



Optimization of the Initiators in the In-situ Synthesis of Polystyrene-Clay Nanocomposites by Response Surface Methodology

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Abstract: *Organically modified nanoclays can be used to enhance the properties of polymers. The properties are being improved by improving the reinforcing effect of the nanofiller and the polymer matrix. Here, in this work in-situ polymerisation is used for the preparation of polystyrene clay nanocomposites. In-situ synthesis can boost the proper and uniform dispersion of nanoclay in the polymer which is not attained by melt mixing. In the in-situ synthesis the amount of initiator plays a major role in improving the polymer properties as well as in clay dispersion. Here, the initiator used is Azobisisobutyronitrile (AIBN). Thus it is intended to optimize the amount of AIBN for the synthesis of polystyrene clay nanocomposites and hence to evaluate the mechanical properties.*

Keywords: *polystyrene clay nanocomposites, design of experiments, optimization, response surface methodology*

I. Introduction

The synergy between nanotechnology and polymer science gave birth to a new class of materials called Polymer Nanocomposites (PNCs). The conventional fillers incorporated in polymers improves its properties to a significant level. But nanofillers have revolutionized the entire polymer modification field. Nanomaterials have very high aspect ratio compared to its parent materials. This property of nanofiller can be advantageously exploited to improve the reinforcement effect of polymers [1]. The study on the mechanism of the property improvement of polymers by nanofillers still need more attention. This can be explained by quantum mechanics in a better way which is out of scope of our present study.

Hwang and his co-workers[2] have prepared HIPS/organoclay nanocomposites with various rubber and organoclay contents. The initiator used was AIBN. The permeability of the NC is found to be proportional to the rubber content and inversely proportional to the clay content. Clay, PS and PB found to be in the increasing order of gas permeability. Thermal stability, tensile modulus, gas barrier properties and viscosity increases with clay content while gas barrier properties decreases with rubber content and impact strength was found to be decreasing with clay content.

Akat and his co-worker[3] have conducted insitu synthesis of PMMA/PS nanocomposites by free radical polymerisation using intercalated chain transfer agent using montmorillonite clay. XRD and TEM analysis showed the formation of exfoliated nanocomposites. The amount of clay loading found to affect the properties. The good dispersion of clay platelets in the PMMA matrix resulted from the efficient intragallery over extra gallery polymerisation due to the chain transfer agent and monomer in the interlayer space of the clay layers. All composites exhibited enhanced thermal stabilities compared to virgin polymer. The authors are claiming that the system can be applied to any free radical polymerizable monomer and monomer mixtures.

Wang et. al. [4] have compared the various methods of preparation of polystyrene/pmma clay nanocomposites like bulk, suspension and emulsion methods. Two different modified clays have been used. The modification of clay as well as the route for the preparation determined whether the clay formed was exfoliated or intercalated. A working hypothesis is that the preparation of an exfoliated nanocomposite is more likely when a double bond is involved in the polymerisation reaction. But, mere presence of double bond not always produce exfoliation. Solution polymerisation yielded only intercalated systems. The other types gave either intercalated or exfoliated systems[4]. The atom transfer radical polymerisation of ethyl acrylate was carried out in bulk polymerisation in the presence of modified clay by Datta et. al [5] A remarkable enhancement of polymerisation rate was observed by the addition of nanoclay. Time of dispersion of clay in the monomer and the loadings of clay were found to have a positive effect on the kinetics of polymerisation. The polymerisation followed first order kinetics and the molecular weights increased linearly with conversion.

Polymer nanocomposites can be used for numerous applications ranging from car bumpers to advanced optoelectronic device[6]. Since the property improvements are at low loading levels of nanofillers compared to high loadings of conventional composites, weight reduction will be there which makes it suitable for military and aerospace applications. They can also be used in tyres, fuel systems, gas separation membranes in fuel cells and seat textiles, timing belt covers, pollution filters, air bag sensors.

Organically modified clays can be used as nanofillers which can give dramatic improvements in the performance aof polymers. Various parameters like the initiators, clay loading etc can affect the properties of

PNCs. Here, it is proposed to do the in-situ synthesis of polystyrene clay nanocomposites and to study the effect of the amount of initiator in the preparation of composites. A background work has been conducted with different types of initiators like Benzoyl Peroxide (BPO) and Azobisisobutyronitrile (AIBN) and found that AIBN give better properties for the composites than BPO. Hence, further experiments are conducted with AIBN as the initiator.

II. Material and Methods

Nanoclays (Plate thickness (SEM) - < 80 nm and average particle size - 100 ± 5 nm) used in this study is nanokaolinite which has been purchased from M/s English India Clays Ltd. Vely, Thiruvananthapuram. with the following specifications. The Unmodified Clay (UC) is Nanocaliber 100. Modified organo clays used are Amino Clay (AC) which is Nanocaliber 100 A and Vinyl Clay (VC) which is Nanocaliber 100 V. The initiator, Azobisisobutyronitrile (AIBN) whose decomposition temperature, 65°C, is purchased from Spectrochem Pvt. Ltd., Mumbai and Styrene from Rolex Chemical Industries Pvt. Ltd. Specimens were tested for flexural properties with Shimadzu Autograph Universal Testing Machine (UTM)) and Impact strength with Resil Impact Testing Machine.

In this work, to achieve better dispersion, in-situ-polymerization is used for the preparation of composites, where the mechanism of polymerisation is free radical. Polymerization takes place in three steps viz., initiation, propagation and termination. Vinyl monomers are highly reactive and can undergo self polymerization. Inhibitors are added to prevent this. Styrene is purified by washing with 5% NaOH followed by washing with demineralised water. The inhibitor along with the alkali solution is separated from the monomer and washing is repeated for four times. Any moisture present in the monomer is removed with molecular sieves.

In the previous study, a comparison of initiators like Benzoyl Peroxide (BPO) and Azobisisobutyronitrile (AIBN) is conducted. The process conditions also got optimized and the results are summarized in Table 1.

Table 1 Comparison of initiators for in-situ polymerisation

Initiator	Temperature (°C)	Amount (wt%)
AIBN	68	0.875
BPO	90	1

Nanocomposites were prepared for both BPO and AIBN, by varying the clay composition from 1 to 4 wt%. Then the prepared nanocomposites are subjected to various tests and characterization and found that the nanocomposites exhibited better properties for AIBN than BPO. Moreover, the amount of AIBN and the temperature required for the process is less than that for BPO. So further experiments were conducted with AIBN as the initiator and the amount of initiator is optimized by Response Surface Methodology.

Design of Experiments with Response Surface Methodology (RSM)

Design of experiment (DOE) is a well-accepted statistical technique able to design and optimize the experimental process that involves choosing the optimal experimental design and estimate the effect of the several variables independently and also the interactions simultaneously. Response surface methodology (RSM) is a statistical method used for experimental modeling and analyzing the relationship between the input and response variables[7]. The effect of variables like AIBN (A) and clay (B) content on the mechanical properties of polystyrene clay nanocomposites was studied using RSM. Factorial designs are effective when more than two factors are involved in the experiment in which all combinations of factors can be determined experimentally[8]. The most common experimental design used in RSM is the Central Composite Design (CCD), which has equal predictability from the center[6].

According to the CCD, the total number of combinations is $2k + 2k + n0$, where k is the number of independent variables and $n0$ is the number of repetitions of the experiments at the center point[7]. The response of the system was expressed by the following second degree polynomial equation:

$$Y = B_0 + \sum_{i=1}^n B_i X_i + \sum_{ij} B_{ij} X_i X_j + \sum B_{ij} X_j^2 \quad (1)$$

where Y is the predicted response. Here, only 2 variables are involved viz., A and B, $n = 2$. Therefore equation (1) becomes,

$$Y = B_0 + B_1 A + B_{12} AB + B_{11} A^2 + B_{22} B^2 + \varepsilon \quad (2)$$

where A and B are AIBN and clay content respectively, B_0 is a constant, B_1 and B_2 are linear coefficients, B_{12} is the interaction coefficient, B_{11} and B_{22} are quadratic coefficients and ε is the experimental error. In this study, mechanical properties like impact strength, flexural strength and flexural modulus were tested using a full factorial central composite design. On the basis of preliminary experiments, the ranges of clay and AIBN content were chosen. The range and the levels of the variables considered in this study are shown in Table 2.

Table 2 Coded value of independent variables and experimental ranges.

Factor Name	Coded lower limit	Coded higher limit	Real lower limit	Real higher limit
A. AIBN (wt%)	-1	+1	0.5	1
B. Nanoclay (wt%)	-1	+1	1	4

During the data analysis for the responses viz., Impact Strength, Flexural Strength and Flexural Modulus, by sequential model Sum of Squares and lack of Fit tests, a quadratic model can be selected. 13 experiments were conducted and analyzed for each case (Table 3). Design Expert software (version 8.0.7.1) was used for regression and graphical analysis of the data obtained. The fit of the regression model was checked by the adjusted coefficient of determination (R^2 Adj).⁵ The statistical significance of the model was determined by the application of Fisher's F test.

Table 3 Design layout of mechanical properties with clay and AIBN as parameters

Experiment No.	Factor 1	Factor 2	Response 1	Response 2	Response 3
	A. AIBN(%)	B. Clay (%)	Impact strength (J/m)	Flexural strength (MPa)	Flexural Modulus (MPa)
1	0.75	2.50	21.91	40.9	2230
2	0.5	1	19.41	38.8	2018
3	0.75	2.5	21.73	41.1	2231
4	0.75	2.5	21.81	40.8	2229
5	0.75	4.62	18.31	37.3	1995
6	0.75	3.8	19.53	38.5	2183
7	0.4	2.5	18.91	38.7	1953
8	1.1	2.5	19.8	38.9	2030
9	0.5	4	18.18	37.5	1984
10	1	1	20.06	38.7	2225
11	0.75	2.5	21.75	40.7	2231
12	0.75	2.5	21.71	41.2	2235
13	1	4	19.31	37.5	1986

III. Results and Discussion

Experimental design using RSM

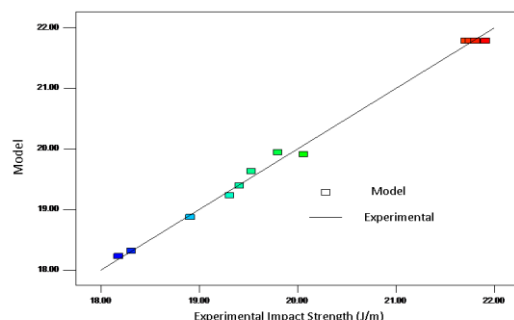
Experimental design was done with Design Expert software, version 8.0.7.1. After evaluating the data gathered from the design, a quadratic model was suggested. Acceptability of the suggested model was confirmed with variance analysis (ANOVA).

Impact Strength

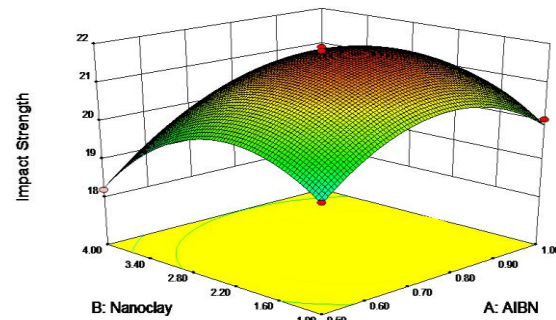
Table 4 Anova results for Impact Strength

Parameter	F-value	p>F	Calculated coefficient	DF	Std. deviation
Constant			21.78	1	0.05
A-AIBN(%)	90.60	<0.0001	0.38	1	0.04
B-clay(%)	134.72	<0.0001	-0.46	1	0.04
AB	4.52	0.0710	0.12	1	0.056
A ²	770.53	<0.0001	-1.19	1	0.043
B ²	1078.53	<0.0001	-1.41	1	0.043
Lack of fit	3.23	0.1438			
Model	373.8	<0.0001			
Std. deviation		0.11			
R ²		0.9963			
Adj. R ²		0.9936			
Pred. R ²		0.9795			

The Model F-value of 373.80 implies the model is significant. Values of "Prob > F" less than 0.0500 indicate model terms are significant. The "Lack of Fit F-value" of 3.23 implies the Lack of Fit is not significant. The "Pred R-Squared" of 0.9795 is in reasonable agreement with the "Adj R-Squared" of 0.9936. Standard deviation of the model is 0.11.

Fig. 1 (a) Model vs Experimental values for Impact strength, (b) 3D Surface plot for impact strength.

(a)



(b)

Model Equation is

$$\text{Impact Strength} = 21.78 + 0.38 * A - 0.46 * B + 0.12 * A * B - 1.19 * A^2 - 1.41 * B^2 \quad (3)$$

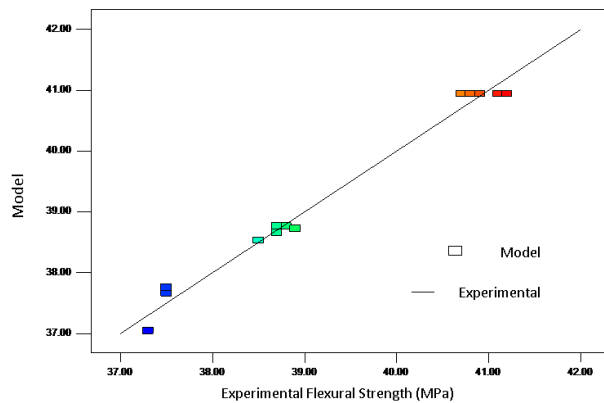
Flexural Strength

Table 5 Anova results for Flexural Strength

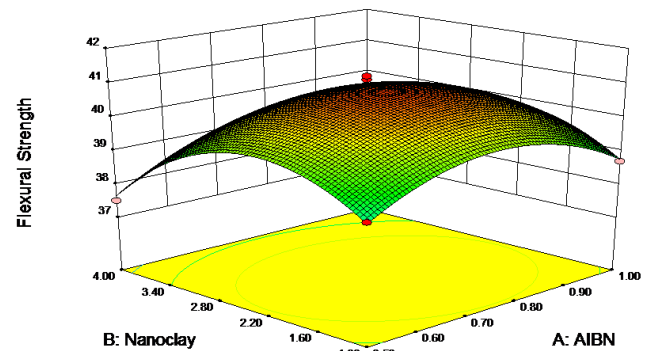
Parameter	F-value	p>F	Calculated coefficient	DF	Std. deviation
Constant			40.94	1	0.10
A-AIBN(%)	0.079	0.7873	0.023	1	0.082
B-clay(%)	41.42	0.0004	-0.52	1	0.082
AB	0.047	0.8345	0.025	1	0.12
A ²	165.97	<0.0001	-1.13	1	0.087
B ²	325.09	<0.0001	-1.58	1	0.087
Lack of fit	1.55	0.3321			
Model	95.89	<0.0001			
Std. deviation		0.23			
R ²		0.9856			
Adj. R ²		0.9753			
Pred. R ²		0.9346			

The Model F-value of 95.89 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. The "Lack of Fit F-value" of 1.55 implies the Lack of Fit is not significant. The "Pred R-Squared" of 0.9346 is in reasonable agreement with the "Adj R-Squared" of 0.9753.

Fig. 2 (a) Model vs Experimental values for Flexural strength, (b) 3D Surface plot for Flexural strength.



(a)



(b)

Model Equation is

$$\text{Flexural Strength} = 40.94 + 0.023 * A - 0.52 * B + 0.025 * A * B - 1.13 * A^2 - 1.58 * B^2 \quad (4)$$

Flexural Modulus

Table 6 Anova results for Flexural Modulus

Parameter	F-value	p>F	Calculated coefficient	DF	Std. deviation
Constant			2231.2	1	6.8
A-AIBN(%)	54.66	0.0002	39.74	1	5.37
B-clay(%)	157.06	<0.0001	-67.36	1	5.37
AB	45.46	0.0003	-51.25	1	7.60
A ²	409.23	<0.0001	-116.60	1	5.76
B ²	138.57	<0.0001	-67.85	1	5.76
Lack of fit	102.37	0.0003			
Model	150.25	<0.0001			
Std. deviation		15.2			
R ²		0.9908			
Adj. R ²		0.9842			
Pred. R ²		0.9350			

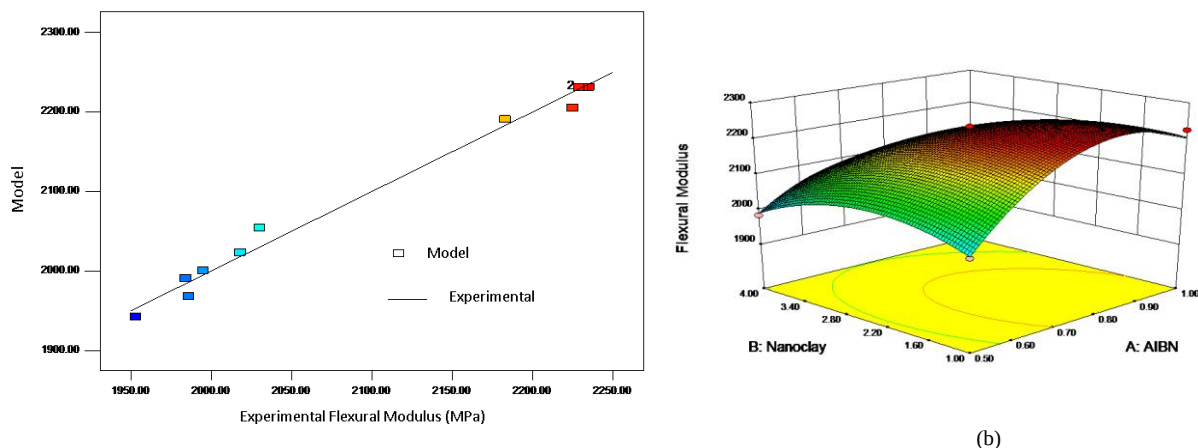
The Model F-value of 150.25 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model

terms are significant. The "Lack of Fit F-value" of 102.37 implies the Lack of Fit is significant. The "Pred R-Squared" of 0.9350 is in reasonable agreement with the "Adj R-Squared" of 0.9842.

Model Equation is

$$\text{Flexural Modulus} = 2231.2 + 39.74 * A - 67.36 * B - 51.25 * A * B - 116.60 * A^2 - 67.85 * B^2 \quad (5)$$

Fig. 3 (a) Model vs Experimental values for Flexural Modulus, (b) 3D Surface plot for Flexural Modulus



Optimization

Optimization is an important and inevitable tool which helps in determining the most suitable conditions for the process [9]. The optimized results for nanoclay and initiator combination is done by design expert software version 8.0.7.1. The optimization problem is formulated in Table 6. The objective is to maximize the properties within the given range in the Table 6 with the given range of variables. The optimized results are shown below in Table 7.

Table 6 Problem Formulation of Optimization with Constraints.

Name	Goal	Lower limit	Upper Limit
A. AIBN(%)	Is in range	0.5	1
B. Nanoclay (%)	Is in range	1	4
Impact Strength (J/m)	maximize	18.18	21.91
Flexural Strength (MPa)	maximize	37.3	41.2
Flexural Modulus (MPa)	maximize	1953	2235

From the results the properties are maximized for the combination of nanoclay and AIBN of 2.25 and 0.77 wt % respectively.

Table 7 Optimized Results for the Responses from Modeling and from Experiments.

Parameters	Optimized results from modeling	Optimized results from experiments
AIBN (%)	0.77	0.77
Nanoclay (%)	2.25	2.25
Impact Strength (J/m)	21.8417	21.65
Flexural Strength (MPa)	40.9776	39.852
Flexural Modulus (MPa)	2243.58	2244.12
Desirability	0.975	

Validation by experimental data

The optimized results have been validated by doing experiments for the optimized combinations of nanoclay and AIBN and the results are found to be matching with the optimized results which confirms the model.

IV. Conclusion

Here, the optimization of effect of the initiator, AIBN on polystyrene clay nanocomposites were studied and found the optimized values. The optimum values of AIBN and Nanoclay was found to be 0.77 wt% and 2.25 wt % respectively. More experiments have to be conducted to do the characterisation of PNCs. Also it is proposed to extend our study to high impact polystyrene. Polymer nanocomposites have tremendous market potential both as replacements for current composites and in the creation of new markets through their outstanding properties. However, the chemical compatibility and hence the dispersion of nanoparticles with the polymer matrix is the main issue facing by the researchers in this field. A homogeneous dispersion of nanoparticles with these existing techniques is very difficult due to the strong tendency of the fine particles to agglomerate. Another major attention is given to the scale up to produce large quantities of nanocomposites and the maintenance of the properties attained during laboratory preparation. Biodegradable polymer based nanocomposites have a great deal of future promise for potential applications as high performance biodegradable material[10].

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