Studies on Development of Polypropylene-Clay Nanocomposite for Automotive Applications

Thesis submitted in the partial fulfillment of requirement for the award of the Degree of Master of Technology

In

MATERIAL SCIENCE AND ENGINEERING

Submitted by
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Project Completed at Tata Autocomp Systems Limited -Tech. Center

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July-2008

DECLARATION

I hereby declare that the thesis titled "Studies on Development of Polypropylene-Clay Nanocomposite for Automotive Applications" is an authentic record of my study carried out at Tata Auto Comp Systems Limited- Tech Center as requirement for the award of the degree of M.Tech in Material Science & Engineering.

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Chapter 1

1. 1 Introduction

Polymer composites are widely used in a variety of applications involving automotive parts, consumer products, and electronics.[1,2] In recent years, polymer clay nanocomposites have drawn great interest from both the industry and academia because they often exhibit remarkable improvements in materials properties at very low clay loading (up to 5 wt. %) when compared to pristine polymer or conventional composites[3]. Since low amounts of fillers are used in the composite, density of the final product can be reduced, leading to improved fuel efficiency and reduced pollution.

Nanocomposites constitute a class of material having nanoscale dispersion, typically 100 nm, of the filler phase in a given matrix. Polymer clay nanocomposites have shown dramatic enhancements in mechanical properties (modulus and strength), thermal properties (heat resistance and flammability), and barrier properties.[4] The need to develop new materials with better barrier properties[5,6] is because of stricter permeation[7] standards, which allow permeation[8] of 2.5 grams/sq. meter/day for < 225 cc engine displacement. Therefore, nanocomposites may be used to manufacture automotive parts with reduced weight, reduced part thickness and overall cost reduction[9] as compared to existing materials.

The fast pace of research in polymer clay nanocomposites has already developed some products that are being used commercially for certain applications[10] such as nylon nanocomposites[11] in automotives[12], and in packaging film[13]. Other nanocomposite systems that have been extensively reported in the literature include polymer matrices[14] such as polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO), etc.

1.2 Scope of present work

This research work focused on the development of PP / clay nanocomposites and their potential application in automotive industry. Two different types of clays were used and comparison between their mechanical, thermal, and barrier properties was made to understand structure property relationship in these materials. A brief literature review is documented in Chapter 2. Chapter 3 describes materials, equipments, and experimental methods used for polymer nanocomposite preparation and characterization. Chapter 4 covers results and discussion of the morphology of the nanocomposites, followed by the mechanical and thermal properties of the polymer clay composite systems. Chapter 5 summarizes the overall conclusions. Chapter 6 suggests future work.

1.3 Challenges

Some challenges in processing polymer clay nanocomposites are: to achieve uniform surface treatment of clay layers; to maximize dispersion of filler particles in the polymer matrix; to increase interaction between polymer matrix and filler particles; and to prevent re–agglomeration of filler particles during processing.

Challenges in materials include: material cost of surface modifier (intercalant) and compatibilizer; limited availability of equipment for clay modification, and characterization of clays and nanocomposites (which will restrict experimental iterations).

Chapter 2

2.1 Nanocomposites

As mentioned in the previous chapter, nanocomposites are a class of materials, which contains fillers with at least one dimension in nanometers (less then 100 nm) dispersed in polymer matrix. Advantages of using nanocomposites are:

- Improved mechanical properties[15]
- Improved barrier properties[16]
- Reduced weight
- Overall system cost effectiveness
- Numerous processing advantages
- Recyability[17]

2.2 Types of polymers used as matrix material

Thermoplastics are the general class of polymers used as matrix material for nanocomposite synthesis. They can be remelted and remolded. Commonly used thermoplastics include PP, PE, poly(ethylene terephthalate (PET), PMMA, PS, polycarbonate (PC), nylon, etc. Out of these some polymers like PMMA, PS, and PC are useful at temperatures below the glass transition temperature (T_g) because they are amorphous. Thermoplastics can be processed by extrusion, injection molding, and blow molding.

2.2.1 Polypropylene

Polypropylene is a versatile polymer used in applications from films to fibers with a worldwide demand of over 21 million pounds. Polypropylene is synthesized by the polymerization of propylene, a monomer derived from petroleum. The range of molecular weights for PP is *Mn* = 38,000 to 60,000 and *Mw* = 220,000 to 700,000. The

molecular weight distribution (*Mn/Mw*) can range from 2 to about 11. The isotactic polymer is the most commercially used form with a melting point of about 165 °C. It is used in applications such as sealing strips, paper laminating, and adhesives.

Polypropylene is less resistant to degradation (particularly high temperature oxidation) than polyethylene, but it has better environmental stress cracking resistance. The decreased degradation resistance of PP is due to the presence of a tertiary carbon in PP, allowing for easier hydrogen abstraction compared with PE. Polypropylene is one of the lightest plastics, with a density of ~0.905. The nonpolar nature of the polymer gives PP low water absorption. Polypropylene has good chemical resistance, but liquids such as chlorinated solvents, gasoline, and xylene can affect the material. Polypropylene has a low dielectric constant, and is a good insulator. Difficulty in bonding to polypropylene can be overcome by the use of surface treatments to improve the adhesion characteristics.

Polypropylene has many applications. Injection molding applications cover a broad range from automotive uses such as dome lights, panels, and car battery cases to luggage and washing machine parts. Filled PP can be used in automotive applications such as mounts and engine covers. Elastomer modified PP is used in the interiors, exteriors, and under the hood applications. New grades of high flow PPs are allowing manufacturers to mold high performance house wares.

2.3 Types of fillers

Fillers are typically incorporated in polymers to improve their processing behavior, physical properties, and to reduce the costs of the final products. Large quantities of particulate fillers are successfully used in PP to improve its performance, and to extend its application envelope to fields where other engineering thermoplastics have been used. For PP, the most commonly used filler is talc, followed by calcium carbonate, and then by glass fiber as reinforcing filler. Other fillers include mica, silica, glass beads, clay, carbon nanotubes (CNTs), etc.

Some of the factors that affect the mechanical properties of the composites are particle size, particle size distribution, specific surface area, hardness, shape, surface free energy and surface treatment, chemical composition, interface chemistry, filler morphology, and degree of purity.

With decreasing particle size, there is an increase in strength and modulus accompanied by a decrease in deformability and impact strength. Also, the tendency of fillers to aggregate increases with increases in numbers of small particles. This can lead to insufficient homogeneity, and the aggregated particles can act as crack initiation sites during impacts. Specific surface area has a direct effect on the adsorption of additives and polymer chains, and the extent of adsorption is proportional to the area of the polymer matrix filler interface. This adsorption affects yield stress, tensile strength, and impact resistance.

The shape of the fillers plays an important role in the reinforcement of the composites increasing with the anisotropy of the particle. Polymer matrix filler interactions affect the mechanical properties of the composite and the particle – particle interactions influence aggregation. Both these interactions are determined by the surface free energies of the filler particles, with nontreated fillers having high energy surfaces. During melt mixing, polymer chains adsorbed onto the active sites of the filler surface form a layer, and the character, thickness, and properties of this interlayer are different from the properties of the matrix. Secondary, van der Waals forces determine the strength of the matrix / nontreated filler interaction and the thickness of the interlayer. Fillers can be broadly classified as inert and reinforcing.

2.3.1 Inert fillers

Inert fillers do not chemically react with the polymer matrix but only the volume occupied by the filler affects the properties of thermoplastics. In particular, these fillers may increase the density, hardness, heat deflection temperature (HDT), and reduce

shrinkage. Examples of this type of fillers are china clay (kaolin), talc, calcium carbonate, etc.

2.3.2 Reinforcing fillers

Interaction of these fillers with polymer matrix is mainly chemical in nature. These are added to improve modulus or tensile strength, HDT, creep behavior, surface finish, barrier properties, etc. Examples of these types of fillers are clay, sand/quartz, silica, carbon black, etc. Table 1 shows effect of filler type on properties.

Table 1. Effect of different type of fillers on polymer properties

Test type	Glass fiber	Talc	Sand/quartz powder
Tensile strength	++	**0**	
Compressive strength	+	+	+
Modulus of elasticity	++	+	+
Impact strength	+		
Reduced thermal expansion	+	+	+
Reduced shrinkage	+	+	+
Better thermal conductivity		+	+
Higher heat deflection temperature	++	+	
Electrical resistance		+	
Thermal stability		+	+
Chemical resistance		**0**	
Better abrasion behavior		+	
Extrusion rate	+		
Machine abrasion		**0**	
Price reduction	+	+	++

++: large influence, +: influence, 0: no influence, : negative influence

Ref: Charles.A. Harper, Handbook of Plastics, Elastomers, and Composites.

2.4 Using clay as filler

Clay is used as low cost filler and extender at 40–50 weight percent loading. The objective is to coax polymer chains between the individual clay sheets to get the sheets to disperse completely in the polymer matrix. The important characteristics pertinent to application of clay minerals in polymer nanocomposites are their richest intercalation chemistry, high strength, stiffness, high aspect ratio of individual platelets, abundance in nature, and low cost. Their unique layered structure[18] and high intercalation capabilities allow them to be chemically modified to make them compatible with polymers, which makes them particularly attractive in the development of clay based polymer nanocomposites. Clay minerals[19] used for polymer nanocomposites can be classified into three groups as 2:1 type, 1:1 type, and layered silicic acids.

2.4.1 Layered Silicates 2:1 Type

The layered silicates used in the nanocomposites belong to the same structural family as the better known minerals talc and mica (*i.e.* 2:1 phyllosilicates). Their crystal lattice consists of two dimensional, 1 nm thick layers, which is made up of two tetrahedral sheets of silica fused to an edge shaped octahedral sheet of alumina or magnesia. The lateral dimensions of these layers vary from 30 nm to several microns depending on the particular silicate. Stacking of the layers leads to a regular van der Waals gap between them called the *interlayer* or *gallery* as shown in Figure1.

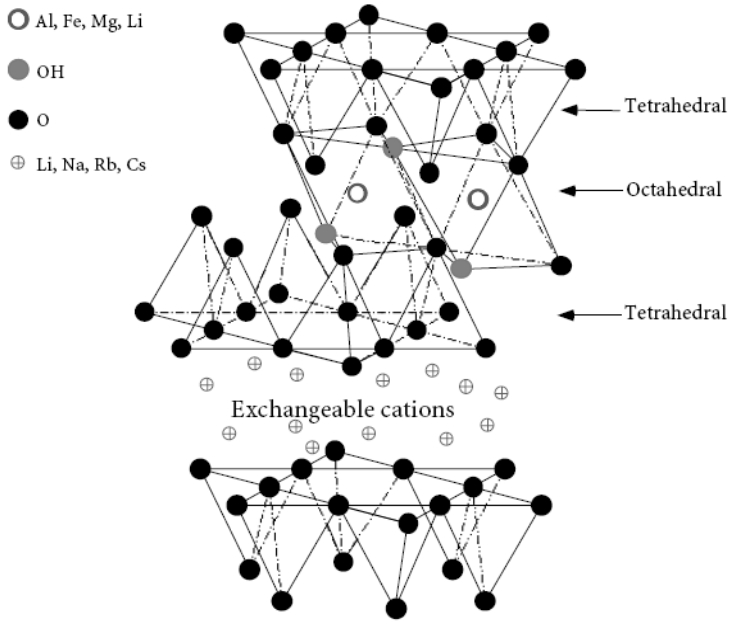

Figure1. The structure of 2:1 layered silicates.[20]

2.4.2 Layered Silicates 1:1 Types

The clays consist of layers made up of one aluminum octahedron sheet and one silicon tetrahedron sheet. Each layer bears no charge due to the absence of isomorphic substitution in either octahedron or tetrahedron sheet. Thus, except for water molecules, neither cations nor anions occupy the space between the layers, and the layers are held together by hydrogen bonding between hydroxyl groups in the octahedral sheets and oxygen in the tetrahedral sheets of the adjacent layers.

2.4.3 Layered Silicic Acids

Clays consists mainly of silicon tetrahedron sheets with different layer thickness. Their basic structures are composed of layered silicate networks and interlayer hydrated alkali metal cations. The silanol groups in the interlayer regions favor the organic modification by grafting organic functional groups in the interlayer regions. They are natural clay

minerals except for octosilicate, but can be synthesized as well. Layered silicic acids are potential candidates for the preparation of polymer nanocomposites because they exhibit similar intercalation chemistry as smectite clays. Besides, they possess high purity and structural properties that are complementary to smectite clays.

All of these clay types are characterized by a large active surface area, layered morphology; characteristic cation for isomorphic substitution (for example, Al^{+3} replaced by Mg^{+2} or Fe^{+2}) generates a negative charge defined through the charge exchange capacity[21] (CEC), depending on the mineral origin, and isomorphic substitution within the layers. The most commonly used clay is 2:1 type with CEC in the range of 0.9 – 1.2 milliequivalence per gram (meq/g). Table 2 shows a summary of clay mineral properties.

Table 2. Properties of clay

Secondary mineral	Type	Interlayer condition/Bonding	CEC [cmol/kg]
Kaolinite	**1:1 (nonexpanding)**	**lack of interlayer surface, strong bonding**	**3 15**
Montmorillonite	**2:1 (expanding)**	**Very weak bonding, great expansion**	**80 150**

2.4.4 Organically modified layered silicate (OMLS)

The physical mixture of a polymer and layered silicate may not form a nanocomposite, rather separation into discrete phases takes place. So clay surface is modified to achieve good exfoliation and dispersion in polymer matrix. Montmorillonite (magnesium aluminum silicate $M_x(Al_{4x}Mg_xSi_8O_{20}(OH)_4)$ is a type of smectite clay, which has a thin layered sheet morphology. They can have lengths upto 1000 nm with thicknesses about 1 nm, which leads to a large surface area, and a high aspect ratio. They are associated with a large net negative charge, located inside the crystal, and a few positive charges on the

edges. However, it is difficult to disperse the clay platelets (hydrophilic) in most polymers (hydrophobic). Therefore, montmorillonite clays are surface treated with long alkyl chain organic molecules, for example. In the case of PP, a compatibilizer, such as maleic anhydride grafted PP, is used to achieve better dispersion leading to exfoliation.

2.4.5 Method of surface modification

It is critical to modify the surface of clays to achieve desired miscibility and dispersion leading to desired properties.[22] Therefore, importance is given to select appropriate organic modifications for layered inorganic clays. Pristine layered silicates usually contain hydrated Na^+ or K^+ ions. Obviously, in this pristine state, layered silicates are only miscible with hydrophilic polymers, such as poly (ethylene oxide), or poly (vinyl alcohol) (PVA). To render layered silicates miscible with other polymer matrices, one must convert the normally hydrophilic silicate surface to organophilic**,** thus making the intercalation of many polymers possible.

Generally, this can be done by ion exchange reactions with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium[23] or alkylphosphonium cations. Alkylammonium or alkylphosphonium cations in the organosilicates lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, and result in a larger interlayer spacing. Additionally, the alkylammonium or alkylphosphonium cations can provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix. A typical schematic of clay modification is given in Figure 2.

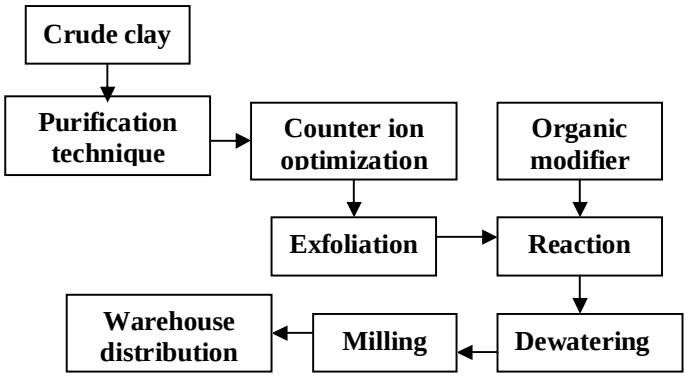

Figure 2. Schematic flow chart for organoclay manufacture.

2.5 Types of nanocomposites

Depending on the strength of interfacial interactions between the polymer matrix and layered silicate (modified or not), three different types of nanocomposites are thermodynamically achievable. A representative schematic is given in Figure 3.

2.5.1 Intercalated nanocomposites

In intercalated nanocomposites,[24] the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio.

2.5.2 Flocculated nanocomposites

Conceptually this is same as intercalated nanocomposites. However, silicate layers are sometimes flocculated due to hydroxylated edge to edge interaction of the silicate layers.

2.5.3 Exfoliated nanocomposites

In an exfoliated nanocomposite,[25] the individual clay layers are separated in a continuous polymer matrix by an average distance that depends on clay loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite.

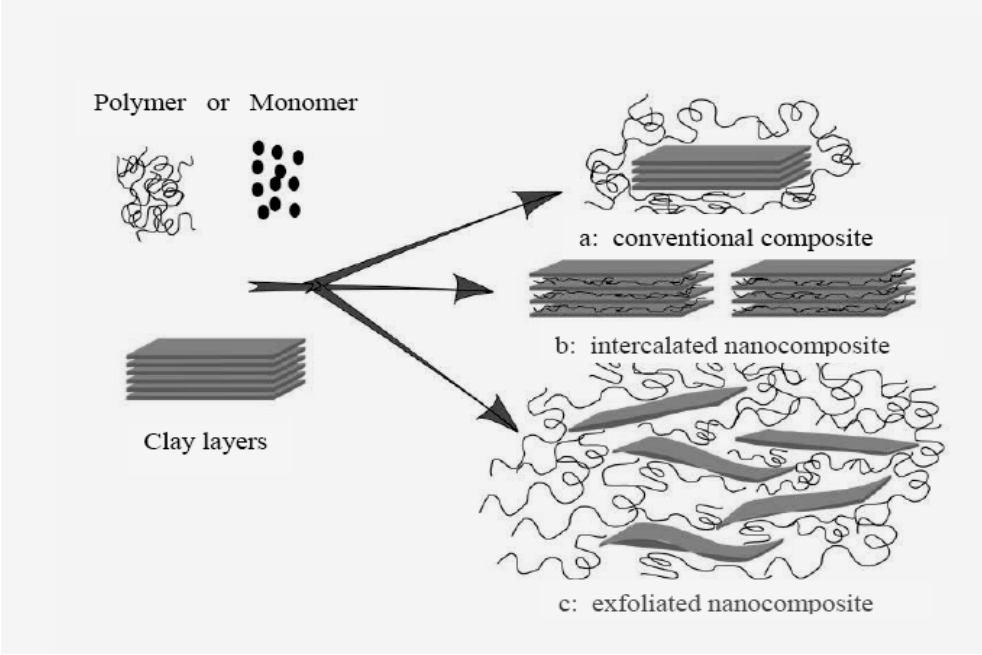

Figure 3. Schematic illustration of three types of polymer nanocomposites.[26]

2.6 Nanocomposite processing techniques

Polymer–clay nanocomposites can be synthesized via four approaches[27,28,29] depending on the starting materials and the processing techniques.

The first approach is via ***in situ*** polymerization, which consists of swelling the organophilic clay layers in the presence of liquid monomer followed by polymerization (Figure 4). It can be initiated by either heat or radiation, by diffusion of an appropriate initiator, or by a catalyst attached inside the clay via ion exchange. The ability of the small monomer molecules to intercalate in the nanolayers for polymer formation to occur makes this technique very successful in achieving fully exfoliated layer.

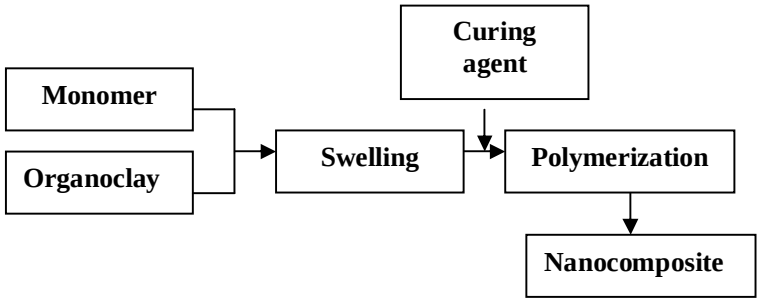

Figure 4. *In–situ* polymerization process.

Emulsion polymerization is another method where the layered silicate is dispersed in an aqueous phase in the presence of a surfactant. The surfactant is not necessarily cationic; it can be anionic or zwitterionic. The monomer is added to the solution and adsorbs onto the clay layers. The advantage of this method is the fact that the clay is modified in the same solution where polymerization occurs rather than functionalizing the clay in a separate stage as done for *in–situ* polymerization.

Along the solution scheme, a third type of synthesis involves dissolving a polymer in a solvent, mixing with organoclay–solvent dispersion where the polymer will displace the solvent and intercalate within the interlayer. Solvent is finally removed, yielding the nanocomposite (Figure 5).

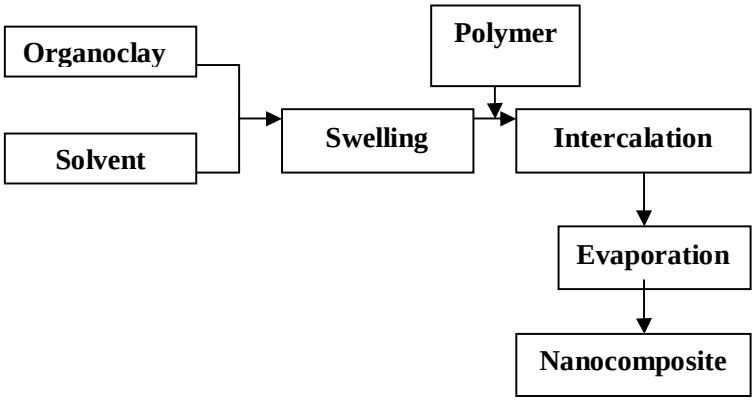

Figure 5. Solution exfoliation.

The fourth technique, melt intercalation,[30] is more industrially favorable due to its ease of implementation and production. This method consists of annealing, statically or under shear, a mixture of polymer and treated clay at a temperature above the glass transition or melting temperature of the polymer (Figure 6). A majority of nanocomposites can be prepared with this approach.

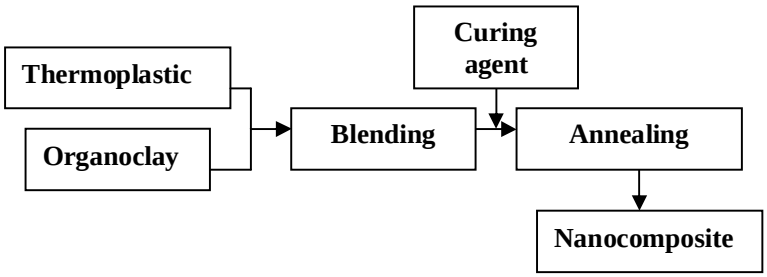

Figure 6. Melt intercalation.

2.7 Characterization techniques for nanocomposites

2.7.1 Morphological characterization

2.7.1.1 Wide Angle X–ray Diffraction (XRD)

Wide angle X–ray diffraction (XRD)[31] is very useful to determine the *d*–spacing of intercalated layered silicates. In general, dry inorganic layered silicates (smectites) show diffraction at about 6–8° (2θ), which corresponds to a *d*–spacing of about 1 nm. The thickness of diffracting clay stacks, number of individual clay platelets per stack, can also be calculated from the breadth of the XRD peak using the Bragg equation: $n\lambda = 2d \sin\theta$,

whereas λ is the wavelength of X–rays; *d* is the spacing between the planes in the atomic lattice; and θ is the angle between the incident ray and the scattering planes.

2.7.1.2 Transmission Electron Microscopy (TEM)

X–ray diffraction alone is not enough to determine the morphology of a nanocomposite. In fact the use of XRD alone can be very misleading since both exfoliated and disordered structures will not be detected by XRD. Nanostructure can be studied by monitoring the position, shape, and intensity of the basal reflections of XRD patterns**.** With XRD morphology, dispersion of clay platelets can be examined. Limitations of XRD technique include absence of information about the spatial distribution of the clay layers or structural non–homogeneities in nanocomposites. In contrast, TEM can provide direct qualitative information of structure, morphology, and spatial distribution of the various components as well as defects in structure.

2.7.2 Thermal properties

There are two purposes for employing thermogravimetric analysis.
(a) To determine the approximate inorganic (clay) content in the polymer clay composite.
(b) To obtain information on the thermal stability of the new material.

Cone calorimetry[32] can be used to determine barrier properties, fire characteristics such as ignition times, weight loss, heat and smoke release rates, heat of combustion as well as the average specific extinction area.

MFI is another property of interest in assessment of molecular mass, and is an inverse of melt viscosity. Knowing MFI is vital to anticipate and control processing parameters during molding of components.

2.7.3 Mechanical properties

Among the many mechanical properties, tensile, flexural, and impact properties are the most frequently considered properties, which are evaluated, and used throughout the automotive industry. These properties are an important indicator of the material's behavior under loading in tension. Tensile testing provides these useful data: tensile yield strength, tensile strength at break (ultimate tensile strength), tensile modulus (Young's modulus), and elongation at yield and break. Another property of interest is the flexural strength, which is the material's ability to resist bending (stiffness of the material).

2.8 Challenges dealing with nanocomposite production

Following are the challenges in the production of nanocomposites:

2.8.1 Exfoliation and orientation

When using clay fillers, it is necessary to separate the particles into the right shape and layer structure called *exfoliation* to achieve required properties. Particle orientation also has an effect on the success of a nanocomposite.

2.8.2 Compatibility and reaggregation

Compatibility between the nanofillers and the polymer substrate may cause issues as well, depending on how they interact with each other. Another concern is during the processing stage there is a possibility of reaggregation where the particles clump together. If this happens, the creation of the nanocomposite is unsuccessful.

2.8.3 The thermodynamic challenge

In general, interplay of entropic and enthalpic factors determines the outcome of whether an organically modified montmorillonite (o–mmt) will be dispersed, intercalated, or exfoliated in a polymer. Dispersion of montmorillonite in a polymer requires sufficiently favorable enthalpic contributions to overcome any entropic penalties. Favorable enthalpy of mixing for the polymer / o–mmt is achieved when the polymer / mmt interactions are more favorable compared to the surfactant / mmt interactions.

For most polar or polarizable polymers, an alkylammonium surfactant (the most commonly used organic modification is adequate to offer sufficient *excess enthalpy*, and promote the nanocomposite formation. However, in the case of polypropylene, the alkylammonium–based o–mmt has surfactants with the same aliphatic apolar nature as PP. Consequently, such systems are at *theta* conditions, and there is no favorable excess enthalpy to promote PP / alkylammonium – mmt dispersion. Thus, the *challenge* with PP is to design systems where the polymer / mmt interactions are more favorable than the surfactant / mmt interactions. There are two ways to overcome this challenge:

1. ***Improve interactions between polymer and montmorillonite*** to become more favorable than the alkyl surfactant / mmt interactions. This can be achieved by PP functionalization *i.e.* by introducing polar or polarizable groups in the polymer.

2. ***Decrease the enthalpic interactions between the surfactant and the montmorillonite***, which effectively will render the PP / mmt contacts favorable. This second route is more challenging, as the alkyl–surfactant / mmt interactions are already very poor (that is exactly the reason these surfactants work so well in dispersing most non aliphatic polymers). However, semi–fluorinated surfactants do have more unfavorable interactions than the hydrogenated polyolefins, and if used appropriately to organically modify the mmt, they will promote PP / mmt miscibility.

2.9 Properties enhanced by using nanocomposites

2.9.1 Mechanical properties

Most of the PP / mmt nanocomposite studies report tensile strength as a function of montmorillonite content. A sharp increase in Young's modulus at filler loadings <3wt% is reported. Analogous results are reported for nylon 6 / montmorillonite systems. Reason for increase in modulus may be attributed to the stiffness of montmorillonite layers as well as the constraining effect of exfoliated montmorillonite layer on molecular motion of polymer chains.

2.9.2 Thermal properties

Nanodispersion of montmorillonite in polymer matrix also promotes higher heat deflection temperature. Improvement in HDT originates from the better mechanical stability of nanocomposite as compared to neat polymer. Enhanced HDT is important for industrial viewpoint as with the increases in HDT, mold cycle time is reduced.

2.9.3 Barrier properties

Polymer / montmorillonite nanocomposites in which montmorillonite layers are fully *exfoliated* to 1 nm thick individual layers, and dispersed in polymer matrix exhibit enhanced barrier properties, due to the increase in effective diffusion length as solutes must travel a tortuous path around well dispersed platelets of high aspect ratio.

2.9.4 Weight reduction

Enhanced mechanical properties can also be achieved by other layered particular fillers like talc, however much higher filler loadings ~30wt% are required. Hence by using

nanocomposites, weight of final product can be reduced, which in turn would affect the final cost (final system cost reduction and / or value addition is required).

2.10 Examples of Polymer Clay Nanocomposites

Nanocomposite technology has reached a variety of polymers systems that can be mixed with layered silicates. Following are the examples of some polymer clay nanocomposites.

2.10.1 Nylon 6 / Clay Nanocomposites

Toyota research group was the pioneer in polymer nanocomposites by synthesizing nylon 6 / clay nanocomposite via *in–situ* polymerization of caprolactam in the clay interlayers. Montmorillonite was modified with amino acids [$H_3N^+(CH_2)_{n-1}COOH$]. It was demonstrated that the surfactant chain length affected the final morphology of the nanocomposite. Mechanical properties showed significant improvements with the addition of only 4.2 wt% of modified mmt. These exfoliated nanocomposites demonstrated significant increase in dimensional stability and barrier property.

2.10.2 Polystyrene / Clay Nanocomposites

Polystyrene is one of the most researched nanocomposite systems, being synthesized via *in–situ* and emulsion polymerization, and by melt intercalation. There are several literature papers on polystyrene nanocomposites[33] from different research groups. Akela and Moet synthesized intercalated nanocomposites by using mmt modified via cation exchange with a polymerizable surfactant, (vinylbenzyl)trimethyl ammonium chloride. Styrene was *in–situ* polymerized in the presence of a solvent to facilitate intercalation. These intercalated polystyrene nanocomposites exhibited enhanced thermal properties than pure polystyrene.

2.10.3 Epoxy Resin / Clay Nanocomposites

Several research groups have studied the use of clay filler with epoxy resin.[34] These studies revealed clay intercalation as well as exfoliation, and were focused on the use of diglycidyl ether of bisphenol A [EPON–828] as epoxy resin. Composites were synthesized via *in–situ* technique. Qutubuddin and coworkers synthesized epoxy resin cured in the presence of organophilic montmorillonite, and intercalation was observed due to high interlayer spacing verified by both XRD and TEM.

2.10.4 Polypropylene / Clay[35] Nanocomposites

One of the most used polyeolefins in the industry is polypropylene. One obstacle for synthesizing nanocomposites in this system is the thermodynamic incompatibility between PP and organoclay since PP does not contain any polar groups in its backbone. However, Toyota research group developed PP / clay hybrid by using simple melt mixing of three components: PP, maleic anhydride(MA) modified propylene oligomers (PP–MA), and clay intercalated with stearylammonium cation. XRD and TEM indicated that both intercalated and exfoliated composites were produced, depending on the type of maleic anhydride groups used: MA (acid value = 52 mmol of KOH/g) for intercalated and MA (acid value = 26 mmol of KOH/g) for exfoilated. It was concluded that two factors influence the exfoliation and homogeneous dispersion of the layers in the composite: (i) Intercalation capability of oligomers in layers. (ii) Miscibility of oligomers with PP.

2.11 Nanomaterials in automotive industry

A "Roadmap Report Concerning the Use of Nanomaterials by the Automotive Sector published by the European Commission" called *Nanomaterial Roadmap 2015* has outlined some interesting information regarding nanomaterials.

Some of the nanomaterials that are being investigated are: carbon black; hydrophobic fumed silica; nanoclay; nanotalc; carbon nanotubes; polymer nanocomposites; oxides such as magnetite, ceria, and titania; aluminum / magnesium / titanium alloys; metal / ceramic coatings; silicon carbide and carbon nanofibers; and metal matrix hybrids.

These materials can be used in the following domains in the automotive industry: frames and body parts; engines and powertrain; paints and coatings; suspension and breaking systems; lubrication; tires; exhaust systems and catalytic converters; and electric and electronic equipment.

Some key drivers and challenges that the scientific community faces are: energy; environment; safety; better performance / engine efficiency; aesthetics / haptics; affordability; recyclability; and weight reduction of vehicles.

Some companies that are involved in nanomaterials and nanocomposites research, development, and commercialization are given below:

Nanoclays: Southern Clay Products, Nanocor, Crystal NanoClay (India)

Carbon nanotubes: Hyperion, Bayer, Arkema, Mitsui, Nanocyl, Nanovatec (India)

Nanocomposite compounds / masterbatches: RTP, PolyOne, Crystal NanoClay (India), Technovinyl Polymers (India)

Nanocoatings: for glass, wheels, antifog, water and dirt repellent, self healing, scratch resistant, optical effects, antireflective coatings in interiors: BASF, Bayer, PPG, Nanovere, Triton, Nanogate, Nanophase

Auto manufacturers: GM, Ford, Toyota, Honda

2.12 Polymer nanocomposites in the automotive industry

As explained earlier, a nanocomposite is a multi phase compound in which one of the phases has a length scale in the nanometer range. There are several reasons as to why nanocomposites are being used in the automotive industry. Some of them are:

1. Significant improvement in mechanical properties of nanocomposites can be achieved because of high aspect ratio (length:diameter) of filler particles.
2. Due to the small filler size, there will be less surface distortion of auto components.
3. Since low amounts of fillers are used in the composite, density of the final product can be reduced, leading to improved fuel efficiency and reduced pollution.

Improvements in mechanical (tensile and flexural), thermal (heat distortion temperature, coefficient of linear thermal expansion), and barrier properties, and higher scratch / mar, chemical, and solvent resistance have been reported for the clay nanocomposites. Equivalent values of flexural modulus and heat distortion temperature of conventional 30 weight per cent filled nylon can be achieved with ~ 8 weight per cent nanoclay filled nylon nanocomposite.

Reduction in molding cycle time and warpage has been observed. Longer lasting components with fewer repairs along with weight reduction are added benefits. These nanocomposites can be used in flame retardant applications where lower heat release rate is required. Some applications of polymer clay nanocomposites have been in timing belt covers, step assists, body side moldings, and bumper fascia (Figure 7 A and B).

Figure 7 (A). Pontiac Aztec door cladding, rear quarter panel.

Figure 7 (B). Denali front fascia.

Besides mechanical property improvements, nanoclay compounds can exhibit improved barrier. The reduction in permeation rate is typically attributed to the increase in effective diffusion length as solutes must travel a tortuous path around well dispersed platelets of high aspect ratio. Nylon 6 nanocomposite film achieved an oxygen transmission rate almost five times lower than the standard nylon 6 film.

The reduction in permeation rates can be important in meeting stricter fuel emission requirements in automotive or other small engine applications. The California Air Resources Board (CARB) and the U.S. Environmental Protection Agency (EPA) will be implementing these requirements from 2008 through 2013. Proposed EPA regulations on lawn and garden equipment will limit fuel permeation to 1.5 $g/m^2/day$. Typical polyethylene resins commonly used today will not meet these new standards. Figure 8 shows the reduction in fuel loss rate between a standard blow molded HDPE tank and several nylon nanocomposite tanks.

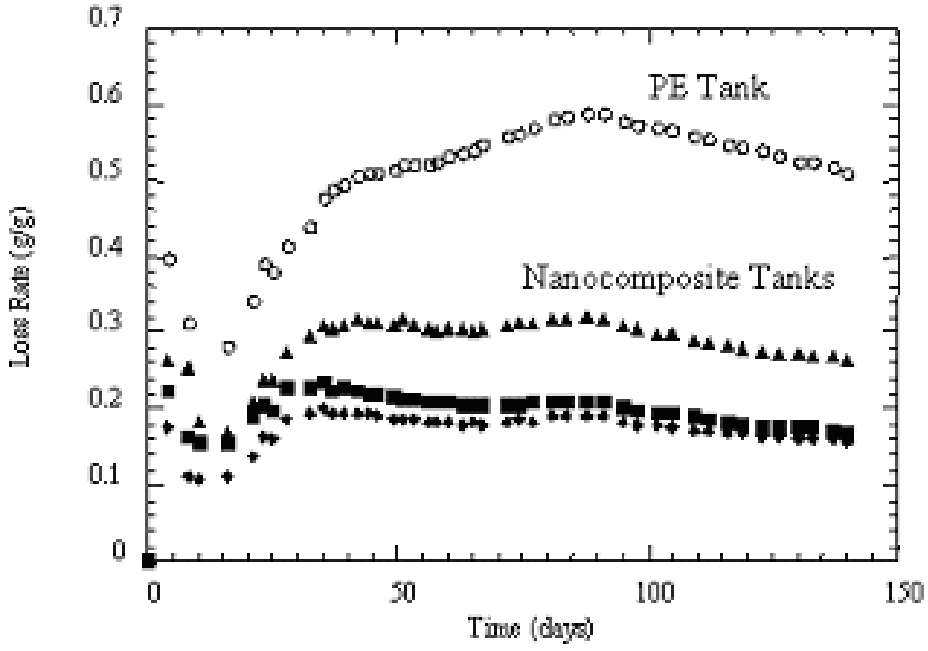

Figure 8. Normalized fuel loss rate comparison of small tanks.

2.13 Scope of present work

This research work focused on the development of PP clay nanocomposites and their potential application in automotive industry. Two different types of clays were used and comparison between their mechanical, thermal, and barrier properties was made to understand structure property relationship in these materials. One of the objectives of this study was to indigenize clay sources and modification, and compounding of PP with clay filler. Clay particles were surface modified using Crystal NanoClay (India) proprietary technique. Modified clays, PP, and MA–g–PP were compounded in an extruder, and pellets were obtained. Tensile, flexural, and impact test specimens were injection molded. Morphology of raw and modified clay was studied using XRD and TEM. Mechanical testing of PP / clay systems was carried out for their tensile, flexural, and impact properties. Thermal stability was determined by thermogravimetric analysis, while flammability was evaluated using burn rate test.

Chapter 3

Materials and Experimental Procedure

3.1 Materials

Two types of organo quaternary ammonium salt modified nanoclays (NC1 and NC2) were obtained from Crystal NanoClay, India. CEC number for NC1 and NC2 are 1.0 meq/g and 0.9meq/g, respectively. Polypropylene copolymer used in this study was obtained from Reliance Industries, India. Maleic anhydride grafted PP (MA–g–PP) used as compatibilizer was obtained from DuPont.

3.2 Nanocomposite Preparation

Polypropylene nancomposites were prepared using two different types of nanoclays and maleic anhydride as mentioned in section 3.1. Pellets of pure PP and MA–g–PP were obtained by extrusion using corotating twin screw extruder with L/D ratio > 36:1. Extruder was maintained at the speed of 300–400 rpm at about 200 °C. This was done to maintain similar thermal history.

Nanoclay powder was dried for 3 h at 90 °C in vacuum oven. NC1 and NC2 clay / PP master batches were prepared with composition of 40 wt% PP + 30 wt% clay +30 wt% MA–g–PP under the same conditions as mentioned above. Master batches were let down into final compositions of 2 wt%, 5 wt%, and 8 wt% for both NC1 and NC2 clays. About 2–2.5 kg of material was extruded for each composition. Sample information is given in Table 3.

Table 3. Nanocomposite sample information

PP	Polypropylene	PP–MAgPP	PP+5 wt% MAgPP
2NC1	PP+MAgPP+NC1 (2 wt%)	2NC2	PP+MAgPP+NC2 (2 wt%)
5NC1	PP+MAgPP+NC1 (5 wt%)	5NC2	PP+MAgPP+NC2 (5 wt%)
8NC1	PP+MAgPP+NC1 (8 wt%)	8NC2	PP+MAgPP+NC2 (8 wt%)

About 20 test specimens for tensile, flexural, and impact testing were injection molded for each composition.

3.3 Characterization of Nanocomposites

Nanocomposite samples were characterized using different techniques to evaluate their morphology and performance. The techniques are described below.

3.3.1 Wide Angle X–ray Diffraction

XRD is the most general technique to probe nanostructures. Hence, XRD patterns were recorded with X–ray diffractometer (Rigaku–Model Geiger, diffractogram) equipped with Cu–K_α X–ray radiation (λ = 1.54 Å). Graph of intensity against 2θ in the range of 2° to 6° was made for raw clays as well as for surfactant treated nanoclays. Scan speed was maintained at 0.5 deg/min.

3.3.2 Transmission Electron Microscopy

Specimens were prepared for TEM by cryosectioning the samples Reichert Jung Ultracut E microtome. The microtome chamber, knife, and samples were maintained at ~ –50 °C. Ultrathin sections were placed on copper TEM grids. Sections were observed using a Zeiss EM 109T electron microscope operating at 80 kV.

3.4 Determination of Mechanical Properties

Mechanical properties were evaluated for all compositions. Table 4 shows the test conditions for determination of mechanical properties.

Table 4. Conditions for mechanical testing

Test Specification	Tensile Test	Flexural Test	Izod (Notched) Impact Test
ASTM Method	ASTM D638	ASTM D790	ASTM D256
Shape of the specimen	Dumbbell shaped	Rectangular	Rectangular
Sample dimensions	150×12.7×3.2 mm^3	125×12.7×3.2 mm^3	64 ×12.7 × 3.2 mm^3
Test temperature	23 °C	23 °C	23 °C
Equipment used	Instron Corporation Series IX	Instron Corporation Series IX	Ceast impact tester
Cross head speed	50 mm/min	2.54 mm/min	NA
No. of specimens tested	Three	Three	Five

3.5 Fracture Analysis using Scanning Electron Microscope (SEM)

SEM (LEO, Model–EV040–7636) was used to study fracture behavior of nanocomposites. After tensile test, the fractured sample was cut in approximately 1 cm size away from fractured surface. Sample was cleaned by ultrasonic cleaning and polished. The fracture surface was coated with thin gold layer and observed under SEM.

3.6 Melt flow index

MFI was determined for each sample according to ASTM1238. Approximately 6.9g of pelletized sample was loaded and compacted in testing cell. Temperature was maintained at 230 °C. An initial load of approximately 1.5 kg was applied for 250 sec. Then a load of 2.16 kg was applied, and melt flow index was noted as flow rate per 15 sec. Samples were weighed using digital balance. Each reading was multiplied by 40 to get MFI in g/10min.

3.7 Thermogravimetric Analysis

Thermogravimetric analysis was done on a Thermal Analysis Q50 instrument Thermogravimetric Analyzer with nitrogen as purging gas. Tests were conducted from 25 to 700 °C at a heating rate of 10 °C/min.

3. 8 Test for flammability

Flammability of nanocomposites was characterized by burn test, which gives a quantitative measure of rate of burning of polymeric samples. Test was conducted according to ASTM D635. Sample dimensions were 150 × 12.7 × 3.2 mm^3. Test samples were placed horizontally in the flammability apparatus (Atlas Model HMV metal flammability cabinet). The free end of specimen was exposed to specified methane gas flame. Ratio of burned length and elapsed time was reported as burn rate (mm/min).

Chapter 4

Results and Discussions

The effect of type of clay and clay loading on the properties of nanocomposites are discussed in the following sub-sections.

4.1 Morphology

4.1.1 X-ray Diffraction

XRD pattern of raw clay NC2 (Figure 9 A) shows one peak at about 2θ = 5.5° with basal spacing of 1.60 nm. Surface treated clay NC2 (Figure 9 B) shows increase in basal spacing of 1.91nm at 2θ = 4.6°. In as received raw NC2 clay scattering peak at 2θ = 5.5° is unsymmetrical indicating the existence of thickness distribution of clay layers. On the other hand in surfactant treated clay peak at 2θ = 4.6 is symmetrical indicating uniform distribution of clay layer thickness. Appearance of a small hump at smaller angle 2θ = 2.6° with basal spacing 3.39 nm is observed in surfactant treated clay, such a shift indicates that the clay gallery has been expanded by incorporating surfactant. Similar morphology is observed for surface treated clay NC1 (Figure 9 C).

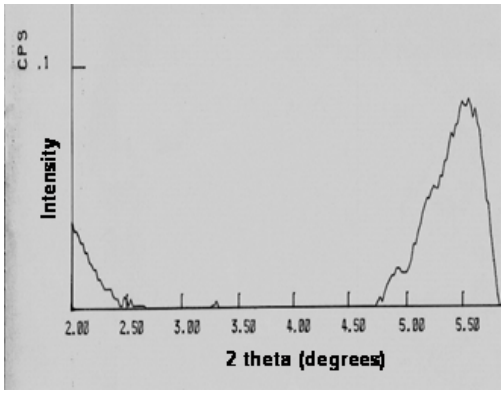

Figure 9 (A). Intensity vs. angle of scattering (2θ) for raw clay NC2.

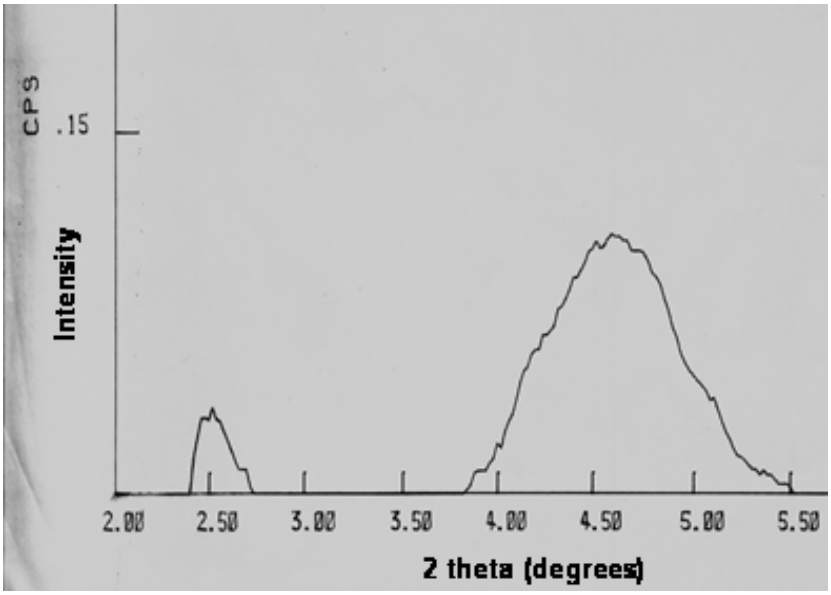

Figure 9 (B). Intensity vs. angle of scattering (2θ) for surface treated clay NC2.

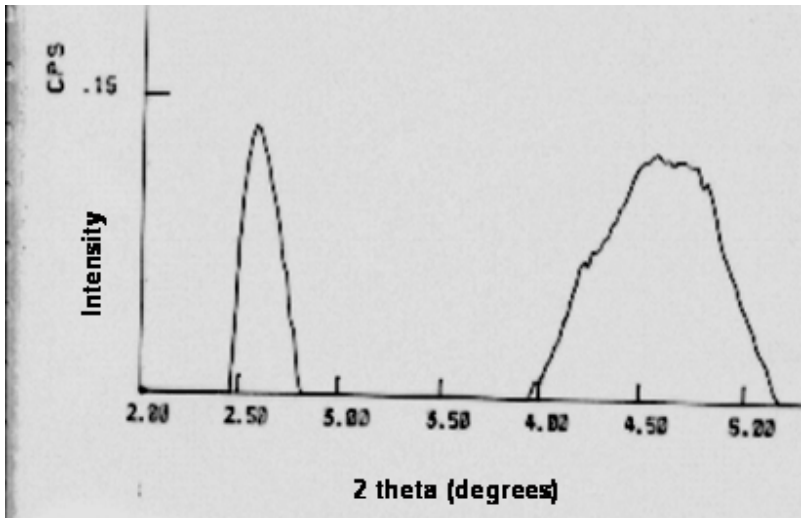

Figure 9 (C). Intensity vs. angle of scattering (2θ) for surface treated clay NC1.

4.1.2 Transmission Electron Microscopy

TEM image of 5NC2 (5 wt% nanoclay type 2) nanoclay composite is shown in Figure 10. This image indicates a mixed morphology, where single, double, or triple layers are exfoliated. Aggregated tactoids are also present. This type of morphology has been reported for PP and polystyrene composites. The ability to exfoliate and randomly disperse the layered silicate in a medium is related to a number of factors such as exchange capacity of silicate, polarity of polymer, chemical nature of organic modifier, and mixing conditions. Similar morphology was observed for 5NC1 (5 wt% nanoclay type 1).

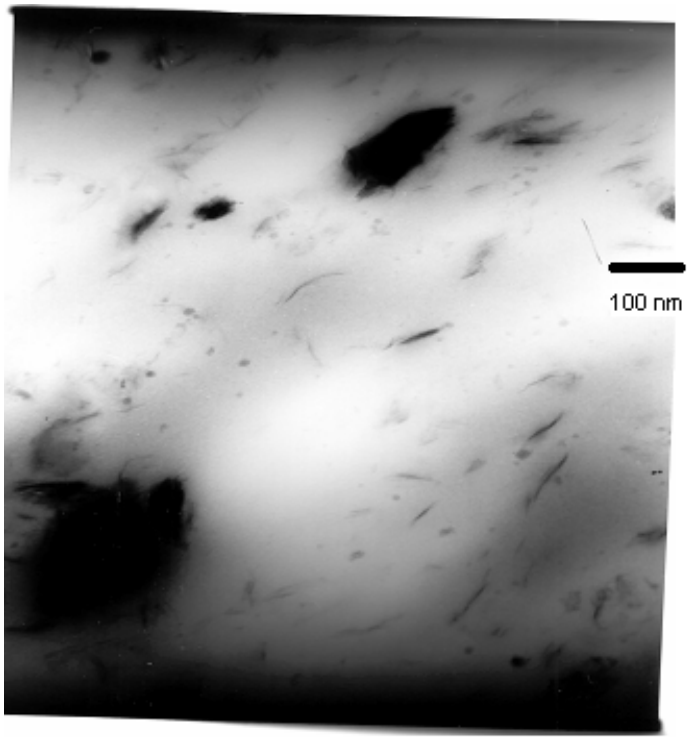

Figure 10. TEM image of 5NC2 (5 wt% nanoclay type 2) nanoclay composite.

4.2 Mechanical Properties

The results for tensile testing are shown in Figure 11. Comparison of Young's moduli from two different clay types is made. Data is obtained from dumbbell shaped samples containing 2, 5, and 8 wt% clay loadings. The characteristic behavior of PP / clay nanocomposite materials is observed. There is an increase in Young's modulus. The amount of change in mechanical properties is directly related to the quantity of clay used in nanocomposite. By the addition of 2 wt% NC1, Young's modulus increases by 2% as compared to pure polymer. However, adding 5 wt% NC1, modulus increases dramatically by 20%, and for 8 wt% NC1 loading it reaches to a maximum of 28%. In the case of NC2, Young's increases by about 12% with 8 wt% clay loadings as indicated in Figure 11.

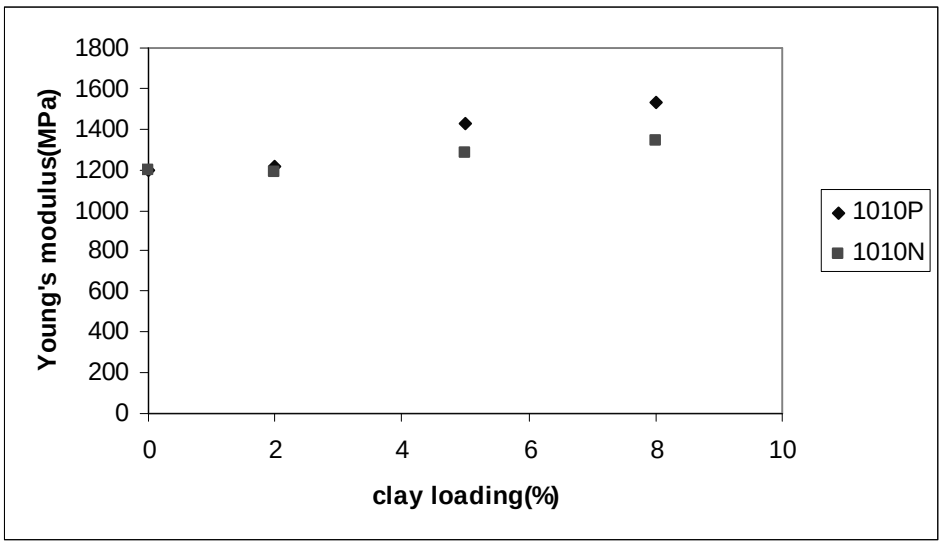

Figure 11. Young's modulus for various clay loadings (1010P – NC1; 1010N – NC2).

The increase in Young's modulus may be attributed to effective stress transfer from polymer matrix to fillers. In present case, increase in Young's modulus is more pronounced by using nanoclay NC1 than NC2. Reason for this may be higher layer charge density (indicated by higher CEC), and subsequently higher alkyl ammonium

content in NC1 than NC2. This may lead to stronger interfacial interaction of NC1 with polymer than NC2. Generally stronger interface interactions reduce the stress concentration, and hence enhances Young's modulus.

Only slight enhancement in tensile strength over pure polymer is observed as shown in Figure 12. Some reasons for this may be: less interaction between polymer matrix and filler layers, more tactoid / intercalation formation compared to exfoliation, amount of MA–g–PP used. The reason for less increase may be attributed to inappropriate MA-g-PP concentration used to prepare nanocomposite. Work by Reichert *et. al.* revealed[36] that considerable tensile strength enhancement could be achieved only when appropriate MA–g–PP compatibilizers were used to prepare nanocomposite. Okada *et. al.* reported only slight improvement in tensile strength[37] compared to virgin PP. Su *et. al.* reported degradation of tensile strength[38] as compared to pure polymer in case of PS / clay nanocomposites.

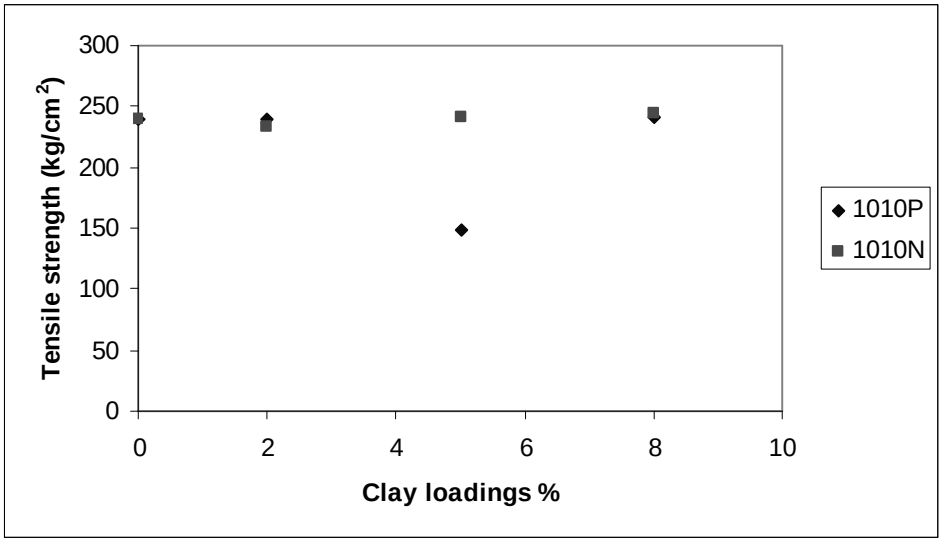

Figure 12. Tensile strength for various clay loadings (1010P – NC1; 1010N – NC2).

Nanocomposite researchers are generally interested in the tensile properties of final materials, there are very few reports concerning the flexural properties of neat polymer and its nanocomposites. Ray *et. al.* reported[39] the detailed measurement of

flexural properties of neat polymer and polymer filled with nanofillers. They have reported a maximum increase of 21% in flexural modulus as compared to neat polymer. In present work, we report an increase in flexural modulus by 15% with 8 wt% loading of NC1, and 6% with 8 wt% NC2 as shown in Figure 13.

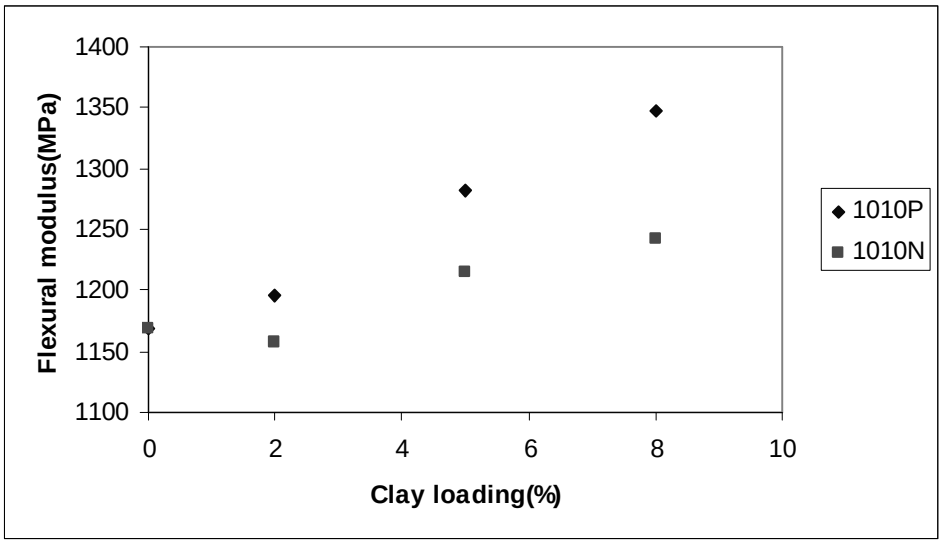

Figure 13. Flexural modulus for various clay loadings (1010P – NC1; 1010N – NC2).

Although significant enhancement in Young's modulus and flexural modulus has been achieved, this improvement is offset by the reduced elongation at break and impact strength of nanocomposite materials. The relationship between elongation at break and clay content is shown in graph. Elongation at break first increases by 8% with 2 wt% NC1. It decreases to 33% with 8 wt% loading. For NC2, the decrease is by 17% for 8 wt% loadings as shown in Figure 14.

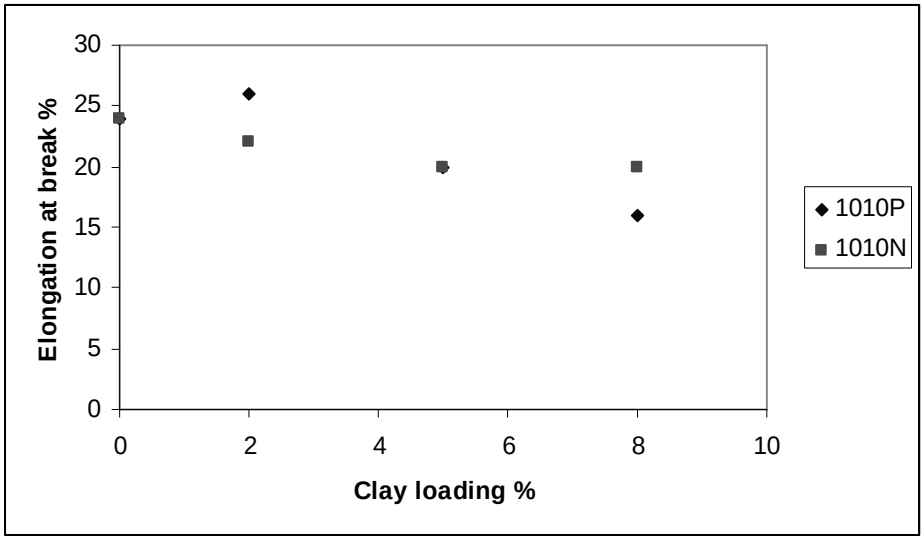

Figure 14. Elongation at break for various clay loadings (1010P – NC1; 1010N – NC2).

There is a decrease in the impact strength of PP nanocomposites compared to the pure PP as expected (Figure 15). This may be due to immiscible aggregates of clay acting as defects and stress concentrators, which might contribute to failure even if they are present only at low concentrations.

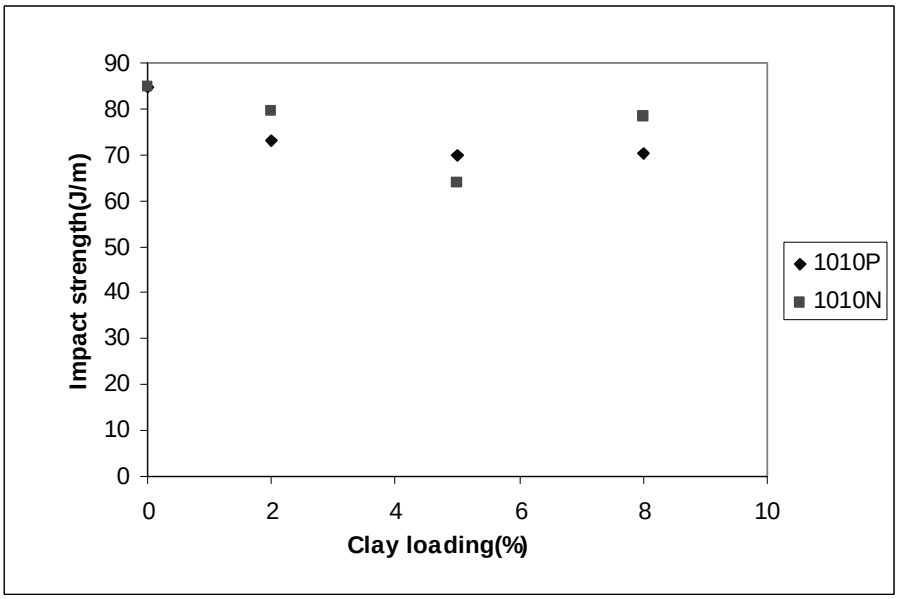

Figure 15. Impact strength for various clay loadings (1010P – NC1; 1010N – NC2).

The relationship between modulus and strength is shown in Figure 16. Modulus and impact strength characterize the potential for end use performance of nanocomposite in automotive industry.

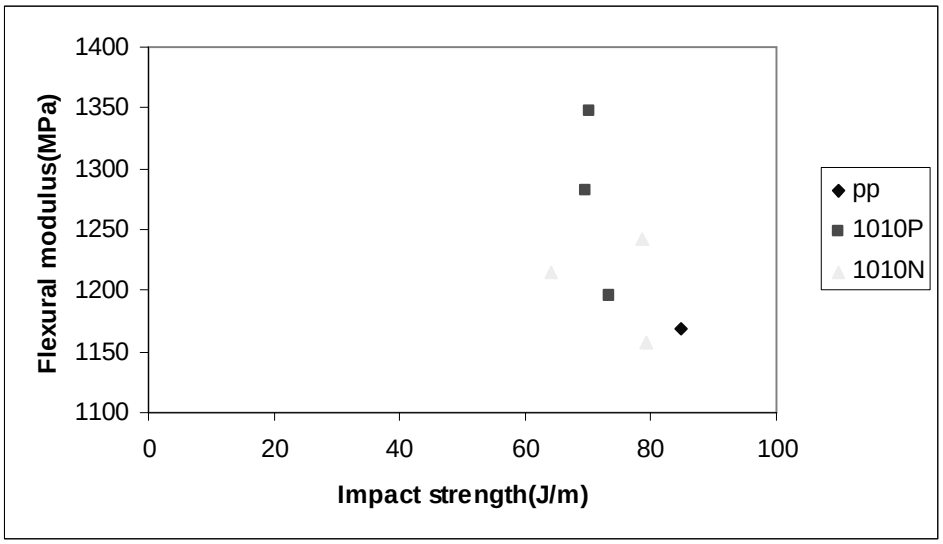

Figure 16. Flexural modulus vs. impact strength for various clay loadings (Pure PP, 1010P – NC1; 1010N – NC2).

Although flexural modulus increases with increasing filler loadings, impact strength decreases. Previous work done by several research groups suggests that mixed intercalated / exfoliated structure can be used to achieve a balance of high modulus and impact.[40]

4.3 Fracture Analysis using Scanning Electron Microscopy

SEM images were taken from fractured surface of tensile samples. The micrographs shows that fracture surface of unfilled PP, 2NC1 (2 wt% NC1), and 8NC1 (8 wt% NC1) are shown in Figure 17 A, B, and C, respectively. Ridges and valleys observed on

fractured surface of unfilled PP indicate ductile fracture mode. This may be correlated to data obtained from elongation at break. Unfilled PP shows more elongation at break than clay filled samples.

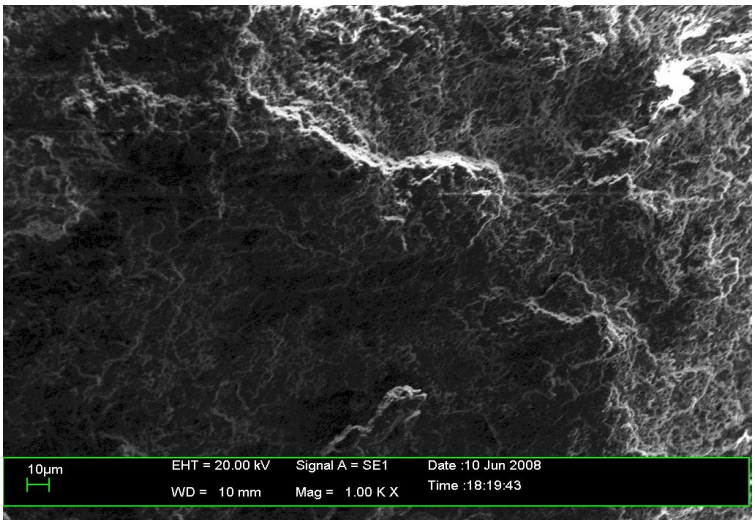

Figure 17 A. SEM image of fractured surface of unfilled PP.

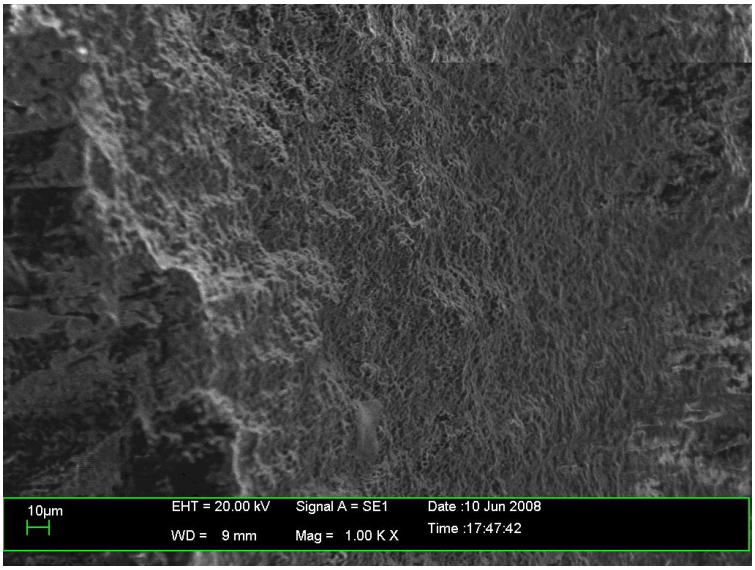

Figure 17 B. SEM image of fractured surface of 2NC1 (2 wt% NC1).

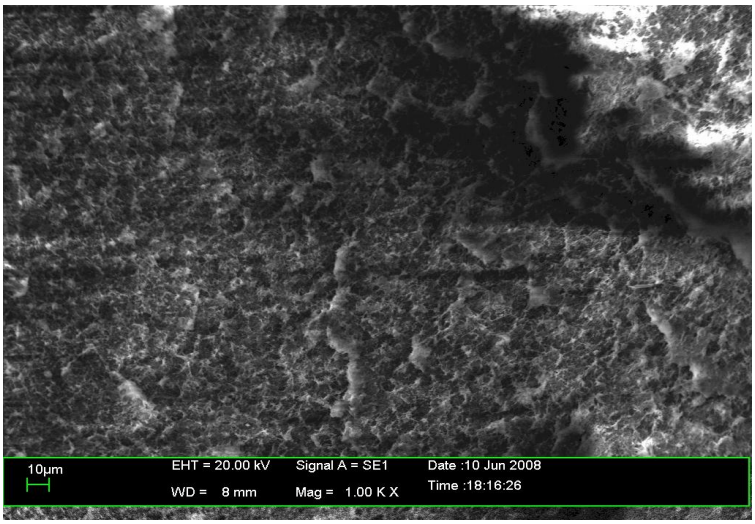

Figure 17 C. SEM image of fractured surface of 8NC1 (8 wt% NC1).

Impact strength behavior can also be explained from SEM micrographs. More surface roughness indicates that more energy was dissipated during fracture of unfilled PP. This explains higher impact strength of pure polymer as compared to PP clay nanocomposites.

4.4 Melt Flow Index Test

Understanding the melt flow properties of nanocomposites is important in gaining a fundamental knowledge of the processability of the material. Figure 18 shows some MFI values for pure PP and NC1 and NC2 clay nanocomposites. MFI decreases from 24 g/10min to about 22, 20, and 16 g/10min for both types of 2, 5, and 8 wt% composites, respectively. Decrease in MFI can be offset by an increase of 20-30% in Young's or flexural modulus, which makes thin walling of auto components more easier.

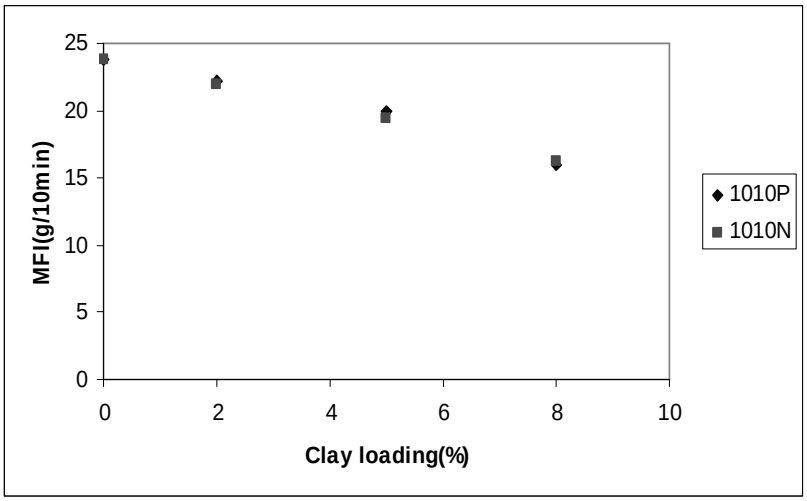

Figure 18. MFI of pure PP, and NC1 (1010P) and NC2 (1010N) clay nanocomposites.

4.5 Thermogravimetric Analysis

TGA curves of filled and unfilled PP are shown in Figure 19. Residue of unfilled PP at 600 °C was almost close to 0%. For filled composites, residue was about 1.2, 2.8, and 4.4 wt% for 2, 5, and 8 wt% loadings of nanoclays which was the targeted amount in the samples. The difference in clay contents may be due to the fact that the volatiles and other organics that were used for surface modification might have decomposed (which would have contributed to the total weight otherwise).

Initial decomposition temperatures of clay filled nanocomposites are higher compared to unfilled PP. At about 410 °C, weight loss of unfilled PP is about 25%, whereas weight loss of clays filled PP is about 10%. Rapid decrease in weight percentage of clay filled nanocomposites is due to the burning of organic molecules present in the organoclay. Unifllled PP and PP+ MA–g–PP being uniform resin molecule showing a gradual trend.

The unfilled PP started to decompose around 380–400 °C, whereas the composites started to decompose around 410–425 °C. This analysis showed delayed

decomposition for the clay filled PP. This type of behavior has been reported earlier for PMMA / montnorillonite clay nanocomposites. Improved thermal stability of nanocomposite was attributed to its structure as well as to restricted thermal motion of polymer in the intergallery of clay platelets. An increase of 40 to 50 °C in decomposition temperature was observed compared to unfilled PMMA. PDMS / clay nanocomposites showed an increase of 140 °C in decomposition temperature compared to pure PDMS network. One reason for this improved thermal stability has been attributed to hindered out diffusion of volatile decomposition products within the nanocomposite.

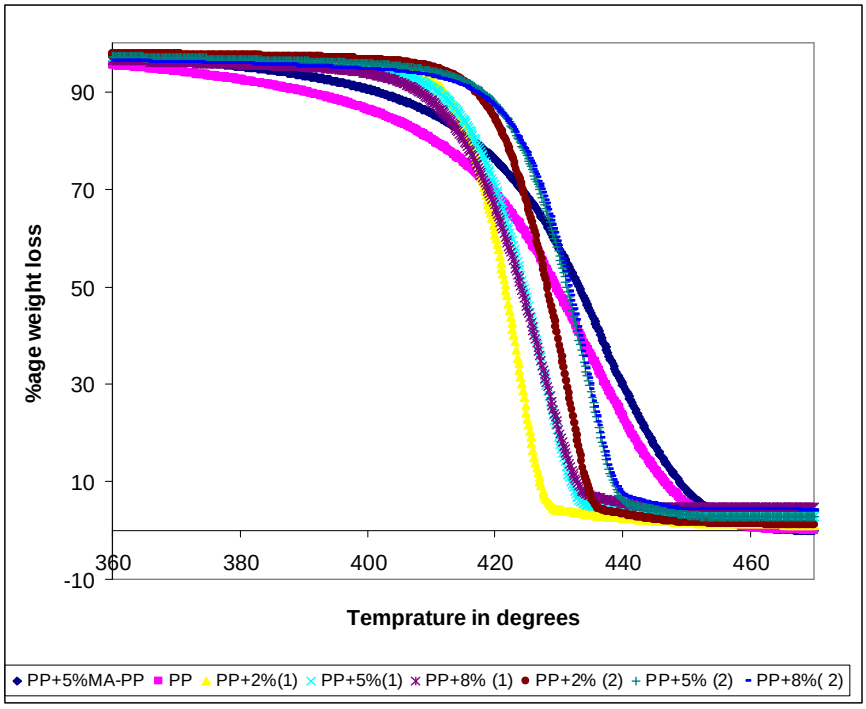

Figure 19: TGA curves for filled and unfilled PP nanocomposites.

4.6 Burn Rate Test

Literature reports[41] suggest that flammability and barrier properties show similar trends, however no direct quantitative correlation is reported. Therefore, to estimate trend of barrier properties burn rate test was conducted on pure PP, 2NC1 (2 wt% filled NC1) and

2NC2 (2 wt% filled NC2). As expected burn rate for 2NC1 decreased by 6%, and for 2NC2, it decreased by 1% from that of pure PP. Role of nanocomposite in bringing about a reduction in burn rate may be due to the formation of a barrier, which impedes mass transport and insulates the underlying polymer from heat source. Higher concentration of organic molecules (present in the clay modifier and MA–g–PP) will increase burn rate. Furthermore, incomplete exfoliation would increase burn rate. Decrease in burn rate, in the case for 2 wt% clay filled PP composites, can be correlated to increased thermal stability of nanocomposites as is indicated by TGA curves. This can be correlated correlated to XRD data, which indicates increased basal *d–spacing* from 1.60 nm to 3.39 nm by incorporating polymer in clay layers. And TEM images exhibit a mixed morphology. However more experiments based on cone calorimeter and oxygen transmission rate would support the enhanced barrier properties of polypropylene clay nanocomposites.

Chapter 5

Conclusions

A comparative study of mechanical, thermal, and flammability properties of PP / clay nanocomposites was done using two different types of clay. XRD and TEM were used to characterize the morphology of the nanoccomposites. XRD indicated that the long alkyl chains (modifier) intercalated between the clay layers increasing the *d* spacing. TEM exhibited a mixed morphology – presence of tactoids, intercalated and exfoliated structures.

Depending on the clay loading and clay type, Young's as well as flexural modulus increased between 10 and 30%. For clay type 1 with 8 wt% loading, Young's modulus increased by 28%, and flexural modulus increased by 15%. For clay type 2 with 8 wt% loading, Young's modulus increased by 12%, and flexural modulus increased by 6%. There were decreases in elongation at break and impact strength for the clay filled PP, but was not significant enough to conclude that the overall mechanical properties deteriorated dramatically. Toughness of the material decreased with increasing clay content. Therefore, to obtain proper balance of flexural modulus and impact strength control over microstructure is required. Scanning electron micrograph images showed that fracture of filled and unfilled PP was ductile in nature.

Thermal gravimetric analysis indicated that the clay filled PP composites showed delayed decomposition. Improved thermal stability of nanocomposite was attributed to its structure as well as to restricted thermal motion of polymer in the intergallery of clay platelets. One reason for this improved thermal stability has been attributed to hindered out diffusion of volatile decomposition products within the nanocomposite. Improvement of 6% in flammability properties with 2 wt% clay type 1 is reported. Burn rate for 2NC1 decreased by 6%, and for 2NC2, it decreased by 1% from that of pure PP. Role of nanocomposite in bringing about a reduction in burn rate may be due to the

formation of a barrier, which impedes mass transport and insulates the underlying polymer from heat source.

Nanocomposite formed from clay type 1 NC1 showed better improvement in mechanical and barrier properties than nanocomposites formed from clay type 2 NC2. The reason for this might be higher CEC number, leading to better interfacial interaction between clay type 1 NC1 and polymer matrix. Therefore, dispersion and extent of exfoliation of clay in polymer matrix is critical to achieve required property enhancement.

Aggregated tactoids or other impurities can act as stress concentrators, where crack initiation and propagation is possible, resulting in deteriorating mechanical properties compared to the unfilled polymer. Since size, shape, type, and properties of fillers, surface treatment of particles, compatibilizer, polymer matrix, degree of dispersion, interfacial interaction, processing conditions, etc. influence the properties of the final composite, care should be taken to establish the factors to obtain materials.

Chapter 6

Future Work

Future research work will include choosing a homopolymer polypropylene and nylon as matrices. Nylon does not need compatibilizer, and it is easier to mix clay with nylon. As the amount of intercalant or MA–g–PP increases, burn rate increases. Therefore, it is imperative to select the optimum amount of surface modifier and MA–g–PP. Challenges (mentioned in Sections 1.3 and 2.8) need to be addressed when the clay is modified, MA–g–PP is chosen, or polymer clay nanocomposite is processed. Some challenges in processing polymer clay nanocomposites are: to achieve uniform surface treatment of clay layers; to maximize dispersion of filler particles in the polymer matrix; to increase interaction between polymer matrix and filler particles; and to prevent re–agglomeration of filler particles during processing.

Differential scanning calorimeter will be used to determine the crystallization temperature of filled and unfilled polymer clay systems. Higher crystallization temperature will translate to reduced mold cycle time, which will lead to cost reduction when molding auto components. Dynamic mechanical analysis will be done to study the effect of temperature on modulus of the materials. Scratch resistance testing will be carried out. Additional experiments for both filled and unfilled polymer clay systems will be carried out for flammability and oxygen transmission rate tests.

If mechanical and barrier properties are satisfactory, and thin walling of auto components is possible, then resistance of filled systems to ultraviolet or Xenon arc will be tested. These tests will be useful to evaluate the feasibility of implementing polymer clay nanocomposites in the automotive industry. Some components that can be made using polymer clay nanocomposites are: instrument panel, body side claddings, bumper fascia, plastic fuel tank, etc.

Finally, if polymer clay composites are to be utilized to their fullest value in terms of price / performance ratio, then the following items have to be taken into consideration: existing challenges need to be understood through research and analysis; innovative solutions should be developed through collaboration between suppliers and original equipment manufacturers; and existing manufacturing infrastructure should be utilized whenever possible.

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