

Investigation of compatibility of Nano fillers and catalysts for the synthesis of polystyrene nanocomposites

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Abstract : The compatibility of unmodified and modified kaolinite nano clays (Vinyl Clay and Amino Clay) in the in-situ synthesis of polystyrene reinforced with kaolinite clay nanocomposites and its effect on mechanical properties were studied. The effect of catalysts/initiators like AIBN (Azo bis iso butyro nitrile) and BPO (Benzoyl Peroxide) were also compared and their operating conditions in the system were optimized. In-situ synthesis was done by altering the process conditions in three distinct methods. In the first method, BPO was used as the initiator and was synthesized without Nitrogen atmosphere in an open system. Nanocomposites obtained were of poor quality which was evident from its molecular weight and conversion. Second and third methods were conducted in Nitrogen atmosphere in a closed system in which BPO and AIBN respectively were used. Proper temperature control and exchange of heat of polymerization were facilitated. Mechanical properties improved drastically and AIBN proved to be the best initiator with less stringent operating conditions than BPO. In all the three cases vinyl clay gave the best properties because of the compatibility and interfacial adhesion of vinyl group with styrene monomer. Here, the same property enhancement is achieved as commercial polystyrene with lesser amounts of nanofiller.

IndexTerms - In-situ polymerization, Azo bis iso butyro nitrile, Benzoyl Peroxide, Kaolinite nano clay, Mechanical properties.

1 INTRODUCTION

Polymer nanocomposites got developed as the material of the modern century due to the enrichment in its properties than conventional composites¹ and also well known for its potential applications. Various nanofillers are used for property enhancement. Clay is the popularly used nanofiller due to its abundance, layered structure and high dispersion properties². Lower nanofiller loadings for the same property compared to conventional fillers reduce the cost, weight and improve the product quality³. The exotic change in properties is mainly due to the high aspect ratio^{3,4,5} of nanofillers which can be explained by quantum confinement. The synergy between nanofillers and polymer matrix is better achieved by the proper dispersion of nanofillers in the polymer matrix⁶. Mechanical properties are indirect measures of better interfacial dispersion of nanofiller in the polymer matrix^{7,4}. Even though melt mixing is commonly used; molecular level dispersion of fillers in the polymer matrix is less achieved here since it is solid-solid interaction. Moreover, operating conditions are stringent and tedious⁸. In-situ polymerisation can guarantee interfacial dispersion⁹ much better than any other methods since the interaction of nanofillers could be attained at monomer level itself. It also boosts the degree of blending between the polymer matrix and nanofiller. Proper dispersion indirectly yields better properties and finally the quality of product. Most commonly used nanofillers for polymers are nanoclays among which smectic clay, montmorillonite is popular. But since it is expensive, here kaolinite clays are used which is cheap and abundantly available which also could produce nanocomposites of identical quality as conventional microcomposites. Polystyrene is a very important and widely used plastic with plenty of commercial applications. But it is brittle in nature. So in this work, it is intended to improve the properties of polystyrene by reinforcing with nanoclay. Modification of clay to change its polarity and to transform it from hydrophilic to organophilic is essential in the preparation of nanocomposites¹⁰. Nanofiller should be compatible with the matrix in order to achieve better properties for the composite. Hence proper selection of nanoclay is important to ensure the diffusion of monomer or the polymer into the interlayer spacing of clay which explains its compatibility. So here, the effect of three kaolinite nanoclays is compared in this study i.e. Unmodified Clay (UC), Vinyl Clay (VC) and Amino Clay (AC). The chemistry between the monomer, nanofiller and initiator should be strong for the prospective quality of the final product. A comparison of the effect of initiators is also done. This sort of quantifying the effect of initiators and selection of nanoclay is important in future works.

Akat and his co-workers¹¹ have conducted insitu synthesis of polystyrene nanocomposites by free radical polymerisation using intercalated chain transfer agent using montmorillonite clay. The authors are claiming that the system can be applied to any free radical polymerizable monomer and monomer mixtures. The atom transfer radical polymerisation of ethyl acrylate was carried out in bulk polymerisation in the presence of modified clay by Datta et. al.¹² 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. Mamaqani et. al.³ prepared clay dispersed polystyrene nanocomposites by in-situ atom transfer radical polymerisation method. The effect of the weight ratio of clay on the thermal properties was also studied. The high values of initiator efficiency signify the controlled nature of polymerisation and the accelerating effect of nanoclay on the polymerisation rate in styrene. The addition of nanoclay broadened the molecular weight distribution of resulting polymers. Wang et. al.¹³ have compared the various methods of preparation of polystyrene/PMMA clay nanocomposites like bulk, suspension and emulsion methods. Solution polymerisation yielded only intercalated systems. The other types gave either intercalated or exfoliated systems. Hasegawa et al¹⁴ has carried out the preparation of polystyrene-clay hybrids by melt blending of styrene vinyl oxazoline copolymer with organophilic clay. The storage moduli of the product were higher than those of matrix polymers at all temperatures. Noh and Lee¹⁵ has synthesized polystyrene clay nanocomposites by emulsion polymerisation and studied the properties. The increased Young's modulus of the product is due to the intercalation of Polystyrene in clay galleries as well as fine dispersion of clay particles into the polymer matrix. Fu and Qutubuddin¹⁶ prepared a reactive cationic vinyl benzyl dimethyl dodecyl ammonium chloride for the intercalation of nanoclay. Attempts to prepare polystyrene nanocomposites by bulk polymerisation of styrene with

stearyl trimethyl ammonium resulted in only intercalated composites. Polystyrene clay nanocomposites showed dynamic modulus higher than pure polystyrene.

This work mainly concentrates on the comparison of the effect of nanoclays, selection and its reinforcement effect on composites. Initiators like AIBN and BPO were used here. The decomposition temperature of BPO is higher compared to AIBN. The operating conditions of both were optimised and results were compared.

2 Experimental

2.1 Materials

Modified and Unmodified nanoclays used in this study were supplied by English India Clays Ltd. Vely, Thiruvananthapuram, India, has the specifications given in Table 1.

Table 1: Specifications of Nanoclays

Property	Unmodified nanoclay (UC)	Vinyl Clay (VC)	Aminoclay (AC)
Appearance	White/off white powder	White/off white Powder	White/off white Powder
Average particle size	100 ± 5 nm	100 ± 5 nm	100 ± 5 nm
Plate thickness (SEM)	< 80 nm	< 80 nm	< 80 nm
Bulk density	0.2 - 0.3 g/cc	0.2 - 0.3 g/cc	0.2 - 0.3 g/cc
BET Specific surface area	28 - 30 m ² /g	28 - 30 m ² /g	28 - 30 m ² /g

BPO (Benzoyl Peroxide) and AIBN (Azo bis iso butyro nitrile) were used as the initiators. AIBN was purchased from Spectrochem Pvt. Ltd., Mumbai, India and BPO from Loba Chemie Pvt. Ltd, Mumbai. Styrene of different grades was used here. Lower grade styrene used for preliminary studies was purchased from Sharon Enterprises India Limited, Kochi, Kerala and Analar grade, from Rolex Chemical Industries Pvt. Ltd. Polystyrene (PS) (REPOL H110MA) supplied by M/s Reliance Industries Ltd., Hazira, Gujarat, India

2.2 Mechanical Characterization

Samples were tested for flexural properties (ASTM D790)¹⁷ with Shimadzu Autograph Universal Testing Machine (UTM)) and Impact Strength (ASTM D 256)¹⁸ with RESIL Impact Testing Machine.

2.3 Methods

Vinyl monomers are highly reactive and can undergo self polymerization. Inhibitors were added to prevent this. Styrene was purified by washing with 5% NaOH followed by washing with demineralised water. The inhibitor along with the alkali solution was separated from the monomer and washing was repeated for four times. Any moisture present in the monomer was removed with molecular sieves.

BPO of different concentrations like 0.5, 0.75, 1 and 1.5 wt% were introduced into washed styrene and during the start of polymerisation, 1% clay was added. The temperature of polymerisation was kept around 85 to 95 °C (decomposition temperature of BPO). The prepared polymers were poured in a mould and kept in a vacuum oven for 2 days to remove any of the unreacted monomer. It is observed that the nanocomposite prepared by adding 1% initiator was better than those with other concentrations. So the experiment has been repeated with 2% clay and got the same observation. Thus the amount of BPO is optimized as 1 wt% and temperature of polymerization as 90°C.

The same experiments were repeated with AIBN as initiator by varying the compositions as 0.5, 0.75 and 1 wt%. The temperature of polymerisation was kept around 65 to 70 °C (decomposition temperature of AIBN). In this case it was observed that the nanocomposite prepared by adding 0.75% initiator was better than those with other concentrations. But it was not as good as the one which was prepared with BPO. So again the initiator amount is changed and the experiments were repeated and found that for 0.875% AIBN gave the best results. Thus the amount of AIBN was optimized as 0.875 wt% and temperature of polymerization as 68°C. Thus the process conditions of both the initiators were optimized.

Experiments were conducted in beaker which was kept on a magnetic stirrer at a speed of 150 rpm for providing proper agitation and was conducted for three different methods. In the first method, hereby called as "BPO without inert atm", lower grade styrene was used with BPO as the initiator. During the start of polymerization, nanoclay at different loadings was added to prepare polystyrene clay nanocomposites.

For all the cases, the effect of three different nanoclays UC, VC and AC were compared. In the second and third techniques, hereby called respectively as "BPO with inert atm" and "AIBN with inert atm", experiments were conducted at inert N₂ atmosphere in a three neck flask on a magnetic stirrer at a speed of 150 rpm. The flask was kept in a water bath to get proper temperature control, which was mounted on the magnetic stirrer. Styrene, being highly volatile, vaporizes at the operating conditions and any of the styrene vaporized would be condensed back to the flask with the help of the condenser which was connected to the three neck flask. Polymerization was catalysed by initiators and during the start of polymerisation, clay at different loadings were added to prepare polystyrene clay nanocomposites. Nanoclays were dried before the incorporation into polymer to ensure the absence of moisture in it. In the second and third case BPO and AIBN were used as the initiators respectively.

Composition of Nanoclay was varied from 0 to 4 wt%. The prepared composites were poured in a mould and kept in a vacuum oven for 2 days to remove any of the unreacted monomer and were subjected to various tests and characterization.

2.4 MOLECULAR WEIGHT DETERMINATION

Viscometry is a useful technique for determining the molecular weight of polymers. Here viscosity of a polymer solution and hence the molecular weight was determined by Mark-Houwink - Sakurada equation¹⁹ (Equation 1).

$$\eta = K \overline{M}_v^a \quad (1)$$

where η is the intrinsic viscosity; \overline{M}_v the viscosity average molecular weight, a and K are constants for a particular polymer/solvent/temperature system. A known volume of polymer solution (polystyrene dissolved in toluene)¹⁹ was taken in the Ubbelohde suspended level viscometer (USLV) and measured the flow time. Subsequent concentrations were obtained by adding known volumes of pure solvent and mixing inside the viscometer itself. The solvent (toluene) flow time (t_0) and the solution flow time (t) for different concentrations were measured using the same viscometer. For each concentration, the corresponding reduced viscosity and the inherent viscosity were calculated from t and t_0 as per the equations given below (Equations (2) to (6)).

$$\text{Relative Viscosity} = \eta_r = \frac{t}{t_0} \quad (2)$$

$$\text{Specific viscosity} = \eta_{sp} = \frac{t - t_0}{t_0} = \eta_r - 1 \quad (3)$$

$$\text{Reduced Viscosity} = \eta_{red} = \frac{\eta_{sp}}{C} \quad (4)$$

$$\text{Inherent Viscosity} = \eta_{inh} = \frac{\ln(\eta_r)}{C} \quad (5)$$

$$\text{Intrinsic Viscosity} = \eta = \left(\frac{\eta_{sp}}{C} \right)_{C \rightarrow 0} = \left(\frac{\ln(\eta_r)}{C} \right)_{C \rightarrow 0} \quad (6)$$

Common ordinate intercept or the average value of the intercepts of the double extrapolation plots of reduced viscosity and inherent viscosity against concentration gives the intrinsic viscosity¹⁹. Then viscosity average molecular weight, \overline{M}_v is calculated using the Equation (1).

3 Results

Since tensile properties were not showing any improvement from the pure matrices (from preliminary works), further experiments were conducted for impact and flexural properties.

3.1 Method 1 - BPO without inert atm

The effect of all the nanoclays on mechanical properties were studied and compared and shown in Fig 1 to 3.

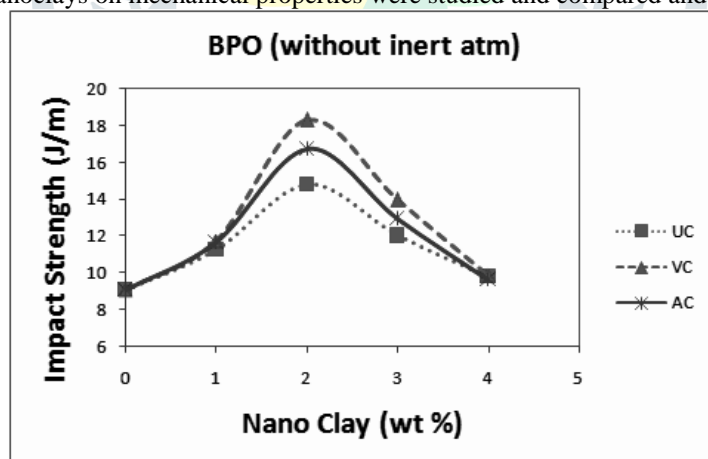


Figure 1: Variation of impact strength with BPO without inert atm.

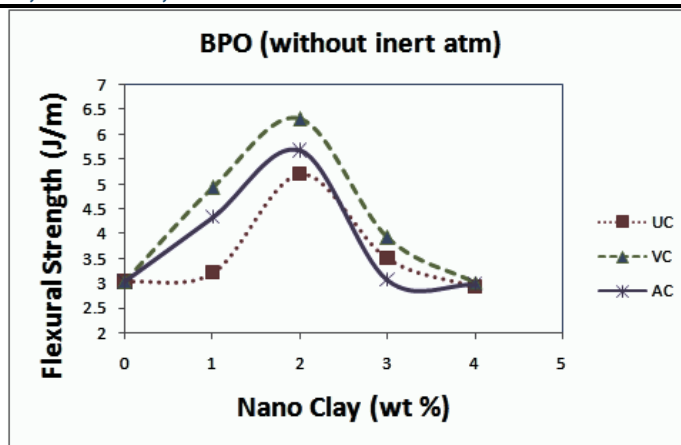


Figure 2: Variation of Flexural strength with BPO without inert atm.

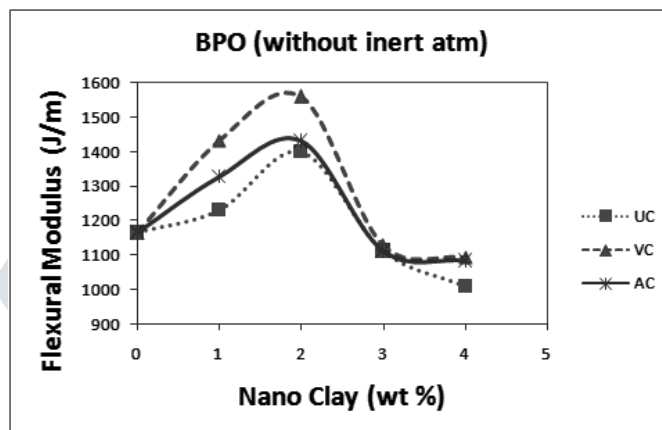


Figure 3: Variation of Flexural Modulus with BPO without inert atm.

All the three curves showed a similar trend where the maximum properties were obtained for vinyl clay at a clay loading of 2 wt %. Aminoclay and unmodified clay showed a lesser effect on mechanical properties. The conversion of polystyrene nanocomposite was calculated by elemental analysis as follows.

$$\begin{aligned} \% \text{ Conversion} &= \frac{\text{Total PS in gm/ monomer charged}}{\text{Weight of monomer charged}} * 100 \\ \text{Weight of monomer charged} &= 78.12\text{gm} \\ \text{Weight of PS} &= 45.62\text{gm} \\ \% \text{ Conversion} &= 58.4 \% \end{aligned}$$

Around 58 % of styrene gets converted into polystyrene by method 1. The remaining styrene might get volatilized during polymerization, since the polymerization was done at 90°C in an open system.

3.2 Molecular weight determination of commercial and in-situ polymerized PS

3.2.1 Method 1- BPO without inert atm

Flow time of solvent, $t_0 = 205$ sec. Intrinsic Viscosity of polystyrene vinyl clay nanocomposites from method 1 (Fig 4) is 0.1775. Intrinsic viscosity of polystyrene (Fig 5) is 0.4285. The values of K and a are 11×10^{-5} dl/g and 0.725 respectively¹⁹. Therefore, molecular weight of polystyrene vinyl clay nanocomposites from method 1 was found to be 26580 and that of commercial polystyrene was 89638.

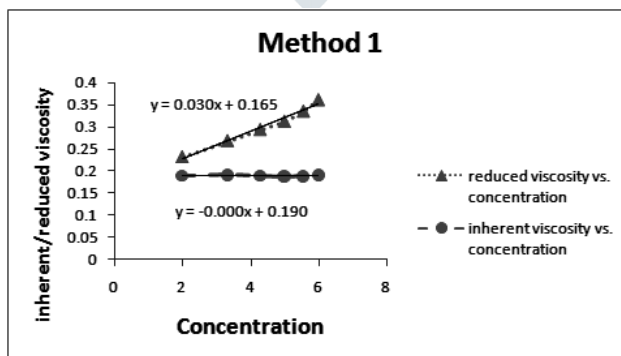


Figure 4: Calculation of intrinsic viscosity of polystyrene vinyl clay nanocomposite from method 1.

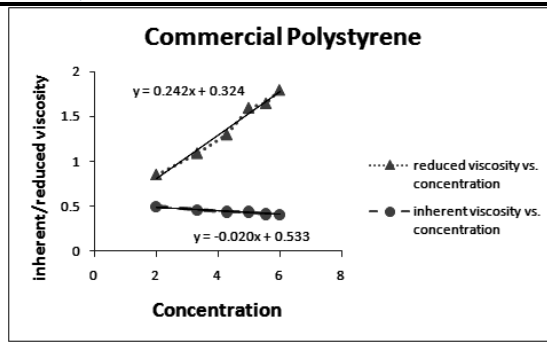


Figure 5: Calculation of intrinsic viscosity of polystyrene.

3.2.2 Method 2 – BPO with inert atm

This method was conducted to overcome the defect of the product obtained in the first method. The product was brittle which was evident from the molecular weight and also since the experiment was conducted in an open system most of the styrene got vaporized at that high temperature which resulted in a low yield of product (58 %). The effect of nanoclays on mechanical properties was plotted in Fig 6 to 8. Here, also the trend was the same and the properties were highest for vinyl clay but better than that of previous method.

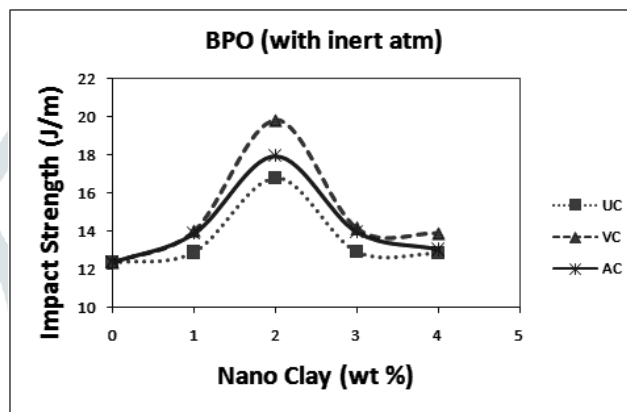


Figure 6: Variation of impact strength with BPO with inert atm.

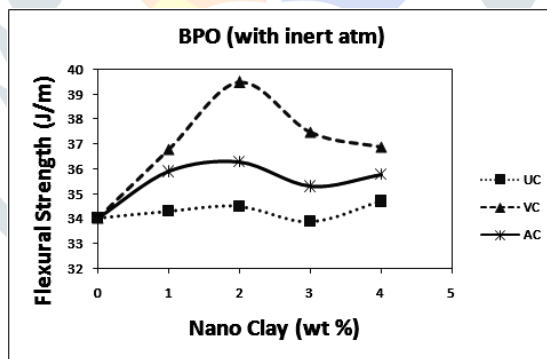


Figure 7: Variation of flexural strength with BPO with inert atm.

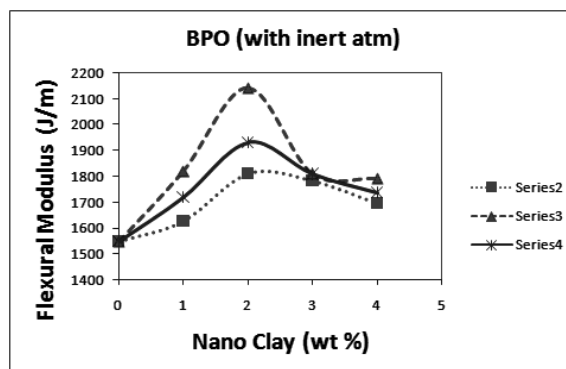


Figure 8: Variation of flexural modulus with BPO with inert atm.

3.2.3 Method 3- AIBN with inert atm

In the third method, AIBN was used as the initiator. Since the decomposition temperature of AIBN is less than BPO, experiments could be conducted at a low temperature ie. At 65 °C. Same trend was observed here also with an added advantage of increase in properties (Fig 9 to 11). Intrinsic viscosity of polystyrene vinyl clay nanocomposites from method 3 (Figure 12) was 0.4465. Therefore, molecular weight of polystyrene vinyl clay nanocomposites from method 3 was found to be 94873 which is much higher when compared to commercial polystyrene. The conversion of polystyrene nanocomposite for method 3 was found to be 92%.

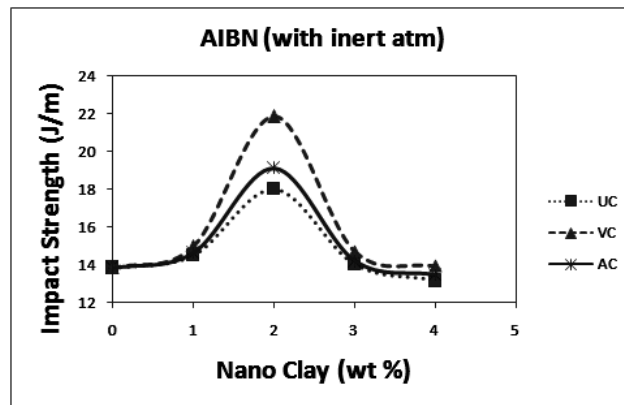


Figure 9: Variation of impact strength with AIBN with inert atm.

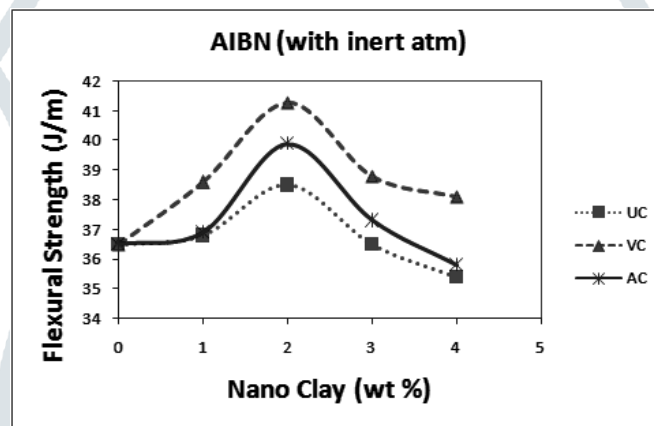


Figure 10: Variation of Flexural strength with AIBN with inert atm.

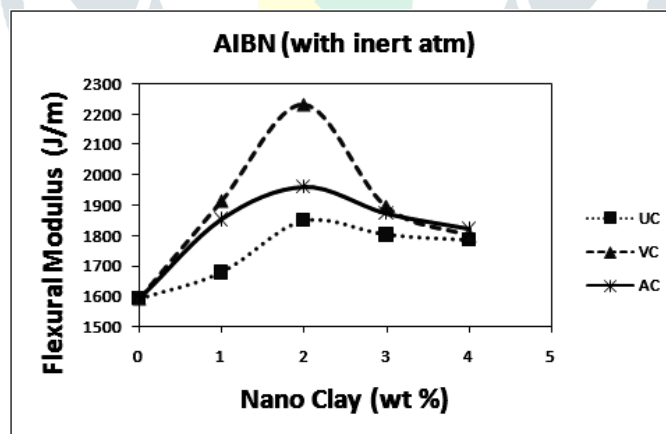


Figure 11: Variation of Flexural modulus with AIBN with inert atm.

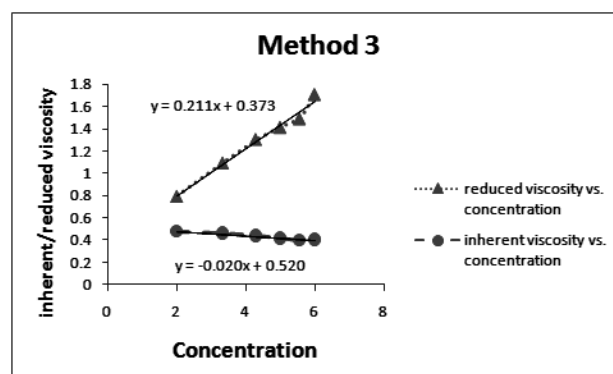


Figure 12: Calculation of intrinsic viscosity of polystyrene vinyl clay nanocomposite from method 3.

4 Discussion

In all the above cases, properties of polystyrene nanocomposites were better for vinyl clay than unmodified and amino clay. For unmodified nanoclay, properties were the lowest. This necessitates surface modification of nanoclay to make it compatible with organic monomers and polymers. When modified nanoclays were used, VC was giving excellent properties at a clay loading of 2 % than AC. This is because of the high dispersion and hence higher interfacial bonding¹ of VC with styrene since styrene is a vinyl monomer. VC shows high compatibility with styrene or polystyrene. The amount of clay loading found to affect its properties¹¹. Datta and coworkers have found that the polymerization rate has a positive improvement and tremendous effect on clay loading¹². Properties are increasing and show a maximum at 2 % and then decreases. This may be due to the agglomeration of nanofillers at higher concentrations.

In the first method, polystyrene clay nanocomposites of very low quality were obtained. Viscosity average molecular weight of the PS nanocomposites was much lower than that of commercial PS. This is obviously due to the lack of control of temperature, catalyst concentration, removal of heat of polymerization etc in this case since it was conducted in an open system without an inert atmosphere. The presence of inert nitrogen atmosphere can improve the molecular weight significantly²⁰ so it is necessary to maintain an inert atmosphere for producing good quality products with considerable yield and degree of polymerisation. Molecular weights of polymers should be large to have strong mechanical properties²¹. So in the second and third method, an inert nitrogen atmosphere was maintained and the experiment was conducted in a closed system. To ensure temperature control water bath was maintained. This led to a drastic improvement in mechanical properties. Also AIBN proved to be the best initiator than BPO. The amount of AIBN required is less compared to BPO. Also the decomposition temperature of AIBN is less which reduces the evaporation of styrene monomer at higher temperatures which ensures higher yield and hence higher degree of polymerization. . Same property enhancement is achieved as commercial polystyrene with fewer amounts of ingredients. When the requirement of components in composite materials is reduced for the same property enhancement, it will significantly reduce the weight of the composite. Thus light weight poly styrene can be prepared which is a remarkable achievement.

5 Conclusion

The effect of various kaolinite nanoclays were compared for the in-situ synthesis of polystyrene kaolinite clay nanocomposites. This shows that surface modification of nanoclay is essential to obtain better mechanical properties. Among the modified nanoclays vinylclay gives better properties due to the compatibility and interfacial interaction of vinyl group with styrene monomer. The effect of initiators like AIBN and BPO were also compared and its operating conditions in the system were optimized. Among the three different methods followed for the in-situ synthesis, molecular weight and hence conversion got improved when synthesis was conducted at inert atmosphere. The presence of oxygen causes inhibition of polymerisation. Molecular weight of polystyrene vinyl clay nanocomposites from method 3 was found to be much higher than commercial polystyrene. Higher conversion is achieved from method 3. Thus in-situ synthesis of polystyrene clay nanocomposites was proved to be best for Vinyl nanoclay with AIBN as initiator under nitrogen atmosphere. With this basis further work can be done by incorporating elastomer also.

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