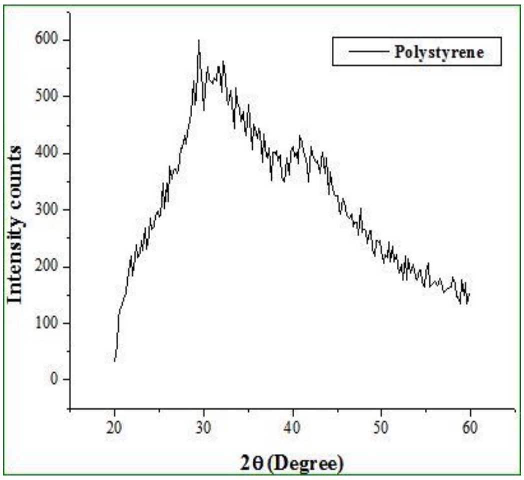


Fig. 3 XRD pattern of PS

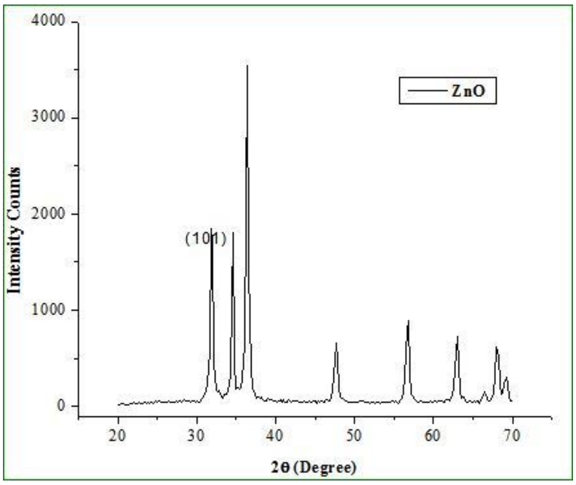


Fig. 4 XRD pattern of Nano-ZnO.

C. ***XRD of Nano ZnO, PS, Composites:-***

Peak details of ZnO Nanopowder obtained by powderx:

The XRD data including d-spacing and peak positions for the ZnO is shown in Table 1.
Sample Name: ZnO Crystal system: Hexagonal Lattice Type: P
Lattice Parameter : a= 4.9168, b= 4.9168, c= 5.4089
Lattice Parameter : Alpha= 90, Beta= 90, Gama=120
Radiation: Cu WaveLength: 1.540598 2Theta Start= 20 2Theta End= 70

Table 1 Peak details of ZnO Nanopowder

H K L	d	2Theta
1 0 0	4.25807	20.845
1 0 1	3.34573	26.622
0 0 2	2.70445	33.097
1 1 0	2.45840	36.520
1 0 2	2.28291	39.440
1 1 1	2.23807	40.263
2 0 0	2.12904	42.422
2 0 1	1.98109	45.763
1 1 2	1.81913	50.104
0 0 3	1.80297	50.585
2 0 2	1.67286	54.835
1 0 3	1.66027	55.286
2 1 0	1.60940	57.191
2 1 1	1.54256	59.916
1 1 3	1.45388	63.987
3 0 0	1.41936	65.737
2 1 2	1.38303	67.692
2 0 3	1.37589	68.092
3 0 1	1.37288	68.262
0 0 4	1.35222	69.452

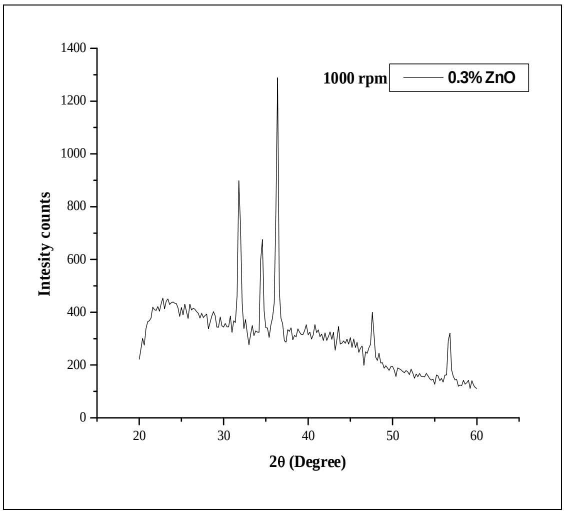


Fig. 5 XRD of composites with 0.3% concentration and 1000rpm.

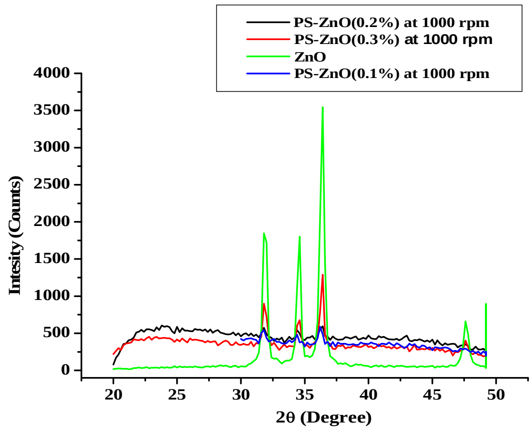


Fig. 6 Comparision of XRD pattern of ZnO with prepared PS/ZnO nanocomposites at concentration of 0.1%, 0.2% and 0.3% at 1000 rpm.

In **Fig. 6** the pattern shows the presence of some nano-ZnO reflections. The nano-ZnO peaks in the composite pattern confirm the formation of Zinc Oxide dispersed PS composite and development of crystallinity in the polymer matrix. All the three composites peaks matches with peaks of Nano-ZnO, indicating the good dispersion of ZnO in the matrix.

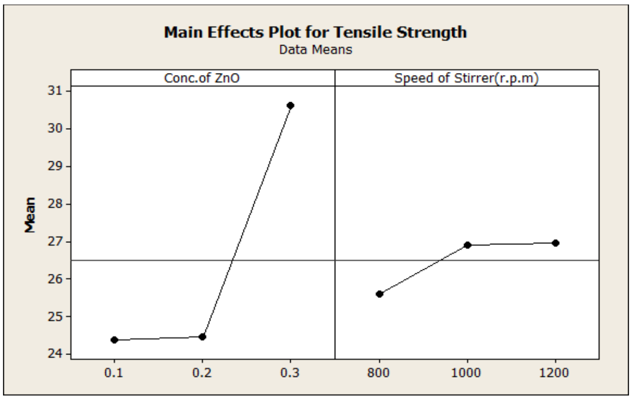
D. *Statistical Analysis of Results*

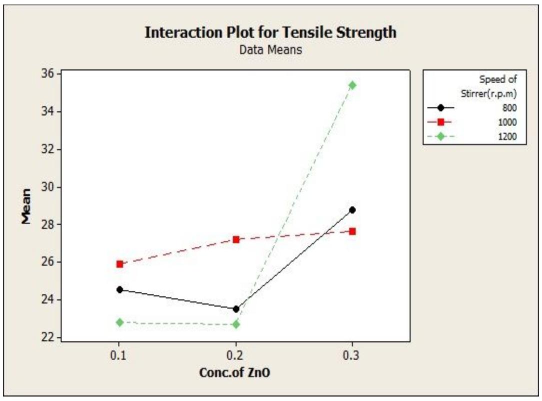
ANOVA Analysis

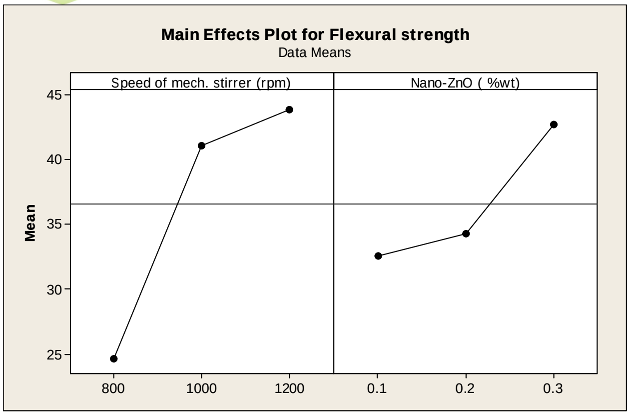
Table shows the two way ANOVA table for Tensile Strength against speed and concentration generated by MINITAB 15. From the table it can be infer that contribution of concentration 58.42% while contribution of speed is 1.31% it means that effect of concentration is more on Tensile Strength as compared to speed. Their contribution of error is 40.27 %. More the error lesser will be the simultaneous effect of input parameter on output parameter [8].

Table 2. ANOVA table General linear Model for Tensile Strength

Source	DF	SS	MS	F	P	Contribution%
Speed of Stirrer (r.p.m)	2	1.608	0.8040	0.07	0.938	1.31
Conc. Of ZnO	2	71.667	35.8334	2.90	0.166	58.42
Error	4	49.399	12.3498			40.27
Total	8	122.674				100.00







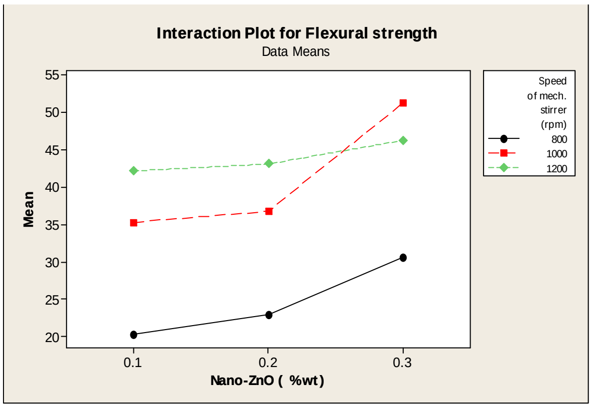


Fig. 7 *ANOVA plot for main effects & interactions.*

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 3. Table 4 Taguchi L9, showing the Tensile Strength values corresponding to each experiment.

Table 3 Process parameters

Variables	Code	Level 1	Level 2	Level 3
Concentration	A	0.1	0.2	0.3
Speed (rpm)	B	800	1000	1200

Table 4 Taguchi L9

Experiment No.	A	B	Tensile Strength
1	0.1	800	38
2	0.1	1000	35
3	0.1	1200	39
4	0.2	800	34
5	0.2	1000	38
6	0.2	1200	40
7	0.3	800	36
8	0.3	1000	32
9	0.3	1200	34

Table 5 Taguchi Analysis: Tensile Strength versus Concentration, Speed

Experiment	Concentration	Speed	Tensile Strength	S/N ratio
1	0.1	800	38	27.7904
2	0.1	1000	35	28.2626
3	0.1	1200	39	27.1473
4	0.2	800	34	27.8995
5	0.2	1000	38	28.6914
6	0.2	1200	40	27.109
7	0.3	800	36	29.1788
8	0.3	1000	32	28.8245
9	0.3	1200	34	30.9948

Table 6 Response Table for Signal to Noise Ratios

Larger is better

Level	Concentration	Speed
1	27.73	28.29
2	27.90	28.59
3[a]	29.67[a]	28.42

Delta	1.93	0.3
Rank	1	2

Optimum level [a]

The results for various combinations of parameters were obtained by conducting the experiment as per the orthogonal array. The Tensile Strength value were analysed using software MINITAB 15. Table 4.Taguchi L9, shows Tensile Strength values which is average of three replications. The effect of input parameters such as concentration and stirring speed on Tensile Strength has been analysed using signal to noise ratio response shown in table 5. Taguchi Analysis: Tensile Strength versus Concentration, Speed. Table 6. Response Table for Signal to Noise Ratios, shows the ranking of process parameters using signal to noise ratios obtained for different levels for Tensile Strength. Figure 8 Effect of process parameters on Tensile Strength, shows the effect of the process parameters on Tensile Strength 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 Tensile Strength obtained at 0.3 % concentration (level 3) and 1200 (level 3).

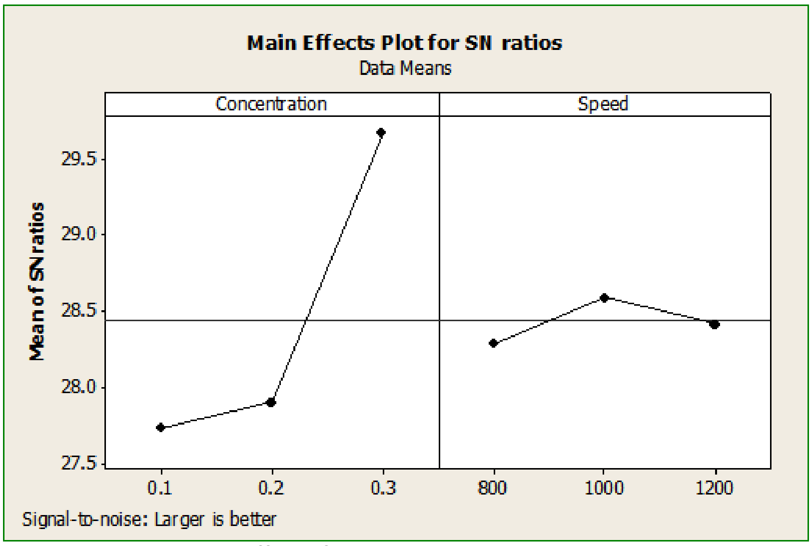


Figure 8. Effect of process parameters on Hardness

IV CONCLUSION

This research focuses on an experimental investigation of the effect of Nano-ZnO and stirrer speed on the Tensile strength and Flexural strength of Prepared polymer Nanocomposites. polystyrene (PS) - Zinc Oxide (ZnO) nanocomposites were synthesized at three different concentration and different stirrer speeds by in-situ polymerization. To show how ZnO are positioned in relation to one another and their dispersion pattern in nanocomposites, two methods i.e XRD and FT-IR were used. Concentration and Speed of stirring during polymerization are the important parameter for the enhancement of mechanical properties. Nano-ZnO gives crystalline nature to nanocomposites.The optimum ZnO content to improve flexural strength property is 0.2 %. At this ZnO content, the increment in flexural strength is 37.82 %. Dispersion of nanopowder enhances the crystallinity of PS. In case of tensile strength, the concentration and stirring speed has an effect of 58.42 % and 1.31 % respectively as analyzed by ANOVA. ANOVA results exhibit that in case of flexural strength, the concentration and stirring speed has an effect of 20.40 % and 74.26 % respectively.

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