Insitu Polymerisation Of Styrene Using Nanoclay And Optimization Of Strength Using Central Composite Design

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ABSTRACT

Polymer nanocomposites have emerged as an area of research in recent years. Nanofillers have revolutionanised the polymer modification field. They are the ultimate reinforcing agents due to their large surface area. They can bring about much higher reinforcement compared to conventional fillers used in polymer modification. This work envisages modification of standard plastic Polystyrene by nanoclay so as to improve its mechanical, thermal and processing properties. The major bottle neck in the development of polymer nanocomposites is the proper dispersion of the nanofillers. Polystyrene clay nanocomposites are prepared with benzoyl peroxide as the initiator by in-situ polymerisation. The compatibility of the initiator and the monomer with clay surface was found to profoundly affect the clay dispersion. The effects of the amount of initiator, polymerising temperature and polymerising time on the conversion of styrene were investigated. The experiments were done with different nanoclays and vinyl clay was found to give the best result. The mechanical properties mainly impact strength were determined. For getting the optimum clay and latex content Central Composite Design of Response Surface Methodology was used. By this method model equations are derived for mechanical properties, using these equations the value of property can be obtained anywhere in the range of experiments. Morphological behavior of the composite was investigated using scanning electron microscopy of fracture surface of impact specimen. Thermal behaviour of composite was done using thermogravimetric analyser.

Key words: central composite design, latex, nanoclay, polystyrene, response surface methodology.

I. INTRODUCTION

Styrene Monomer is the building block of plastic industry. Nowadays, High Impact Polystyrene (HIPS) are available in our commercial markets. They are low cost plastic materials that are easy to machine and fabricate. HIPS are often specified for low strength structural applications when impact resistance, machinability, and low cost are required. But one of the major drawbacks of the material is the reduction in the properties i.e., stiffness and transparency. Here, we intended to develop high impact PS (polystyrene) in the presence of nanoclay to maintain the properties of the polymer. Nanotechnology is broadly defined as: the creation, processing, characterization, and utilization of materials, devices, and systems with dimensions on the order of 0.1–200 nm, exhibiting novel and significantly enhanced physical, mechanical, chemical, and biological properties, functions, phenomena, and processes due to their nanoscale size[1]. Nanocomposites are found in nature, for example in the structure of the abalone shell and bone; the use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials. Jose-Yacaman et. al. investigated the origin of the depth of color and the resistance to acids and bio-corrosion of Maya-blue paint, attributing it to a nanoparticle mechanism. In the mid 1950s, nanoscale organo-clays have been used to control flow of polymer solutions (eg: as paint viscosifiers) or the constitution of gels (eg: as a thickening substance in cosmetics, keeping the preparation in homogeneous form). By 1970s polymer/clay composites or nanocomposites are common in use.

II. MATERIALS AND METHODS

Styrene used for this work was supplied by Sharon Enterprises India Ltd. Benzoyl peroxide was purchased from Loba Chemie Pvt. Ltd, Mumbai. SB Latex from Jubilant industries, nanoclays (Unmodified clay, amino clay, vinyl clay) was supplied by M/s English Clays Ltd. Vinyl monomers are purified either by washing away the inhibitor with dilute alkali or by the distillation of monomers, the latter being done carefully to avoid polymerization due to excess heating. The monomer used is styrene which is vinyl monomer. To remove the inhibitors, styrene is washed with 5% NaOH.

This method is useful only in the case of water-insoluble monomers. The inhibitors react with the alkali, and the reaction product being water-soluble, comes out of the monomer phase. The monomer is then washed with distilled water to remove the alkali traces [6].

III. IN-SITU POLYMERIZATION OF STYRENE.

Here, the mechanism of polymerisation is free radical with benzoyl peroxide (BPO) as initiator at 90^0C[4]. Polymerization takes place in three steps; initiation, propagation and termination. Nanocomposites were prepared by in-situ addition of nanoclay, in different loadings (1%, 2%, 3%, 4%) to monomer styrene during polymerization[3]. Similarly PS nanocomposites were developed using different types of clays (unmodified, amino and vinyl clay) and elastomers (Styrene butadiene rubber and styrene butadiene latex). Central Composite Design (CCD) [2] of RSM was used to study the effect of latex and clay content in PS composites. The design consists of 13 runs and experiments were done based on this runs [7].

IV. TESTING OF COMPOSITES.

Table 1. Variations of strength of PS with unmodified clay content

Unmodified Clay [%]	Impact strength [J/m]	Flexural strength [N/mm^2]	Flexural modulus [N/mm^2]
0	9.08	3.03	1165.70
1	11.69	3.22	2231.26
2	16.76	5.21	4153.70
3	12.94	3.51	2446.10
4	9.65	2.93	1951.45

Table 2. Variations of strength of PS with amino clay content

Amino Clay [%]	Impact strength [J/m]	Flexural strength [N/mm^2]	Flexural modulus [N/mm^2]
0	9.08	3.03	1165.70
1	11.25	4.34	1329.02
2	14.82	5.68	6244.10
3	12.02	3.07	4329.26
4	9.82	2.98	2415.81

In the case of vinyl clay (Table 3) the pattern of variation of strength is same as that of unmodified clay. But the maximum value obtained at 2% of clay is higher than that obtained for unmodified clay. It is due to the better interaction between the vinyl monomer styrene and vinyl clay.

The specimens obtained after moulding were tested for flexural properties in a Shimadzu Autograph Universal Testing Machine (UTM)), impact strength in Resil Impact Testing Machine. Thermal analysis is done in TA-Q 500 series instrument in nitrogen atmosphere for a temperature range of 40^0C to 1020^0C at 200C/min and SEM images were taken with JSM 6390 with an accelerator voltage 20 kV on a vacuum atmosphere.

V. RESULTS AND DISCUSSION

Mechanical properties of the composites with different types of clays are given in the following tables. In the case of (Table 1) unmodified clay, the mechanical properties of the composites are increasing with increase of clay content and reach a maximum at 2 wt% of clay[4]. Further addition of clay decreases the strength; it is due to the agglomeration which takes place at higher clay content. Table 2 lists the properties of PS with amino clay content. Here also the variation is same as that of unmodified and vinyl clay.

Table 3. Variations of strength of PS with vinyl clay content

Vinyl Clay [%]	Impact strength [J/m]	Flexural strength [N/mm^2]	Flexural modulus [N/mm^2]
0	9.08	3.03	1165.70
1	11.74	4.98	2033.02
2	18.32	6.31	7443.82
3	13.95	3.92	4070.28
4	9.9	3.01	2495.36

Experimental design. 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 modelling and analysing the relationship between the input and response variables. With the help of response surface methodology, optimization can be done for finding the values of the process variables that produce desirable values of the response.RSM consists of mainly two designs that are Box-Behnken Design (BBD) and Central Composite Design (CCD). BBD starts with three factors; hence it cannot be used to study two factors. Thus CCD can be used to study the effect of minimum two factors on the response.

There are Central Composite designs for any number of factors, starting with two factors.

The design is called composite because it can be thought of as the union of three separate pieces:

- the eight corners of the cube, which form a two level full factorial
- the six points in the centres of each face, known as the axial points or the star points
- the centre point.

It is called central to distinguish it from non-central designs in which the centroid of the star is displaced relative to the centre of the cube. For brevity we will call it a CC design. These types of experimental design are frequently used together with response models of the second order [2].

Table 4. Model equations and R^2 value for the mechanical properties

Property	R^2	Model Equations for the mechanical properties
Impact strength	0.7316	55.4459-13.2687A-5.7576B+0.6416A*A+0.1349B*B+1.3211A*B
Flexural strength	0.8374	-14.6716-0.3831A+6.2357B-0.2061A*A-0.4528B*B+0.1044A*B
Flexural modulus	0.9497	40483.2-9680.6A-5885.1B+222.2A*A+175.1B*B+1074.4

Analysis of the experimental data obtained from Central Composite design (CCD) runs is done on MINITAB software using full quadratic response surface model (2nd order polynomial equation) as given by.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i x_i + \sum_{i<j=1}^{3} \beta$$

The model equation for the mechanical properties are given in Table 5. The R^2 value which is the degree of agreement between the experimental results with those predicted by the model is obtained in the range of 0.78-0.99 for all the responses (Table 4). The range achieved for R^2 in this study is an indication of very good fitting of experimental data by the model equations.

Contour plot is a series of curves which shows the combination of variables for the response, it is a two dimensional plot. From the contour plot of impact strength (Fig. 1) it is clear that the strength is reaches maximum where clay content is between 0.5 to 1% and latex content between 5.5 to 6%. From the contour and surface plots of flexural strength (Fig. 1) it is clear that the strength increases as the clay and latex content increases. Maximum flexural strength is attained when clay content is between 1 to 1.5% and latex 6.5%. This is due to better interaction between the clay and latex.

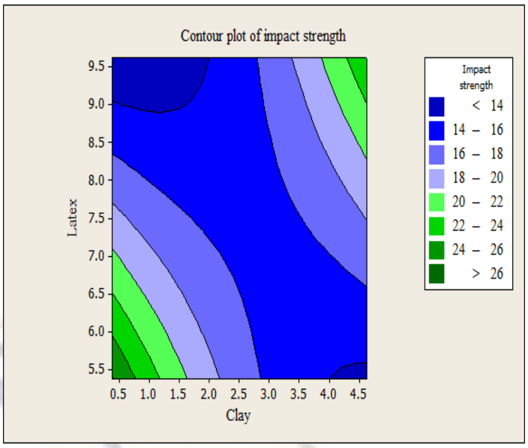

Figure 1 a. Contour plots of impact strength

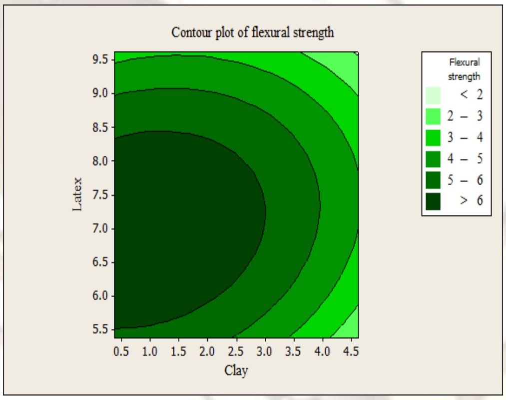

Figure 1 b. Contour plots of flexural strength

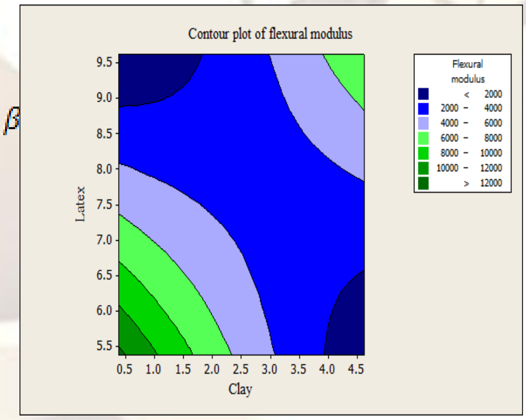

Figure 1 c. Contour plots of flexural modulus.

VI. THERMAL AND MORPHOLOGICAL CHARACTERIZATION

Thermo gravimetric analysis. In the case of pure polystyrene,(Fig. 3) onset of thermal degradation is obtained at 268.99^{0}C and it is completely degraded at a temperature of 413.63^{0}C. In the case of unmodified clay composite onset of thermal degradation is at 268.41^{0}C and it is completely degraded at a temperature of 383.45^{0}C. For modified clay (amino clay) composite onset of thermal degradation is at 347.60^{0}C and it is completely degraded at a temperature of 425.88^{0}C.. For modified clay (vinyl clay) composite onset of thermal degradation is at 376.39^{0}C and it is completely degraded at a temperature of 426.37^{0}C. . For clay and styrene butadiene latex composite onset of thermal degradation is at 295.88^{0}C and it is completely degraded at a temperature of 412.01^{0}C. Thus TGA analyses of all the nanocomposites prepared reveal significant effect of nanoclay addition plays an important role in determining their thermal stability. The addition of clay increased the decomposition temperature of clay composites.

VII. SCANNING ELECTRON MICROSCOPY

The fracture surface SEM images of polymer-fibre composite and optimum hybrid composite are given in Fig. 2. The pictures give a much better feel of the particles in 3 D space. SEM images Fig. 2(a) and Fig. 2 (b) shows give the better dispersion of nanoparticles. As a result impact strength; flexural strength and flexural modulus of the polymer nanocomposites are higher as compared to pure polystyrene. In the case of Fig 2(c) better interaction between latex and clay particles are there. As a result in this case also strength of the polymer composites is higher.

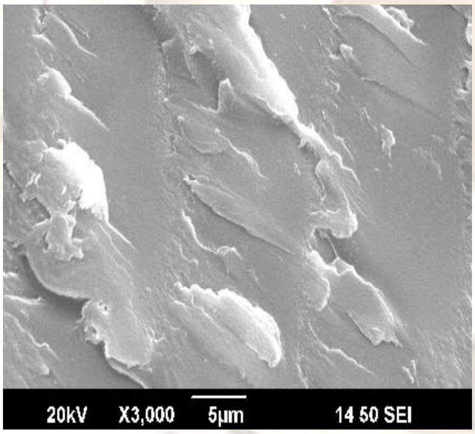

Figure 2 a. SEM of fractured surface of pure polystyrene

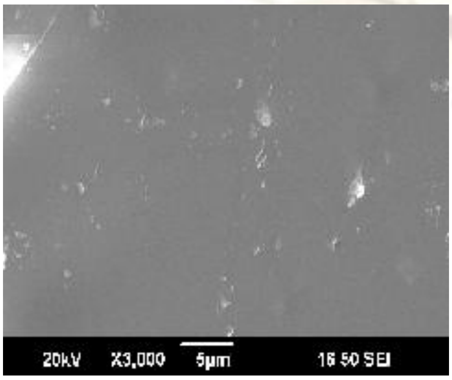

Figure 2 b. SEM of fractured surface of 2% vinyl clay

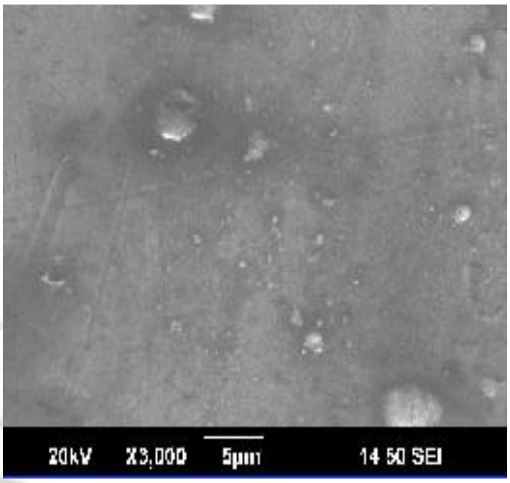

Figure 2 c. SEM of fractured surface of PS+1% vinyl Clay and 6% SBR latex

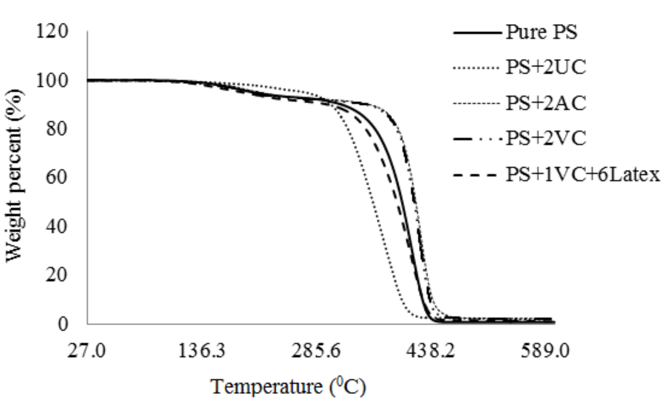

Figure 3. TGA Curves of Pure PS, PS+2UC, PS+2AC, PS+1VC+6Latex

VIII. CONCLUSION

From the above studies, the impact strength, flexural strength and flexural modulus of the composites were found to be higher than that of pure polystyrene. Among the three clays, vinyl clay gives the maximum strength which is due to proper dispersion of clay particles in the polymer matrix. To improve the impact strength of polystyrene further, the combined effect of nanoclay and styrene butadiene latex were also investigated. The Central composite Design of RSM shows that, the maximum strength has been attained for 6% latex and clay content varies from 0.4 to 1%. TGA results show that nanoclay addition increases the thermal stability. But in the case of polystyrene/clay/latex composite thermal stability decreases this is due to the presence of SBR latex particle which decreases the thermal stability lightly. SEM images shows that nanoclay and latex particles are properly dispersed in the polymer matrix which increases the strength. Thus in-situ addition of nanoclay and latex to polystyrene can increase the strength as compared to pure polystyrene prepared by this method.

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References

[1] C. Buzea, I. Pacheco, K. Robbie, Nanomaterials and Nanoparticles: Sources and Toxicity. Biointerphases. 2 (2007) 17–71.
[2] D. Montgomery, Design and Analysis of Experiments, John Wiley and Sons, New York, 2005.
[3] Hand book for fillers and plastics, 1998.
[4] R. C. Surej, P. N. Praseetha, K. E. George, In-situ addition polymerisation of styrene using nanoclay and evaluation of properties, Global Journal of Engineering and Applied Sciences, 1 (2011) 133-135
[5] V. J. M. Raj, Y. C. Orchid, Nanoparticles – A Review, Chemicals & Pharmaceuticals Limited, Chennai, IndiaSchool of Pharmacy, Curtin University of Technology, Perth, Australia.
[6] V. R. Gowariker, N. V. Viswanathan, Jayadev Sreedhar, Polymer Science, New Age International Publisher, First ed., 1986.
[7] Z. Lazi, Design of Experiments in Chemical Engineering: A Practical Guide (Wiley-VCH VerlagGmbH&Co., KGaA, Morristown, USA, 2004.