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Thermoplastic Nanocomposites and Their Processing Techniques

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1. Introduction

Nanotechnology is one of the most up-to-the-minute areas in essentially all technical disciplines of chemistry, electronics, high-density magnetic recording media, sensors and biotechnology, etc. During the last decade, due to the emergence of a new generation of high-technology materials, the number of research groups involved in nanotechnology has increased exponentially covering a broad range of topics such as microelectronics (now known as nanoelectronics, because the critical dimension scale for modern devices has decreased to and /or below 100 nanometer (nm) (Paul & Robeson 2008)), polymer-based biomaterials (Haider et al., 2007), nanoparticle drug delivery (Omer et al., 2011), miniemulsion particles (Zhang et al., 2007; Wu et al., 2010)], layer-by-layer self-assembled polymer films (Lee & Cui 2009), electrospun nanofibers (Haider & Park, 2009; Haider et al., 2010), imprint lithography (Stephen et al., 1996), polymer blends and nanocomposites (Kim et al., 2005). The dimensional shift of materials from micro to nano produced theatrical changes in their physical properties and one such change is large surface area for a given volume (Haider et al., 2007). Therefore nanoscale materials can have substantially different properties from their corresponding large-dimensional materials of the same composition. Surface area per unit volume is inversely proportional to diameter, thus, the smaller the diameter, the greater the surface area per unit volume (Luo & Danie, 2003). Common particle geometries and their respective surface area-to-volume ratios are shown in Figure 1.

The surface area/volume ratio for the fiber and layered nanomaterials is subjugated by the first term ($2/r$ or $2/t$) in the equation. The second term ($2/l$ and $4/l$) has a very small influence as compare to the first term (Frazana et al., 2006). Hence, understandably, altering the particle diameter, layer thickness, or fibrous material diameter from the micrometer (μm) and nm range, will affect the surface area/volume ratio by three orders of magnitude (Thostenson et al., 2005). The nanomaterials, which are under investigation most recently are, nanoparticles (gold (Au), silver (Ag), iron oxide (Fe_3O_4), titanium oxide (TiO_2), silicon oxide (SiO_2), and quantum dots

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(QDs),etc.), carbon nanotubes(CNTs) (SWCNTs (single walled carbon nanotubes), DWCNTs (double walled carbon nanotubes), MWCNTs (multi walled carbon nanotubes), fullerenes, electrospun nanofibers (Haider et al., 2011) and nanowires (Tsivion et al., 2011).

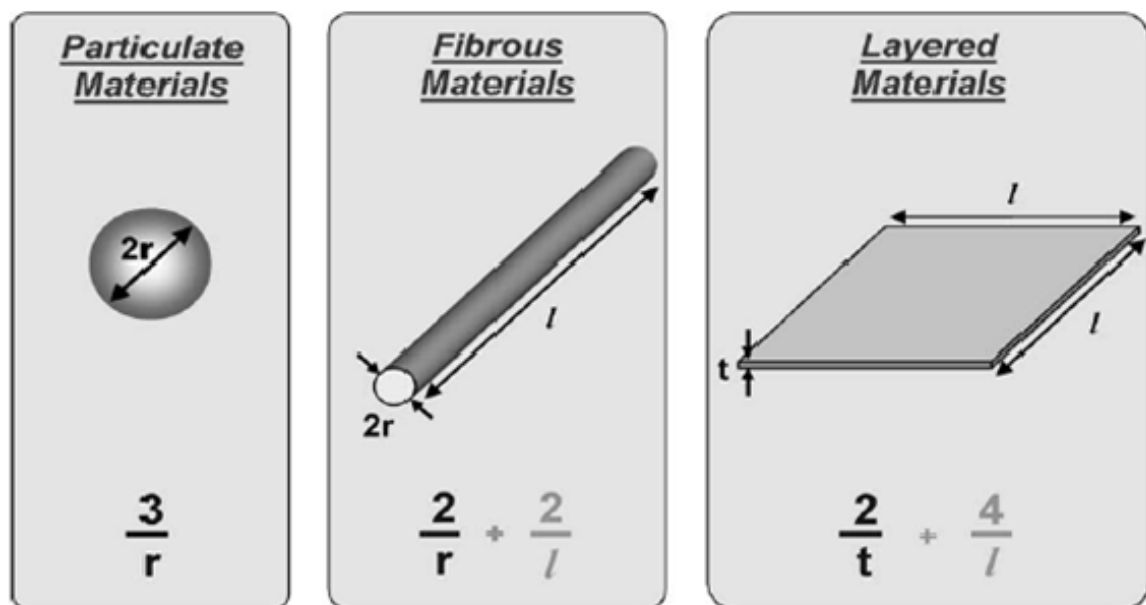


Fig. 1. Nanoparticles geometries and their surface area to volume ratio (Thostenson et al., 2005)

These materials are generally classified by their geometries into three broad classes, and these are particle (gold (Au), silver (Ag), iron oxide (Fe_3O_4) titanium oxide (TiO_2), silicon oxide (SiO_2), etc), layered (materials with nm thickness, high aspect ratio (30–1000) and plate-like structure ,e.g organosilicate), and fibrous (CNTs and electrospun nanofibers, etc) materials(Schmidt et al., 2002; Alexandre & Dubois2000). Nanomaterials provide reinforcing efficiency due to their high aspect ratios, when mixed with other matrix to produce composite material (Luo and Danie., 2003). Composite with different properties could be obtained and this mainly depends on the components (particles, layered or nanofibrous material, cation exchange capacity, and polymer matrix) and the method of preparation [Park et al., 2001]. The interest in polymer matrix based nanocomposites has emerged initially with interesting observations involving exfoliated clay and more recent studies with CNTs, carbon nanofibers, exfoliated graphite (graphene), nanocrystalline metals and a host of additional nanoscale inorganic filler or fiber modifications. Nanotechnology is not new to polymer science as prior studies involving nanoscale dimensions before the age of nanotechnology were not particularly referred to nanotechnology until recently (Paul & Robeson 2008). In the last two decade, there has been increasing interest in the development of polymeric composites, where at least one of the phases is dimensionally in the nm size range (Mirkin, 2005). The story of nanotechnology and nanocomposites is manifested by several significant events. In 1980s the heave in nanocomposites development, has been facilitated to a great extent by the invention/introduction of powerful characterization tools i.e., scanning tunneling microscopy (STM), atomic force microscopy (AFM) and scanning probe microscopy (SPM). These tools made the researchers capable to see the nature of the surface structure and manipulate individual atoms and molecules on solid surfaces. (Royal

Society & the Royal Academy of Engineering, 2004). At the same time, the speedy development of computer technology has made it easier to characterize and predict properties at the nanoscale *via* modeling and simulation (Mirkin, 2005). In general, the unique nanomaterial's characteristics (such as size, mechanical properties, and low concentrations) coupled with the advanced characterization and simulation techniques, have generated much curiosity in researchers for studying nanocomposites. Furthermore many polymer nanocomposites were fabricated and processed in ways, which were similar to those of conventional polymer composites, making them predominant from manufacturing point of view. Nature has mastered in the fabrication of nanocomposites by utilizing natural reagents and polymers (such as carbohydrates, lipids, and proteins) and as always the case researchers have learned from nature. Nature makes strong nanocomposites such as bones, shells and wood, etc by mixing two or more phases such as particles, layers or fibers, where at least one of the phases is in the nanometer size range. The quotation "Nature is a master chemist with incredible talent" by Oriakhi explains all (Paul & Robeson 2008). In recent years, preparation of hybrid organic-inorganic composites has attracted much attention since (such hybrids may show controllable properties such as optical, electrical and mechanical behaviors) by combining the properties of both organic and inorganic compounds (Chiang et al., 2003), e.g. Nylon-6 nanocomposite have shown pronounced improvement of thermal and mechanical properties with very small amount of nanofiller loading resulted in a pronounced improvement of thermal and mechanical properties (Kojima et al., 1993; Saeed et al., 2009). This is not always the case, as the properties of nanocomposite materials depend not only on the properties of the individual parent materials but also on the morphology and interfacial characteristics. Due to the huge potential of the nanotechnology, federal funding for nanotechnology research and development in United State of America (USA) has considerably increased from \$464 million since the inception of National Nanotechnology Initiative (NNI) in 2001 to \$982 million in 2005 (Paul & Robeson 2008) and, this amount is expected to increase to \$2.1 billion in 2012 (<http://www.nano.gov/about-nni/what/funding>). These incredible funding in nanotechnology are focused more on efficient manufacturing processes and the production of novel nanomaterial based products for a wide range of applications.

2. Thermoplastic polymers and their nanocomposites

Plastics are the basic ingredients of animal and plant life and form a part of the larger family called polymers. They offer advantages such as low density, lightness, transparency, resistance to corrosion and colour, their applications vary from domestic articles to medical instruments (Lia et al., 2000). Plastic are broadly classified into; (i) thermoplastics and (ii) thermosetting plastics. Both are long chain-like molecules but differs in their bonding. In thermoplastics the long chain molecules are held together by weak vander waal forces where as in thermosetting, the long chain molecules are held together by strong bonds. Some of the common thermoplastic polymers are; acrylonitrile butadiene styrene (ABS) [Zheng et al., 2004], Acrylic (PMMA) (Khaled et al., 2007), Ethylene vinyl alcohol (EVOH) (Artz et al., (2002), Polyacrylonitrile (PAN)(Zhang et al., 2009), Polyamide-imide (PAI) (Ma et al., 2010), Polyamide (PA or Nylon)(Bourbigot et al., 2002), Polyethersulfone (PES) (Wang et al 2011), Polypropylene (PP)(Lee et al., 2009) Polystyrene (PS) (Meinke et al., 2003) Polytrimethylene terephthalate (PTT) (Hu et al., 2004) and Polyvinyl chloride (PVC) (Awad et al., 2009), etc. As mentioned above the weak

vander waal force can be overcome at high temperatures, resulting in a homogenized viscous liquid, which can be further moulded into various shapes. After cooling, thermoplastic polymers retained their newly reformed shape. Some of the common applications of thermoplastics are; bottles, cable insulators, tapes, blender and mixer bowls, medical syringes, mugs, textiles, packaging, and parts for common household appliances. Nanomaterials reinforced thermoplastic nanocomposites have shown significant growth, as research on the development of novel reinforcing methods intensified. Several methods such as melt blending, solution mixing, coating (Kalaitzidou et al., 2010), in-situ polymerization (Alexandre & Dubois, 2000), nanoinfusion, etc (Lentz et al. 2010) are reported in the literature mostly aiming on the dispersability of the nanomaterials. The nanocomposites prepared using the above mentioned methods has a huge potential for applications in automotive (seat frames, battery trays, bumper beams, load floors, front ends, valve covers, rocker panels and under engine covers, etc) (Garces et al., 2000), aerospace (missile and aircraft stabiliser fins, wing ribs and panels, fuselage wall linings and overhead storage compartments, ducting, fasteners, engine housings and helicopter fairings, etc) (Zhao et al., 2010), optical devices (Ritzhaupt-Kleissl et al., 2006), electrical and actuator devices (Koerner et al., 2004), and as flame retardant. The fabrication of thermoplastic nanocomposites with CNTs, Caly and graphene are discussed in detail as below sections.

2.1 Clay (silicates)-based nanocomposites

After the ground breaking discoveries by Toyota research group (preparation of Nylon-6 (N6)/montmorillonite (MMT) nanocomposite) (Paul & Robeson 2008) and Vaia et al. (dry melt-mixing of polymers with layered silicates) (Vaia et al., 1994), research on polymer/clay nanocomposites accelerated, both in industry and in academic worlds. Since then a number of groups studied the preparation of thermoplastics/silicates nanocomposites e.g. ethylene-vinyl alcohol copolymer/clay (melt blending, solution-precipitation (Artzi et al., 2002; Jeong et al., 2005)), PAN/silicate (in situ polymerization (Choi et al., 2004)), PP/clay (melt-mixing and melt compounding (Parka et al., 2008)) and PS/ clay (in situ polymerization, melt intercalation and solution casting (Panwar et al., 2011)), etc., and found significant improvements in their material properties. Based on the interaction of silicates with polymer, polymer/layered silicate nanocomposites are classified into (Figure 2); (a) intercalated nanocomposites (inserted polymer chains in the layered silicate structure in a crystallographically regular fashion, irrespective of the polymer to clay ratio with a repeat distance of few nm), (b) flocculated nanocomposites, (intercalated and stacked silicate layers flocculated to some extent due to the hydroxylated edge-edge interactions of the silicate layers), and (c) exfoliated nanocomposites (separated individual silicate layers in the polymer matrix; the distance depends on the clay loading) (Ray & Okamoto, 2003). The strong interactions of polymer with layered silicate in polymer/silicates nanocomposites lead to the dispersion of organic and inorganic phases at the nm level, resulting in improved tensile properties (Haider and Park 2009), high moduli (Vaia et al., 1999), increased strength and heat resistance, (Pattanayak et al., 2005), thermal stability (Xu et al., 2004), decreased gas permeability (Kojima et al., 1993), and flammability (Gilman et al., 2000), and increased biodegradability (Gloaguen et al., 2001), not shown by their conventionally filled micro-counterparts (Ray & Okamoto 2003).

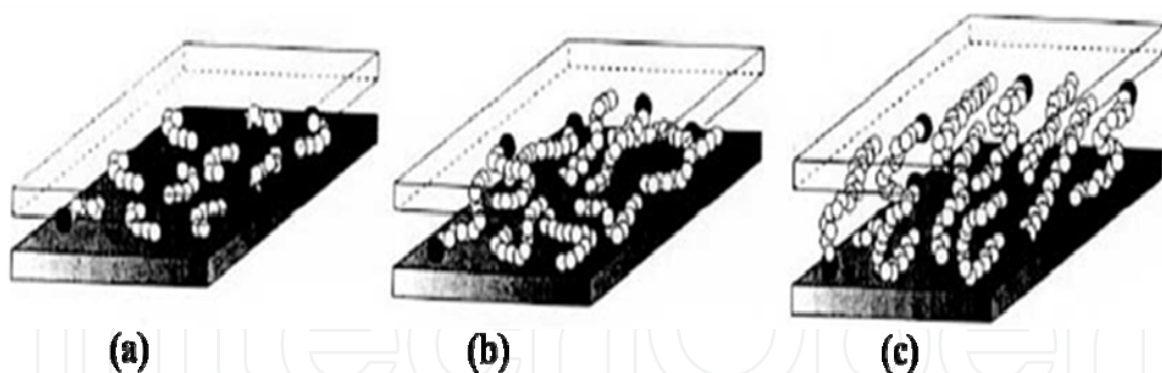


Fig. 2. Interaction of silicates with polymer (a) intercalation, (b) flocculation and (c) exfoliation (Vaia et al., 1994).

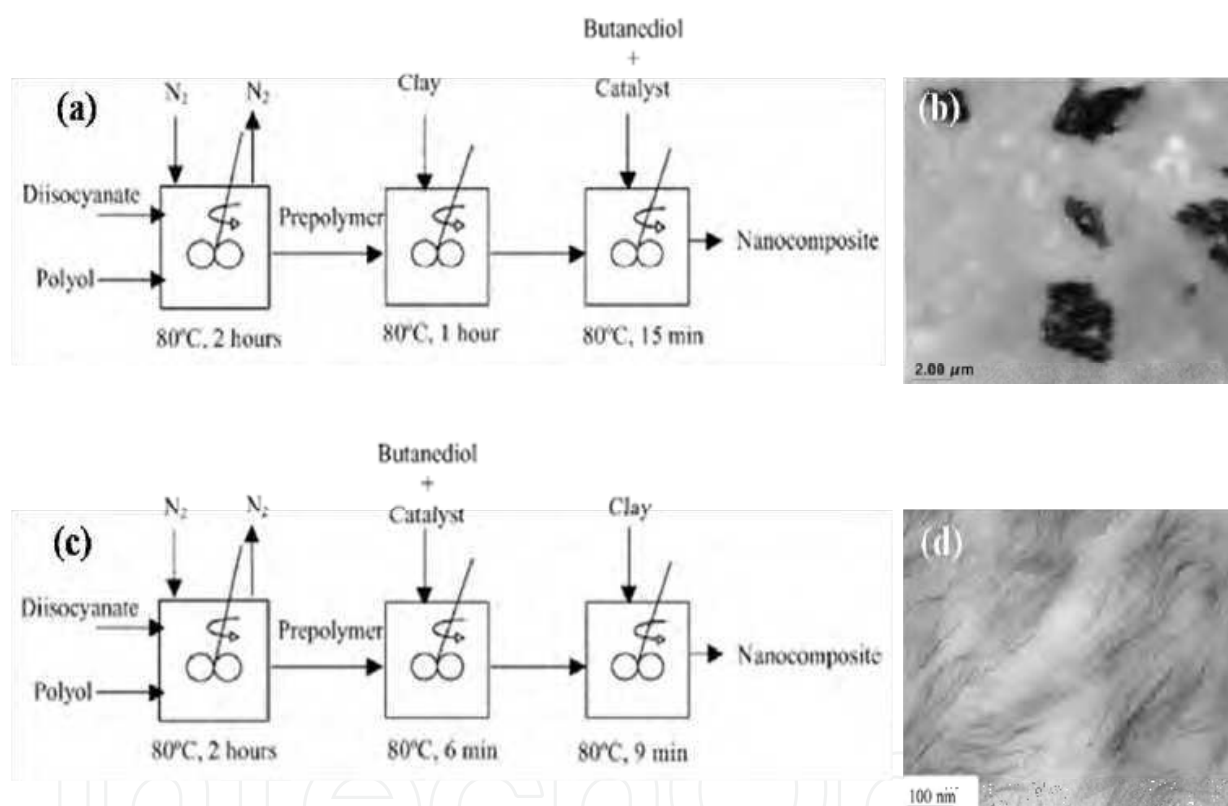


Fig. 3 Schematics of clay/polyurethane nanocomposite preparation and their respective TEM images; (a) method I and (b) TEM image of 4 wt% clay/polyurethane nanocomposite prepared by method I, (c) method II and (d) TEM image of 5 wt% clay/polyurethane nanocomposites prepared by method II.

Pattanayak and Jana prepared thermoplastic polyurethane and reactive silicate clays nanocomposites by bulk polymerization. They used two different methods as shown in Figure 3. In the first method pre-polymer and in the second method chain-extended polymer molecules with residual -NCO groups were involved in tethering reactions with clay during mixing. The morphologies studies of the nanocomposites showed that both shear stress of mixing and the reaction between polymer and clay are the main forces that determine the exfoliation of clay. In first method (Figure 3a) more clay-tethered to polymer

chains, but the clay particles did not exfoliate (Figure 3b) due to low shear stress of mixing. In the second method (Figure 3c) due to the high shear stress of mixing and good reaction, the clay particles are well exfoliated to the scale of individual clay layers (Figure 3d). In the later case best improvement in tensile properties was observed (Pattanayak & Jana, 2005). Gloaguen et al., studied the preparation of nylon 6/clay hybrids *via* in situ polymerization, to obtain a nylon matrix strongly bonded to the delaminated clay platelets and polypropylene/organophilic clay *via* melt dispersion of organophilic clay in polypropylene, to obtain reduced degree of polymer-clay interaction. Extensive cavitation behavior was observed from plasticity results, while retaining a fairly large strain at break, as long as deformation is performed above the glass transition temperature of the matrix. In case of nylon6, it was clear that the usual shear banding plastic deformation mode was altered in its initiation step. Localised interfacial damage promoted extensive polymer matrix brillation and fracture occurred predominantly in areas where delamination of the clay platelets was not fully achieved (Gloaguen & Lefebvre, 2001).

Heterocoagulation method was also employed to prepare PMMA/clay nanocomposites. In the first step a cationic PMMA emulsion was prepared by emulsion polymerization using a cationic initiator in the presence of free surfactant, followed by mixing with aqueous clay slurries of montmorillonite (MMT), synthetic hectorites and fluorohectorites, in the second step. Based on hetero and homocoagulation processes three types of morphologies (Figure 4 (i. exfoliated (a, b, and c), ii. mixed (d) and iii. intercalated (e))_ were predicated. TEM images confirmed the predicted morphologies (Figure 4a, b,d,e). The enhanced thermal stability for these systems was attributed partially to barrier properties (Gloaguen & Lefebvre, 2001).

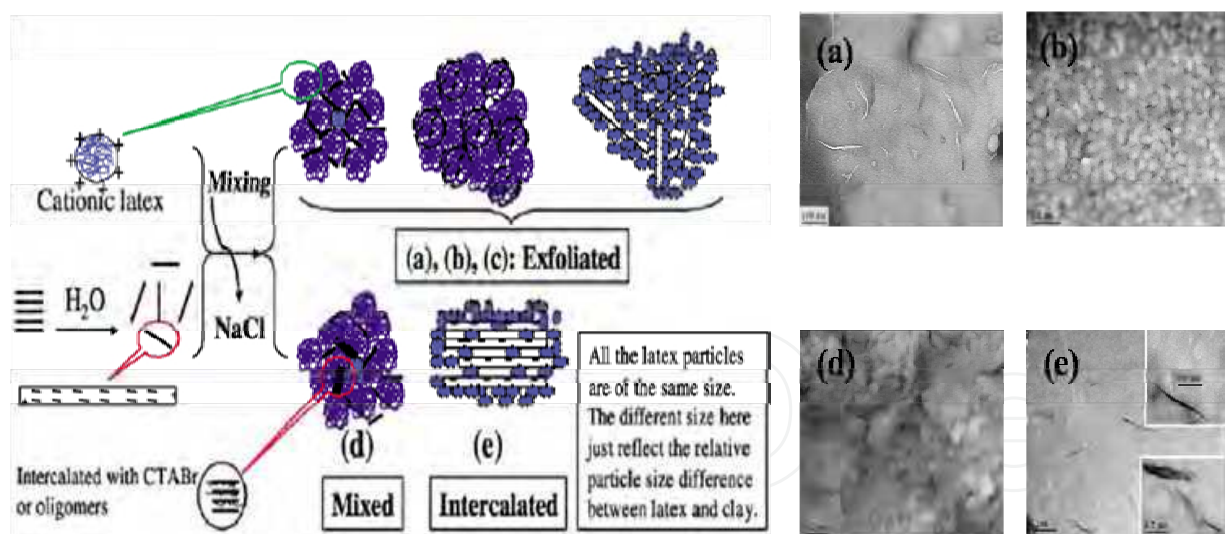


Fig. 4. Schematic representation of the predicted morphologies for coagulation process and TEM images confirming the predicted morphologies (Vaia et al., 1999).

2.2 CNTs -based nanocomposites

Synthetic polymers lack the necessary stiffness (with Young's modulus, 3000- 4000 MPa for amorphous and 3000 MPa for semi-crystalline polymers) for many engineering applications. Polymer industry is therefore in continuous search for new materials, which may not only potentially enhance the stiffness of synthetic polymer but could add some new properties

(such as thermal stability, electric conductivity and air stability, etc.) at lower costs. CNTs with superb mechanical properties (Young's modulus 1TPa and tensile strength 100-150 GPa), electrical conductivity as high as 10^8 S/m, high aspect ratio, small diameter, light weight, air stabilities and thermal stabilities could be one such material. Hence, CNTs have been extensively studied since the discovery by Iijima in 1991 (Ando, 2010). Having said this, pristine CNTs did not yet met early expectations; however their incorporation into polymer materials to prepare nanocomposites, have extend their applications, despite inconsistencies in properties due to (i) CNTs synthesis method and the resultant aspect ratio, (ii) their post-processing (such as purification), and (iii) the characteristics of polymer matrix and the nanocomposite fabrication procedure (such as solution blending, melt blending, or in situ polymerization) (Silva et al., 2011). It is therefore necessary to entertain a compromise between the properties and processing, since only low loadings of nano-filler are needed to reinforce the matrix, which might exhibit improved stiffness without scarifying toughness (Chang et al., 2006).

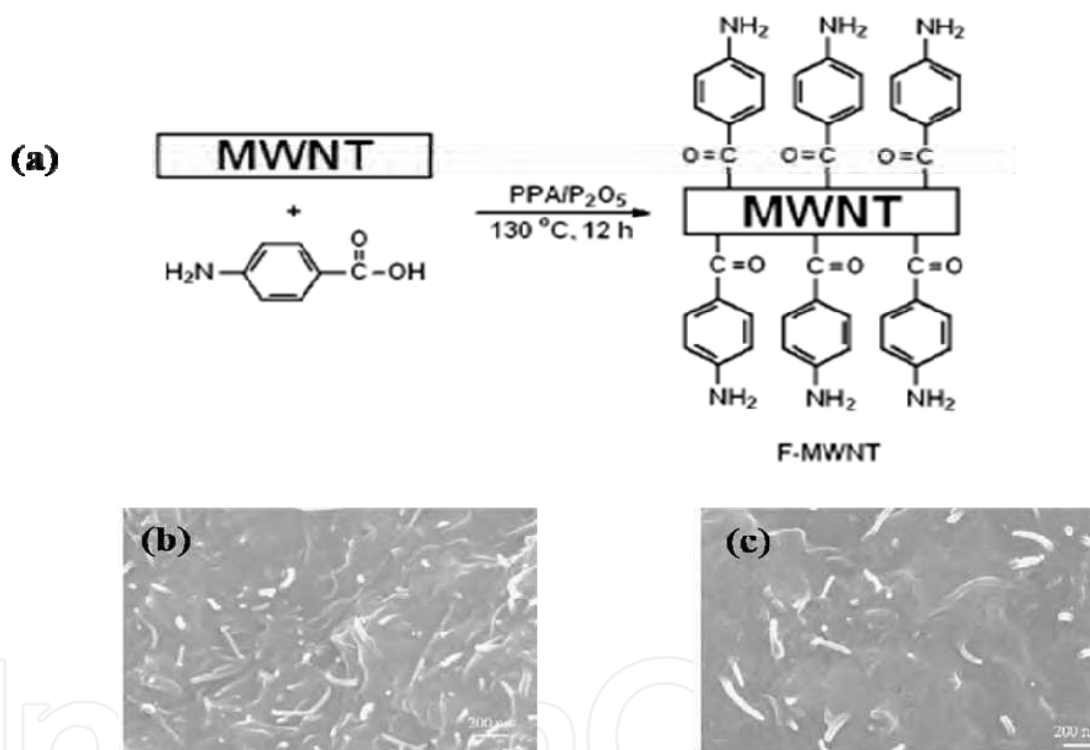


Fig. 5. (a) Schematic of the Side-wall functionalization of MWNTs (F-MWNTs) by Friedel-Crafts acylation, (b) SEM images of the fractured surfaces of a P-MWNT (5 wt%)/nylon-6 and (c) F-MWNT (5 wt%)/nylon-6 (Saeed et al., (2009)

CNTs reinforced thermoplastic nanocomposites have shown considerable growth with increase in the research on the development of novel reinforcing methods. Several methods have been reported in the literature to incorporated CNTs into the thermoplastic polymer matrix. These methods include, solution blending (PAN/MWCNT (Saeed & Park 2010), melt blending a (PMMA/MWCNT, (Yu et al., 2008), PP/SWCNT (Bhattacharyya et al., 2003)), in situ polymerization (Nylon/MWCNT (Saeed et al., 2009), PP/MWCNT (Koval'chuk et al., 2008), PMMA/MWCNT (Cui et al., 2009), PS/MWCNT (Lahelin et al., 2011)), solution casting (PAI/SWCNT (Kim et al., 2007) PTT/MWCNT (Xu et al., 2008)), and Solution

Polymerization (PS/MWCNT (Kim et al., 2007). The properties of the final matrix obtained by the above mentioned methods, depends largely on the dispersion of the CNTs in the polymer matrix because nanoscale diameter and the resultant high aspect ratio gives CNTs very larger surface area, which induces significant entanglement between nanotubes. This entanglement of CNT must be worked out to realize its high potential in practical applications. Various approaches have been use to obtain good dispersion (e.g. chemical functionalization and physical wrapping (Saeed et al., (2009), etc) of the CNTs in polymer matrix. Khalid et al prepared Nylon/MWCNTs nanocomposite by in situ polymerization with both pristine (Figure 5b) and chemically functionalized MWCNTs (Figure 5c). The MWCNTs were functionalized by Friedel-Crafts acylation (Figure 5a), which introduced aromatic amine ($\text{COC}_6\text{H}_4\text{-NH}_2$) groups onto the side wall. Homogenous dispersion of the MWCNTs (Figure 5c) was observed in nylon, which results in an increase in both thermal and mechanical properties for the nanocomposite as compared to the neat polymer (Saeed et al., 2009).

2.3 Graphite-based nanocomposites

Graphene, a monolayer of sp^2 hybridized carbon atoms arranged in a two-dimensional lattice, is a cheap and multifunctional material (Potts et al., 2011). Graphene is considered to be better nanofiller compared to CNTs and other conventional nanofillers, as it improve the mechanical, thermal, and electrical properties of the nanocomposites to a great extent with a very small loading. However, the dispersion of pristine graphene in polymer matrices, as is the case with nanoscale materials, is very poor (Kuila et al., 2011). Poor dispersion drastically effect mechanical, thermal, and electrical properties of the nanomaterial reinforced nanocomposites. Currently work is intensified on making these nanofiller homogeneously dispersible in the polymer matrix. Different types of nano graphite forms, such as expanded graphite (forcing the crystal lattice planes apart due to the insertion of some foreign particles), intercalated (insertion of metal between lattice planes) and surface modified graphene have been used to obtain homogeneous dispersion and produce nanocomposites with improved physicochemical properties. The mechanism of polymer-graphene interactions in polymer/graphene nanocomposites is mainly governed by (i) polarity, (ii) molecular weight, (iii) hydrophobicity, (iv) polymer functionalities, (v) graphene functionalities and (vi) graphene-solvent interaction. In the literature three main approaches are devised for incorporating polymer between graphene layers; (i) In situ intercalative polymerization, (ii) solution intercalation and (iii) melt intercalation. The first methods, is commonly used for the preparation of the homogeneously dispersed graphene. In this method pristine or expended, intercalated or surface modified graphene is first swollen within the liquid monomer and after the diffusion of a suitable initiator, polymerization is initiated either by heat or radiation (Kuilla et al., 2010). A number of thermoplastic polymers/graphene nanocomposites with much improved mechanical, thermal and electric properties were prepared by this method, e.g PMMA/graphene (enhanced storage moduli , glass transition temperatures and thermal stability (Kuilla et al., 2011)), PP/graphene (effective dispersion and high electric conductivity (Huang et al., 2010)), Nylon/graphene (increased Young's modulus (Xu & Gao 2010)) and PS/graphene (improved thermal properties (Patole et al., 2010)), etc. Solution intercalation, not so common, is based on the adsorption of polymer or pre-polymer onto graphene layers. During the process polymer or pre-polymer is solubilized in solvent system, followed by graphene swelling of pristine or modified graphene layers in the same solution. When the

polymer or pre-polymer adsorbs onto the delaminated sheets, the solvent is evaporated and a sandwiched nanocomposites is formed (Kuilla et al., 2010). As mentioned, this method is rarely used for the preparation of thermoplastic polymer/graphene nanocomposites, only PP/graphene nanocomposite is reported recently (increased electric conductivity (Kalaitzidou et al., 2007)). In the melt intercalation technique, no solvent is required and graphite or graphene or modified graphene is mixed with the polymer matrix in the molten state (Kuilla et al., 2010), e.g. PTT/graphene (substantially improved thermal stability and dynamic mechanical moduli (Li & Jeong 2011)).

2.4 Processing techniques

Processing conditions are the factors, which need to be optimized to enhance the performance of thermoplastic polymers and / or their nanocomposites. The processing of polymeric materials (such as plastics, elastomers and composites, etc) is characterized by a wide variety of distinct techniques such as extrusion (Vaia et al., 1994), film blowing (Golebiewski et al., 2008), sheet thermoforming (Feng et al., 2009), blow molding (http://www.petmachine.in/type_of_blow_moulding.htm), and injection molding (Chandra et al., 2007), etc. Extrusion is the continuously shaping of a fluid polymer and/or its nanocomposite through the orifice of a suitable tool (die) (Figure 6a), followed by solidifying it into extrudate of constant cross section. The feed material is usually thermoplastics powder or pellets. In this process, the feed material is heated first to a fluid state *via* a screw extruder, followed by pumping into the die, which is finally solidified by cooling. Extrusion products are often subdivided into groups that include filaments of circular cross-section, profiles of irregular cross section, axis-symmetric tubes and pipes, and flat products such as films or sheets. Another technique used for the processing of thermoplastics into tubular product several times of its initial diameter that can be use directly or made into film, is known as film blowing (Figure 6b). Films produced by the film blowing process are widely used for agricultural, construction, and industrial applications, including covers for silage, greenhouses, chemical/solar ponds, flat cars, etc., or for a variety of packing applications, such as wrapping, can lining, fabricated bags such as garbage, etc (<http://www.whatisplastic.com/?cat=9>).

Blow molding (Figure 7) is the simplest type of molding, in this process, a hot tube of plastic material is dropped from an extruder and captured in a water cooled mold halves. Once the molds are closed, air is injected through the top or the neck of the container; just as if one were blowing up a balloon. The material solidifies into a hollow product. Packing is the major area of application of small to medium-size disposable blow molded products. Blow molded containers are also used for cosmetics, toiletries, pharmaceutical, medical packaging and a variety of household products.

The injection molding process involves the rapid pressure filling of a specific mold cavity with a molten material, followed by the solidification of the material into a product. This process is used for molding thermoplastics, thermosetting resins, and rubbers, etc. Injection molding of thermoplastics can be classified into a several stages. At the plasticity stage, the feed unit operates as an extruder, melting and homogenizing the material in the screw/barrel system. The screw, however, is allowed to pull in, to make a reservoir for the molten materials. At the injection state, the screw works as a ram, which transfer the molten material rapidly from the reservoir to the cavity between the two halves of the closed mold.

Since the mold is kept at a temperature below the solidification temperature of the material, it is essential to inject the molten material rapidly, to ensure filling of the cavity completely. The cavity pressure rises rapidly during the filling stage, which is followed by the holding stage. A high holding/packing pressure is normally exerted, to partially compensate for the thermal contraction of the material upon cooling. After the cooling stage, the mold can be opened and the solid product removed
(http://www.petmachine.in/type_of_blow_moulding.htm).

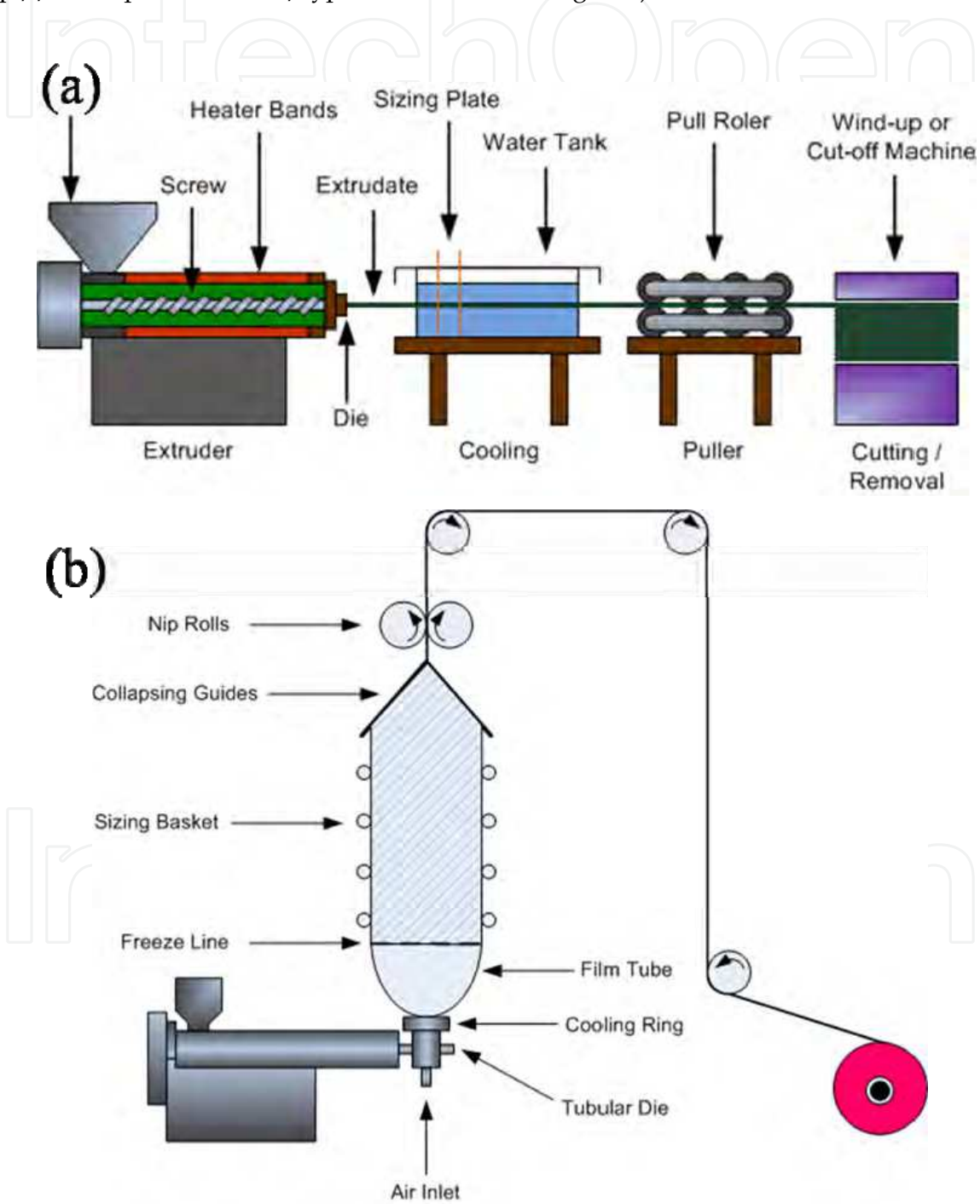


Fig. 6. Schematic for processing of thermoplastic polymers and its nanocomposite (a) Extrusion and (b) film blowing

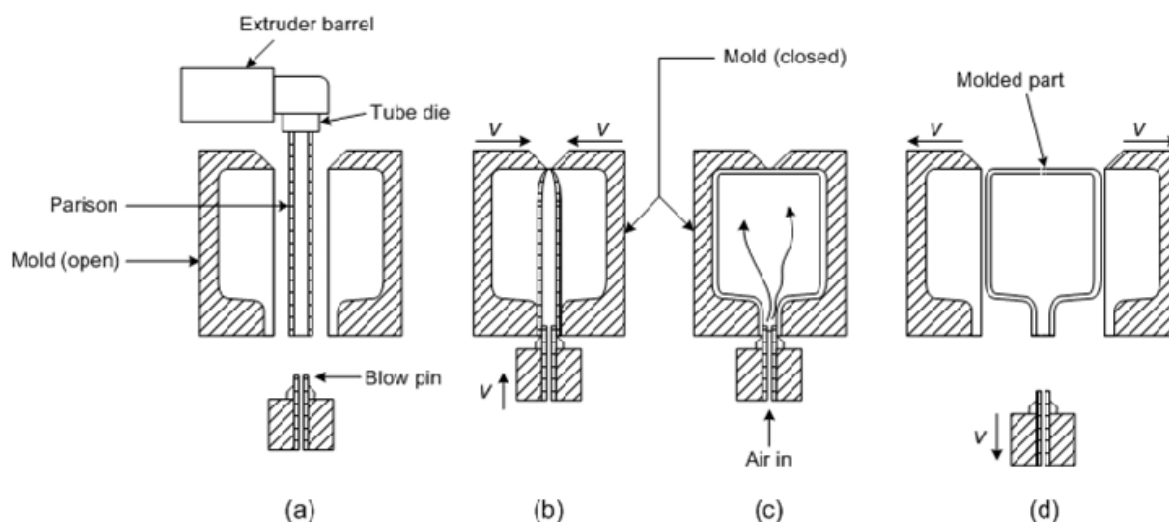


Fig. 7. Extrusion blow molding: (a) extrusion of parison; (b) parison is pinched at the top and sealed at the bottom around a metal blow pin as the two halves of the mold come together; (c) the tube is inflated so that it takes the shape of the mold cavity; and (d) mold is opened to remove the solidified part (http://www.petmachine.in/type_of_blow_moulding.htm).

At high pressures, a polymer melt is compressible; allowing additional material to be packed in the mold cavity after mold filling is complete. This is necessary to reduce non-uniform part shrinkage, which leads to part warpage. Excessive packing results in a highly stressed part and may cause ejection problems whereas insufficient packing causes poor surface, sink marks, welds and non-uniform shrinkage. All thermoplastics are, in principle, suitable for injection molding, but since fast flow rates are needed, good fluidity thermoplastic are normally preferable. The pressure distribution inside the mold cavity changes with distance from the inlet gate. Further away from the gate, pressure rises slowly and it decays quicker than at the points closer to the gate. The pressure in the mold cavity should be more uniform to minimize part warpage. A major disadvantage of injection molded products is the incorporation of fine details such as bosses, locating pins, mounting holes, ribs, flanges, etc., which normally eliminates assembly and finishing operations. (Schey, 1987; Strong, 2000). Thermoforming is another very useful process for producing various devices. Thermoforming involves the heating of thermoplastic sheet above the glass transition temperature T_g for non-crystallizing thermoplastics or near the melting temperature T_m for crystallizing polymers, followed by forming of the softened material into a desired shape by cooling. Products made by sheet thermoforming include skin and blister packs, individual containers (for jelly or cream, vials), cups, tubs, trays and lids. Larger products are generally made from cut sheets at much slower rates; the heating stage often is the limiting factor. Transparent products, such as contoured windows, skylights and cockpit canopies, are often made by this method (<http://www.thermopro.com/FormingMethods.html>).

3. Characterization techniques for nanocomposites

Characterization is critical for analyzing the physical and chemical properties of polymer nanocomposites. Various characterization techniques such as scanning electron microscope (SEM), transmission electron microscopy (TEM), Atomic force microscope (AFM), Raman

and Fourier transform infra red (FT-IR) spectroscopy wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), have been reported in the literature. SEM is used pre-dominantly for imaging the surface texture of materials, however; it can also be used for particle sizing and aggregation. Conventional SEM requires UHV environment and dehydrated samples (dry samples), which lead to uncertainty in getting accurate data in case of wet samples. The problem has been overcome and nowadays the liquid (aqueous) surface and substances close to the surface can be imaged in in-situ material characterization while maintaining UHV conditions around the electron gun with commercially available emission scanning electron microscopy (ESEM). TEM is an entrenched direct electron imaging technique under ultrahigh vacuum (UHV) conditions for studying shape, morphology, particle size distributions and aggregation of nonmetallic and in particular of metallic nanomaterials, though in the former case electron field transmission electron microscope (EFTEM) might be used due to the energy filtering discrepancy (Haider et al., 2011). AFM uses a sharp tip to scan across the sample for measuring three dimensions morphology of the surface. FTIR and Raman spectroscopy has also proved a useful probe of the functionalities in the polymer matrix and their interaction with the nanomaterials (Gajendran & Saraswathi 2008). WAXD is commonly used to probe the nanocomposite structure (Monticelli et al., 2007) and kinetics of the polymer melt intercalation (Li et al., 2003). In layered silicate nanocomposite, a fully exfoliated system is characterized by the absence of intensity peaks in WAXD pattern, which corresponds to a d-spacing of at least 6 nm (Lia et al., 2000). Therefore, a WAXD pattern concerning the mechanism of nanocomposite formation and their structure are tentative issues for making any conclusion. Small-angle X-ray scattering (SAXS) is typically used to observe structures on the order of 10 Å or larger, in the range of 0.5°–5°. The TEM, AFM, and SEM, are also required to characterize nanoparticle, carbon nanofiber dispersion, or distribution (Hussain et al., 2006). TGA is a useful tool for analyzing the amount of the nanomaterials loaded in the matrix and the thermal stability of the nanocomposites whereas DSC provides us the information of the glass transition and melting temperature of the nanocomposites, the results can be compared with the neat matrix and conclusion could be drawn about the interaction of the nanomaterials and matrix.

4. Future outlook

The huge potential of nanocomposites in various disciplines of research and industrial applications is attracting increasing investment in many parts of the world from governments and business companies. The federal funding for nanotechnology research and development in United States of America (USA) has considerably increased from \$464 million, since the inception of National Nanotechnology Initiative (NNI) in 2001, to \$982 million in 2005 (Paul & Robeson 2008) and this amount is expected to increase to \$2.1 billion in 2012 (<http://www.nano.gov/about-nni/what/funding>). Over 300 nanomaterials products were available in the market until 2007. Even if these numbers are below expectation, they highlight the tremendous technological and economical potential associated with polymeric nanocomposites including not only clay but also other inorganic and organic nanofillers, such as carbon nanotubes, SiO₂, SiC, and Si₃N₄. To prepare these nanomaterials on macroscale, various issues surrounding the incorporation of nanomaterials into polymer matrix, strategies for property improvement, and the

mechanisms responsible for those property improvements still remain critical. Thus, polymeric nanocomposites expected to spread through all aspects of life in the mid and longer-term, similar to the way plastics did in the last century. Clearly a diverse range of sectors such as aerospace, automotive, packaging (particularly food but also solar cells), electrical and electronic goods, and household goods etc., will significantly profit from a new range of materials, offered by nanotechnology. In the short term (<5 years), the commercial impact may include inkjet markets, cosmetics, automotive (body moldings, engine covers), catalytic converters and computer chips, (Paul & Robeson 2008; Hussain et al., 2006), while in the medium term (>5- <15 years) (10 years), memory devices, biosensors for diagnostics, advances in lighting applications. The time-scale for automotive, aerospace, bio-nanotechnology is a long-term prospect (>15 years) as these are risk-averse sectors and thereby for large-scale production it is necessary to carry out strict testing and validation procedures (Hussain et al., 2006).

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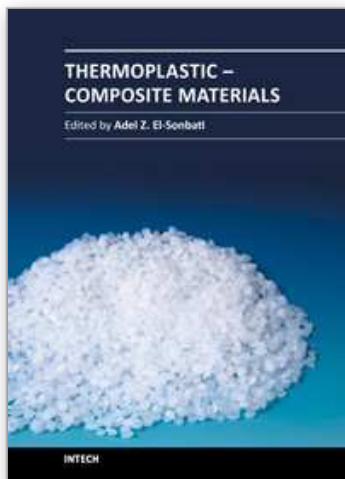
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