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THE EFFECT OF DECAHYDRONAPHTHALIN ON THE MECHANICAL PROPERTIES OF MONTMORILLONITE REINFORCED POLYPROPYLENE NANOCOMPOSITES

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ABSTRACT

The exceptional property exhibited by nanoparticles such as carbon nanotubes and silicate layers has been the major drive for research into advanced nanocomposites. The solution method is used to prepare polypropylene/clay nanocomposites with loadings of 2% and 5%. Decahydronaphthalin was used to disperse the clay and dissolution of the polypropylene matrix. The intercalation of macromolecular chains into the organoclay was evident from XRD and confirmed by SEM studies. Decahydronaphthalin was observed to have a considerable effect on the polymer matrix properties and the tensile moduli of the nanocomposites compared to the pristine polypropylene. Tensile moduli of nanocomposite treated with decahydronaphthalin have been observed to be lower than those of pristine polypropylene. The moduli of both the 2% and 5% PP/clay nanocomposite was 528 MPa and 547 MPa respectively. The pristine PP had a modulus of 794 MPa and that of the PP dissolved in decahydronaphthalin alone was found to be 639 MPa.

Keywords: polypropylene (PP), decahydronaphthalin, young's modulus, SEM, montmorillonite.

1. INTRODUCTION

In recent years, polymer based nanocomposites have generated a lot of interest in the field of nanotechnology because exfoliated clays, carbon nanotubes, carbon nanofibers, exfoliated graphite and nanocrystalline metals can generate significant mechanical properties that are advantageous to the modification of polymeric systems (PH Nam *et al.*, 2002; M. Alexandre *et al.*, 2000).

Several composites have been developed by adding reinforcing compounds to polymers to enhance their thermal, mechanical and barrier properties. However, most of these reinforced materials have poor interactions at the interface with the matrix. Macroscopic reinforcing components usually contain defects, which become less important as the particles of the reinforcing are reduced in size (L. N. Luduena, *et al.*, 2007).

An understanding of changes in properties of a particle or fibre reinforcers at the nanometre scale is very critical in optimizing the properties of nanocomposites. The use of polymer-clay nanocomposites is very popular in the automobile industry after commercial exploitation of nylon-clay composites for engine components by Toyota Automotive Corporation in 1989 (PH Nam *et al.*, 2002). Nanocomposites have also been used as packaging materials, construction materials, flame retardants, protective films and so on (H M.C. de Azeredo, 2009).

The combination of clays and polymers do not always results into nanocomposites, therefore, modifications of either the clay or the polymer is necessary to form a nanocomposite. Structurally, two forms of polymer-clay nanocomposites are distinguishable, intercalated (the penetration of polymer chains into the interlayer regions of the clay and interlayer expansion) and exfoliated (if the penetration of the polymer occurs extensively such that, delamination of the clay layers and dispersion of individual nanometre platelets is observed) which normally provides high aspect ratio and surface area.

The most commonly used clays in polymer nanocomposites is Montmorillonite (MMT) whose structure is made up of several silicate layers stacked together by van der Waal's attraction with a layer thickness between 1.2-1.5 nm and a lateral dimension of 100 - 200 nm (Marchant *et al.*, 2002). These layered silicates may consist of tetrahedrally-substituted or octahedrally substituted structure. In the tetrahedrally-substituted configuration the negative charge is located on the surface of silicate layers; thereby allowing more readily interaction with the polymer matrices converse to octahedrally-substituted configuration.

Single layer thickness and the interlayer gap represents the repeated unit of the multilayer material, called d-spacing or basal spacing (d_{001}), and is calculated from the (001) harmonics obtained from X-ray diffraction patterns (Alexandre *et al*., 2000).

In considering clays for nanocomposites, characteristics that the clay should possess include the ability of the silicate particles to disperse into separate layers and the ability to modify their surface chemistry through ion exchange reactions with organic and inorganic cations.

It is important to state that, since clay is a naturally hydrophilic material, there is a difficulty in exfoliating within a polymer matrix; however, it can be rendered more hydrophobic to facilitate exfoliation through surface treatment. This surface treatment can usually be achieved through ion-exchange reactions with cationic surfactants composed of primary, secondary, tertiary or quaternary alkylammonium cations (Fornes 2002). This modification also leads to expansion of the basal spacing between the silicate layers due to the presence of alkyl chain intercalated in the interlayer to finally obtain organoclay (OMMT). It is worth noting that, formation of the stable PP nanocomposite is achieved by

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reducing the enthalpy of the interaction between the surfactant and the clay. The macromolecule chains exfoliate the silicate layers and make them disperse evenly in the polymer matrix.

Nanocomposites usually exhibit significantly improved mechanical and physical properties as compared to those of pristine polymers containing a small amount (<5 wt. %) of clay. These improvements include increased biodegradability of biodegradable polymers; increased strength, heat resistance, decreased gas permeability and flammability. These have been attributed to the stronger interfacial interaction between the matrix and the clay, as compared with conventional filler-reinforced systems.

In order to improve the low temperature and toughness characteristics of Polypropylene (a foam making polymer), nanoparticles containing polar groups have been added by researchers to overcome these undesirable characteristics (F. Hussain, *et al.*, 2006). The optical properties of polypropylene composites are exploited in the commercial packaging applications as the exfoliated nanosilicate layers generate a tortuous path for oxygen and water vapour penetration of the neat polymers especially for polyolefins like polyethylene and polypropylene (J.S. Ma, *et al.*, 2006), a very important property for increasing the shelf life of food with durable packaging.

In this paper, we investigate the effect of addition of organic solvent to different concentrations of organically modified clays (Closite ® 20A) with polypropylene. The properties of the composites have been characterized from the morphological, microstructural and mechanical properties point of view.

2. EXPERIMENTAL

2.1. Materials and specimens

Polypropylene with a melting temperature of 162ºC was supplied by Fibertex. Montmorillonite (Cloisite 20A, Lot no.20060922AL-049) was purchased from Southern Clay and further modified with alkyl ammonium. Decahydronaphthalin was supplied by Merck Schuchardt OHG, Germany. The injection molding of the test specimens was performed on an industrial-sized Ferromatik Milacron, Malterdingen, Germany K110 injection-molding machine and dispensing it into the dog bone mould.

2.1.1. Preparation of the organically modified montmorillonite (OMMT)

The organic modification of the Montmorillonite is based on the traditional methods of ion exchange reaction between alkyl ammonium cations and Na$^+$-MMT. In the typical modification case, 30 grams of MMT was dispersed into 350 mL deionized water and under magnetic stirring at a temperature of 85 ºC for about 30 mins to allow for homogeneous dispersion. A 0.1M hexadecyltrimethylammonium chloride (HTAC, Aldrich) solution was mixed together with 5ml HCl in 100 ml deionized water. The solution was then poured into the hot clay-water mixture and continuously stirred at a temperature of 85ºC for about 2 hours leading to the formation of a white precipitate. The clay slurry was then filtered and washed with copious amount of water to remove all the chloride ions. The final filtrate (organoclay) was then oven dried at 70ºC for 48 hours.

2.1.2. Preparation of polymer/Montmorillonite (OMMT) nanocomposite

The solution method for nanocomposite preparation was employed in the polypropylene/OMMT nanocomposite (with OMMT loading of 2wt %, and 5wt %). The OMMT was first oven dried at 100ºC for 24 hours to get rid of retained moisture. Measured quantities (2wt % and 5wt %) of the as-prepared OMMT were each dispersed in 60ml of decahydronaphthalin using a low power sonicator horn for 40 mins. 10g of PP was added to each of the dispersion under continuous stirring at 100ºC until complete dissolution of the PP leading to the formation of a very viscous suspension. The as-formed nanocomposite was further dried in an oven for 72 hours to remove any excess solvent in the nanocomposite. As a control, raw PP was also dissolved in the organic solvent without any OMMT which was also dried for 72 hours.

2.1.3. Moulding of dog bones

Dog bone samples were prepared by slicing the composites prepared into pieces as test dog bone specimens (see Figure-1) used for the mechanical, XRD and SEM studies.
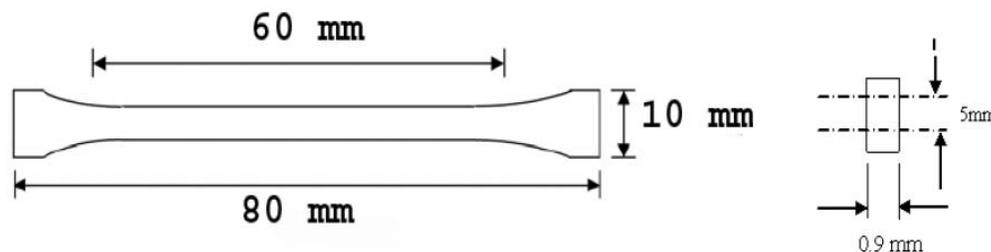
Figure-1. Dog bone specifications and dimensions produced by the injection moulder.

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Injection moulding device (Ferromatik Milacron) with a programmable temperature was used in melting the polymer/clay mixtures and were then casted into dog bone shapes. The heating temperature used was 145ºC. This condition was chosen in order not to exceed the melting temperature of the polymer which may eventually affect the mechanical properties of our sample. The injection moulder, has a pressurized piston which rotates to thoroughly mix the composition together for dispensing the molten mixtures into the dog bone mould which is clamp at the bottom. The melt was then pressed into the mould, after which it was removed and placed in a water bath to cool. The dog bone sample was later opened apart from the mould.

2.2. Characterization techniques

X-ray powder diffraction (XRD) patterns were collected on a Rigaku D/Max-(III) Bragg-Bretano diffractometer with a copper Kα radiation (λ=0.154nm) at 40 kV and 30 mA. The XRD patterns were recorded in the 1º-50º 2θ range with a step size of 0.05º and a counting time of 10s per step.

A Hitachi S-4100 Scanning electron microscope (SEM) equipped with an EDS analyzer was employed for the morphological, microstructure and the investigation of the degree of dispersion of the clay and the nanocomposite: prior to investigation, specimens were sputtered with a thin film of gold to make them conductive; improve image resolution and avoid charge accumulation on nanocomposite during SEM examination.

Tensile testing of the nanocomposite was performed at room temperature using a Zwick Z100 tensile test machine (Zwick Roell, Germany) equipped with a computer-controlled mechanical tester with a clip-on gauge extensometer. The test was conducted at a crosshead speed of 5mm/min. A minimum of five tests was performed for each reported value. Stress-strain curves were then recorded for the various specimens.

3. RESULTS AND DISCUSSIONS

From the XRD data (Figure-2a), OMMT shows a diffraction peak at 2θ = 4.76º which is assigned to the interlayer platelet spacing (001 diffraction peak) with a spacing of 1.86nm. The interlayer spacing for the OMMT was calculated using the Bragg's equation, λ=2dSinθ. The sharp peaks in the XRD patterns of the pristine PP (Figure-2b) indicate the crystalline nature of the PP. In the PP-OMMT nanocomposite (Figure-2c), no observable peak of OMMT was found which could be attributed to the intercalation of the macromolecular chains in the basal spacing of the OMMT/ polymer matrix. With increased loading of the clay in the polymer matrix, there was an increased tendency in agglomeration of the nanoclays particles. This is further confirmed in the scanning electron microscopy images of the 2% and 5% nanocomposite respectively as shown in Figure-3. This indicates that, although the clay aggregates were dispersed during the sonication process, there is an immediate agglomeration stage during the formation which could be attributed to the presence of weaker van de Waals forces that existed between the particles (K. Yano, et al., 1991).

The wetting capability of the polymer matrix with the organoclay is observed to be very low, which may be associated with difference in polarity. It is worth stating that, in the ideal situation, the organoclay is expected to form a partial bond (non-covalent bond) with the polypropylene matrix, due to the fact that the organoclay structure consist in part of some hydrophobic intermolecular chains incorporated in its layers; however this seems not to be the case with PP composite, leading to agglomeration of the nanoclays, as observed the 2% and 5% nanocomposite.

The mechanical properties of the various samples (as-received polypropylene; polypropylene-decahydronaphthalin; 2% OMMT clay/PP composites and 5% OMMT clay/PP composites) are presented in Figure-4 and Table-1 taking into account the tensile modulus and tensile strength (stress).

It can be observed that, the tensile modulus of the as-received polypropylene was higher than that of the composites and that of PP dissolved in decalin.

Tensile modulus expresses the stiffness of a material at the onset of the tensile testing and generally increases when a nanocomposite is formed. The incorporation of the polymer chains into the silicate layers leads to an increase in the surface area of interaction between the clay and the polymer matrix, thus causing an improvement in modulus over the entire composition. There was no any significant increase in the moduli of the composites as compared to the raw PP. The modulus of the composite at 2% loading was 528 MPa and that of the 5% loading was 547 MPa. These values were far below that of the raw PP which is 794 MPa and that of PP dissolved in decalin is 639 MPa.

These low modulus values for the nanocomposites recorded is attributed to the organic solvent used, which can affect the PP chains, reducing the surface area of interaction between the clays and the PP chains. Also as seen in the modulus value of PP/decalin, the reduction in modulus is caused by the presence of the decalin in the final composition as it interferes with the mechanical properties of the polypropylene. The decalin shrinks the PP making it brittle during drying.

The slight increase in modulus in the 5% nanocomposite as compared to the 2% nanocomposite may be due to the volume loadings of the composite used. In order to take advantage of the "nano - effects" it is necessary to ensure there is some form of bonding or interaction between the PP and the clays (J. Lie, et al., 2003) however, the use of decalin hinders the interactions between the PP and the clay, hence the low modulus values recorded in both the composites and the PP dissolved in decalin as compared to the raw PP.

There was no any significant change in the tensile stress as can be seen in Table-1. This certainly suggest that, the clays were neither exfoliated or intercalated during the dispersion process to cause any improvements in strength of the nanocomposites with respect to the raw

PP and PP dissolved in decalin. Both the 2% and 5% loadings of the nanocomposite had a tensile strength of 27 MPa, which is similar to that of the raw PP and PP dissolved in decalin.

Usually, tensile strength of a nanocomposite depends on the interaction between the clay and the PP (S.R Lee, *et al.*, 2000). The PP is non-polar and the clay is polar and so it is important to modify the clay surface. Modified nanoclay which has an alkyl chain was therefore used to compatilize the clay with the PP. However, there was no any noticeable change in the tensile moduli of the composites. This might also suggest that, the clay did not exfoliate in the PP or interaction of the PP did not occur to cause any changes, they rather re-aggregated as was seen in the SEM images shown in Figure-2.

The stress-strain curves of the nanocomposite are show in Figure-3. From the graphs, it is clear that, the filler content contributes to the low elongation to break due to the stress concentrations that causes the composite to fail in a brittle manner with regards to the pristine PP, resulting in a lowering of the elongation at break of the 5% composite in comparison with the 2% and that of the raw PP and PP/decalin.

(a)

(b)

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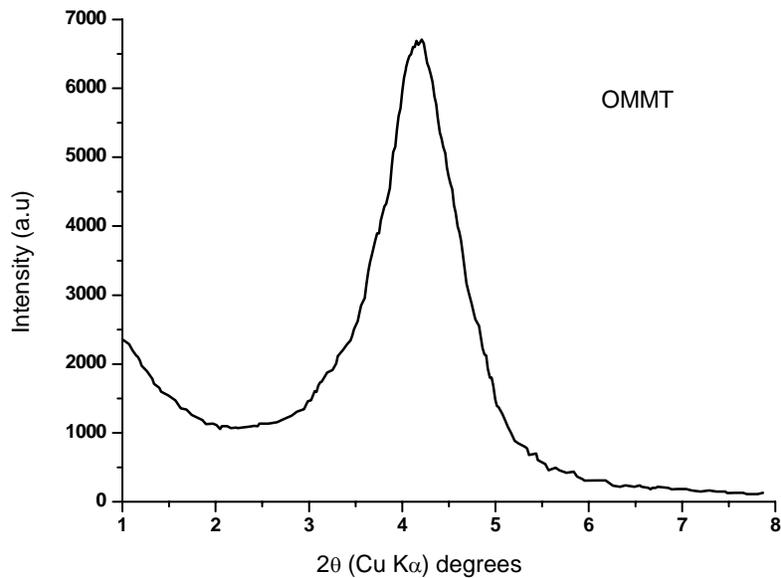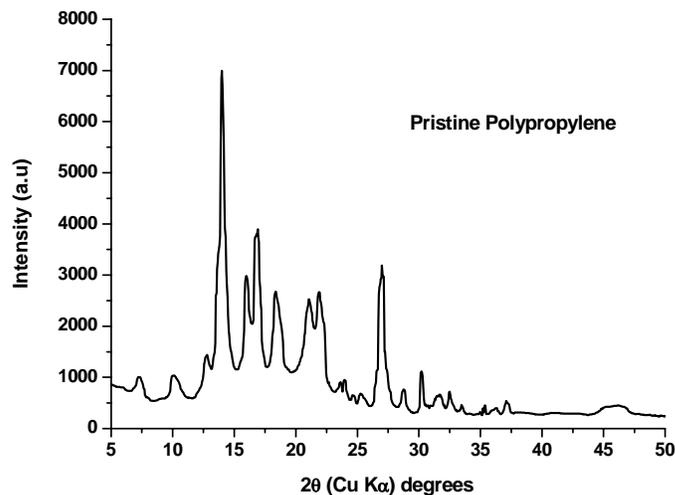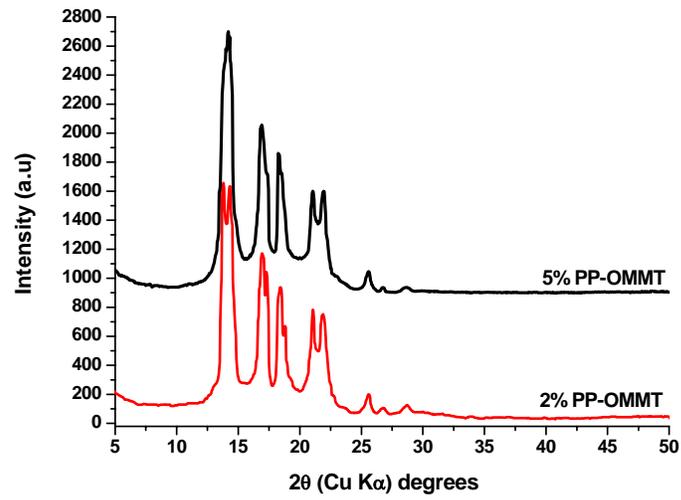
(c)

Figure 2. XRD patterns of (a) OMMT, (b) Pristine (raw) Polypropylene, (c) 2% and 5% PP-OMMT.
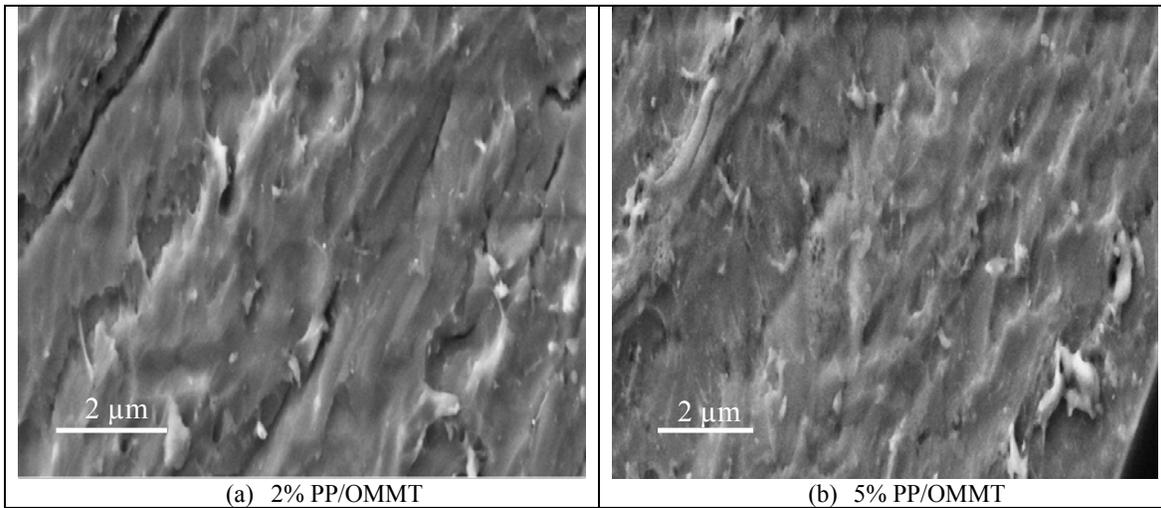
Figure-3. SEM images of (a) 2% PP/OMMT and (b) 5% PP/OMMT loading.

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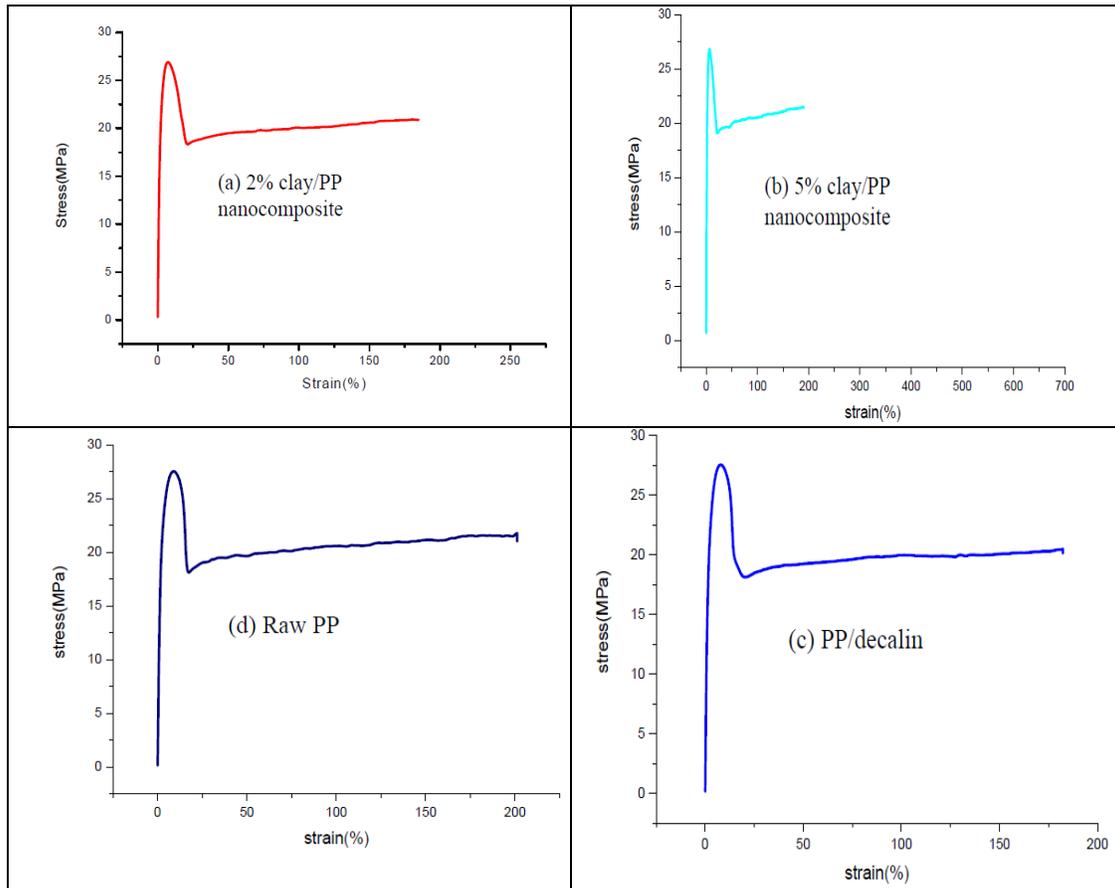
Figure-4. Stress-strain curves (a) 2% clay/PP, (b) 5% clay/PP (c) PP/decalin, (d) Raw PP.

Table-1. Mechanical properties of the various samples.

Compositions	Tensile modulus (MPa)	Tensile stress (MPa)
Raw PP	794	27
PP dissolved in decahydronaphthalin	639	27
2% PP/ OMMT clay composites	528	27
5% PP/ OMMT clay composites	547	27

4. CONCLUSIONS

Polypropylene based nanocomposite containing organically modified montmorillonite (OMMT) was prepared by the solution method. The OMMT clays were obtained by ion exchange reaction using long alkylammonium molecules to facilitate exfoliation of the silicate layers within the polypropylene matrix. X-ray diffraction data showed that the basal (interlayer) spacing of modified montmorillonite increased from ≈1.43nm (literature value) to 1.86nm which promotes the penetration of macromolecules into the silicate spacing for intercalation. The intercalation of macromolecular chains into the organoclay was evident from XRD and was confirmed by SEM study.

In using this solution method of nanocomposite formation, it was observed that, the decalin (organic solvent) used for dispersing the clay and dissolving the polymer, had an adverse effect on the mechanical properties of the PP.

It was clear that by dissolving the PP in the organic solvent (decalin); the young's modulus was decrease by 20%. Also, there was no any improvements in the tensile strengths of the PP, which suggested that, nanoclays remained agglomerated after the dispersion and where not probably exfoliated.

Increasing the loading of the nanoclays also caused stress concentrations in the PP making it to fail in a brittle manner as could be seen from the stress-strain curve for the 5% clay loading where the elongation to break was quite low compared to pristine PP.

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