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# Preparation of Polypropylene Nanocomposites Using Supercritical Technology

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## 1. Introduction

In recent years polypropylene (PP) nanocomposites have attracted great interest in academia. The attractiveness of this new class of material lies in the large improvements in both mechanical and thermal properties, as well as in gas barrier and fire resistance (Grunes et al., 2003). Nanofillers, being additives of nanometre scale, are dispersed in PP matrix, offering multifunctional and high-performance polymer characteristics beyond those possessed by traditional filled materials.

Many methods have been employed for preparing PP nanocomposites (Wu & Lerner, 1993; Andrews et al., 2002; Zhao et al., 2003; Garcia-Leiner and Lesser, 2004). Among them, supercritical CO<sub>2</sub> technology has been intensively studied in recent years. The main advantages of this technology are that CO<sub>2</sub> is a 'green' non-combustible and non-toxic solvent and the addition of scCO<sub>2</sub> into the polymer can cause plasticization, which brings the opportunity to lower polymer viscosity, leading to improved dispersion, and to process the polymer at lower temperatures (Behles & Desimone, 2001; Cansell et al., 2003). Furthermore, CO<sub>2</sub> can act as a transport medium, which facilitates the diffusion of monomers, initiators and molecules into a polymer matrix (Kikic & Vecchione, 2003). The aim of this chapter is to provide a review of the use of supercritical CO<sub>2</sub> technology in the preparation of PP nanocomposites. In this chapter, the different nanofillers used, the processing methods based on using supercritical CO<sub>2</sub> technology and the resulting properties of the nanocomposites will be discussed in detail. The progress and challenges on various aspects of PP nanocomposites will also be discussed.

## 2. Nanofillers

The term 'nanofillers' is vague and no precise definition exists. Nanofillers are understood, in essence, to be additives in solid form, which differ from the polymer matrix in terms of their composition and structure. Nanofillers are of the order of 100 nm or less in at least one dimension.

Nanofillers are often added to enhance one or more of the properties of polymers. Inactive fillers or extenders raise the quantity and lower the cost price, while active fillers bring about targeted improvements in certain mechanical or physical properties. Common nanofillers include calcium carbonate, ceramic nanofillers, carbon black, carbon nanotubes (CNTs), carbon

nanofibres, cellulose nanowhiskers, nanoclays, gold particles, kaolin, mica, silica, silver nanoparticles, titanium dioxide, etc. Because of their impressive intrinsic mechanical properties, nanoscale dimensions and high aspect-ratio, nanofillers such as CNTs or nanoclays are among the most promising due to the fact that small amounts (less than 5 %) of them can provide the resulting nanocomposite material with significant property improvements.

### 2.1 Carbon Nanotubes (CNTs)

CNTs are considered to be ideal candidates for a wide range of applications in materials science because of their exceptional mechanical, thermal, and electronic properties (Baughman & Zakhidov, 2002). Carbon nanotubes exist as two types of structures: singlewall carbon nanotubes (SWNTs) and multiwall carbon nanotubes (MWNTs). Fig. 1 shows the schematic pictures of different types of carbon nanotubes. SWNT can be considered as graphene sheet rolled cylinders of covalently bonded carbon atoms with very high aspect ratios of 1000 or more. MWNTs consist of a number of graphene cylinders concentrically nested like rings in a tree trunk with an interlayer distance of  $\sim 0.34$  nm.

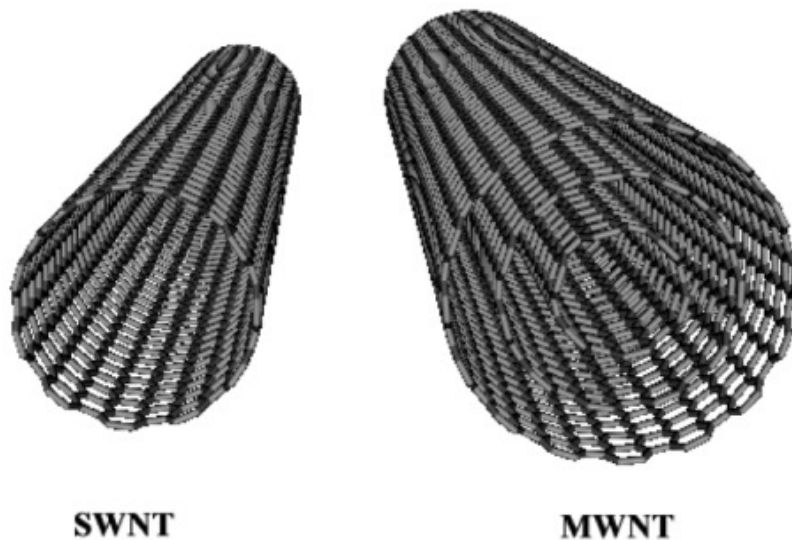


Fig. 1. A schematic illustration of a single-walled carbon nanotube and a multi-walled carbon nanotube (Dresselhaus et al., 2003).

The carbon-carbon covalent bonds in graphite and carbon nanotubes are considered to be one of the strongest atomic bonds in nature. The mechanical properties of CNTs have been extensively studied, both experimentally and theoretically (Yakobson et al., 1996; Lu, 1997). CNTs possess tensile moduli and strengths as high as 1 TPa and 150 GPa respectively. Especially in terms of strength CNTs are exceptional as this value is more than an order of magnitude higher than for high strength carbon fibres. Their density can be as low as  $1.3 \text{ g.cm}^{-3}$ , which is lower than commercial carbon fibres at  $1.8\text{-}1.9 \text{ g.cm}^{-3}$ . CNTs are thermally stable at up to  $2800 \text{ }^\circ\text{C}$  in vacuum. Their thermal conductivity is about twice as high as that of diamond, while their electric-current-carrying capacity is 1000 times higher than that of copper wires (Thostenson et al., 2001).

Since the first CNTs and polymer composites were made in 1994 (Ajayan et al., 1994), large amounts of work have been done on polymer/CNT composites. Incorporating nanotubes

into plastics can potentially provide structural materials with a dramatic increase in both stiffness and strength. Extensive studies have been carried out producing strong polymer/CNT composites (Coleman et al., 2006; Moniruzzaman & Winey, 2006; Ahir, 2005, Wang et al., 2007). The effective use of CNTs as reinforcements still presents some major difficulties (Wang et al., 2007). The key challenge still remains in breaking down bundles of aggregated CNTs and reaching a fine dispersion in the selected polymer matrix. Much work needs to be done to optimise the conditions required for the potential dispersion of nanotubes, especially at higher CNT loadings, as well as a good interfacial interaction (Moniruzzaman & Winey, 2006).

CNTs have extremely low electrical resistance and their electric-current-carrying capacity is 1000 times higher than copper wires (Thostenson et al., 2001). Devices have been developed using CNTs such as field-emission displays (Fan et al., 1999). CNTs have also been widely used to produce conductive polymer composites (CPCs). It has been reported that the percolation threshold in CPC can be as low as 0.0025 wt% in the case of low viscosity thermosetting resins (Bryning et al., 2005). In thermoplastics the percolation threshold is typically around 1 wt%, but can be significantly lower using latex technology (Lu et al., 2008) and is highly dependent on processing history (Zhang et al., 2009; Deng et al., 2009a and 2009b).

## 2.2 Nanoclays

Clay is a natural, earthy, fine-grained material and is the main constituent of the sedimentary rocks in marine sediments and in soils. Clay minerals belong to the family of phyllosilicates (or layered silicate) and have particles less than 2  $\mu\text{m}$  in size as stated in ISO 14688 (Moore & Reynolds, 1997). There are three main groups of clays: kaolinite, montmorillonite-smectite and halloysite, and most clay are a mixture of these different types. The shape of clay minerals is of a distinctive character. Montmorillonite, which has irregular flakes, is the most commonly used nanoclay in polymer/clay nanocomposites (Fig. 2a). Recently, sepiolite, a fibrous shaped mineral, has gained increasing attention as nanofiller reinforcement (Y.P. Zheng & Y. Zheng, 2006). Sepiolite is a needle-like shaped nanoclay composed with elemental particles of lengths of 0.2-4  $\mu\text{m}$ , widths of 10-30 nm and thicknesses of 5-10 nm (Fig. 2b). Sepiolite can have a surface area as high as 200-300  $\text{m}^2\text{g}^{-1}$  and normally it is found stuck together as bundles of fibres which can form micro-agglomerates. Sepiolite is a hydrous magnesium silicate with  $[\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}]$  as the unit cell formula.

Compared with layered montmorillonite, the morphology of fibre-like sepiolite provides a lower specific surface area and smaller contact surface between the nanoclay particles. Therefore, polymer chains have a better chance not only of interacting with the external surface of the sepiolite, but also of penetrating into the structure, which facilitates a more even dispersion of the clays in the polymer matrix. Sepiolite provides a pseudoplastic and thixotropic behaviour which make it a valuable material in multiple applications to improve the processability, application or handling of the final product. Sepiolite has been successfully used to reinforce different polymers, such as poly (hydroxyethyl acrylate), epoxy, PP, etc (Bokobza et al., 2004; Y.P. Zheng & Y. Zheng, 2006; Bilotti et al., 2008).

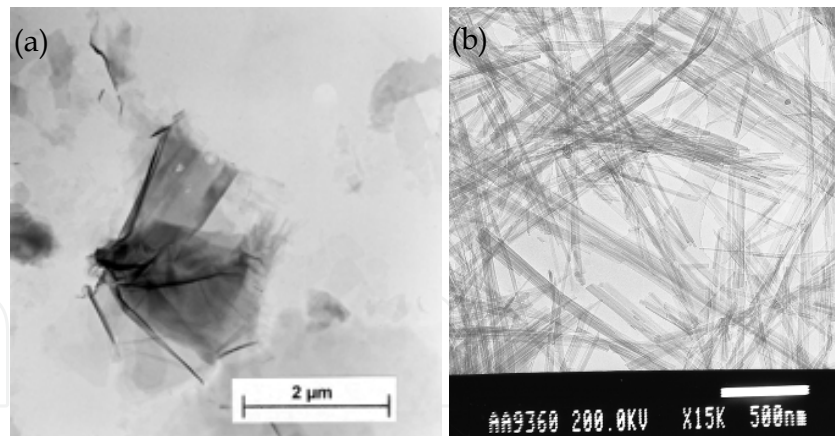


Fig. 2. The structure of (a) montmorillonite (Beermann & Brockamp, 2005) and (b) sepiolite (Bilotti et al., 2008)

### 3. Polypropylene nanocomposites

For decades we have been dealing with polymer microcomposites, where the length scale of the fillers is in micrometres. In the case of polymer nanocomposites, nanofillers, being additives of nanometre scale, are dispersed in a polymer matrix, offering multifunctional, high-performance polymer characteristics beyond those possessed by traditional filled polymeric materials. Improvements in physical and mechanical properties have been well documented in the literature (Dubois & Alexandre, 2006; Thostenson et al., 2001; Koo, 2006). Apart from mechanical enhancements, the value of polymer nanocomposites comes from providing value-added properties not present in the polymer matrix, without sacrificing the inherent processability and mechanical properties of the matrix. The multifunctional features consist of improved thermal, fire, and moisture resistance, decreased permeability, charge dissipation, and chemical resistance (Moniruzzaman & Winey, 2006; Bokobza et al., 2004; Koo, 2006). Because of PP's good balance between properties and cost and its wide usage in industry, PP nanocomposites have been extensively studied in recent years (Deng et al., 2009, 2010; Bilotti et al., 2008; Andrews et al., 2002; Liu & Wu, 2001).

The properties of nanocomposites can be greatly affected by the dispersion of the nanofillers in the polymer matrix (Ray & Okamoto, 2003). Generally, the better the dispersion, the better is the properties of the final nanocomposite. However, nanofillers are, in essence, agglomerates due to their high surface energy, and it is very difficult to disperse them in most polymers. Due to the lack of polar groups in PP, many efforts have been attempted to improve the dispersion of inorganic fillers such as clay and CNTs into a PP matrix for the preparation of effective PP nanocomposites and enhanced mechanical properties. The achievement of well-dispersed nanofillers is the most investigated research topic worldwide (Coleman et al., 2006; Koo, 2006; Ray & Okamoto, 2000; Lu et al., 2008).

## 4. Preparation methods

### 4.1 Traditional processing methods

Polymer nanocomposites are generally prepared by three methods: solution intercalation, in-situ polymerisation or melt compounding.



Solution intercalation has been known for over a century and has proved to be one of the most successful methods for incorporating nanofillers into polymers. Nanocomposites with water-soluble polymers such as poly (ethylene oxide) and poly (vinyl alcohol) and organic solvent-soluble polymers such as HDPE, have been successfully prepared via this method (Wu & Lerner, 1993; Ogata, et al., 1997; Joen et al., 1998; Wang et al., TP, 2007). In terms of PP nanocomposites, the poor solubility of PP in most organic solvents has severely limited the use of this method. Although PP nanocomposites have been reported being produced using xylene, tetrahydronaphthalene and decalin as solvents (Chang et al., 2005; Grady et al., 2002), elevated temperatures are necessary for the evaporation of these high-boiling solvents. Also, their application on an industrial scale is still hindered by the involvement of large quantities of organic solvent.

In-situ polymerisation has been intensively investigated in recent years. The advantage of this process is that the polymer chain can be grafted onto the nanofillers on a molecular scale. This gives excellent dispersion and the potential for good interfacial strength between the nanofillers and the polymer matrix. A relatively good dispersion can be maintained even with high nanotube loading in the matrix. Successful investigations have been reported in the literature from different groups on PP nanocomposites (Ma et al., 2001; Zhao et al., 2003; Koval'chuk et.al, 2008; Funk & Kaminsky, 2007). PP/ MMT nanocomposites were prepared by in-situ polymerization using a Ziegler-Natta catalyst (Zhao et al., 2003). PP/ MWNT nanocomposites have been fabricated by Funck and Kaminsky (2007) using a metallocene/ methylaluminoxane (MAO) catalyst. However, the molecular weight of the polymer is often significantly lower with a wide distribution by comparison with other methods.

Melt compounding is the most common method used to create thermoplastic polymer nanocomposites because it is a cost-effective technology for polyolefin-based systems and is compatible with current industrial practices, such as extrusion, injection moulding, etc (Andrews et al., 2002). However, melt compounding, especially in the case of PP matrices, is generally less effective at dispersing nanofillers such as CNTs and clays, and is limited to low nanofiller loadings due to the high viscosity of the composite systems caused by the addition of nanofillers (Andrews et al., 2002). Moreover, the high shear rates and high temperatures utilised can also cause thermal instability of the molten polymers (Potschke et al., 2003). One approach is using the masterbatch process, where a pre-mixed highly loaded nanofiller composite is diluted with a fresh polymer melt (Prashantha et al., 2009).

Much effort has been expended to facilitate the achievement of good dispersion of nanofillers and efficient stress transfer. The de-agglomeration of CNTs is necessary for dispersing individual nanotubes before mixing them with the polymer matrix. The ultrasonication process is the most common method, but severe sonication may make the tubes shorter (Saito et al., 2002, Inam et al., TP, J. Comp Materials, 2011). Milling and grinding is considered to be a cheap and fast method for industrial processes although it is the most destructive method for CNTs (Pierard et al., 2001). Non-covalent functionalizations, such as surfactants, are often utilised to overcome carbon nanotube entanglements resulting from Van der Waals forces (Bonduel et al., 2005). Covalent functionalization of CNTs helps to break up the CNT bundles and improves the polymer / CNT interfacial adhesion (Liu et al., 2005). Polymer wrapping has been proposed as an alternative method to achieve a good dispersion of the CNTs without destroying their electrical properties (Star et al., 2001). Dissociated CNTs were produced by grafting polymer chains directly onto the CNTs to achieve a homogeneous polymer coating on the CNT

surface (Peeterbroeck et al., 2007; Dubois & Alexandre, 2006). High-density polyethylene has been used to coat MWNTs when producing PP nanocomposites and composites in other polymer matrices such as ethylene-vinyl acetate, polycarbonate and polyamide (Deng et al., 2010; Star et al., 2001; Peeterbroeck et al., 2007; Dubois & Alexandre, 2006; Pötschke et al., 2008). Compared with the direct incorporation of CNTs in polymer melts, enhanced dispersion and improved properties have been reported.

There are two ways to modify the surface of hydrophilic clays in order to improve their dispersion in the polymer matrix. The first one is to modify the surface with cationic surfactants to make the silicate surface organophilic via ion exchange reactions (Lan & Pinnavaia, 1994; Shi et al., 1996). The second method is based on grafting polymeric molecules through covalent bonding to the hydroxyl groups existing on the particles. However, for polyolefin polymers such as PP and PE, they are non-polar and incompatible with silicate surfaces even after modifying them with non-polar long alkyl groups. Therefore, a compatibilizer is often needed to facilitate the interaction between the polymer and the clays (Hasegawa et al., 2000; Garcia-Lopez et al., 2003). Compatibilizers are usually polar functional oligomers providing both a hydrophobic part (which can be easily mixed with a polymer) and a hydrophilic part (which is compatible with clay). Maleic anhydride grafted polypropylene (PP-g-MA) is a commonly used compatibilizer to aid the dispersion of clay or CNTs in PP matrix (Bilotti et al, 2008 and 2010).

#### 4.2 The supercritical fluid technique

In recent years, supercritical technology, especially supercritical carbon dioxide ( $\text{scCO}_2$ ), has been widely applied in the processing of polymer nanocomposites. A supercritical fluid is defined as “any substance, the temperature and pressure of which are higher than their critical values, and which has a density close to, or higher than, its critical density” (Darr & Poliakoff, 1999). Fig. 3 shows a schematic representation of the density and organization of molecules of a pure fluid in solid state, gas state, liquid state and the supercritical domain. No phase separation occurs for any substance at pressures or temperatures above its critical values. In other words, the critical point represents the highest temperature and pressure at which gas and liquid can coexist in equilibrium.

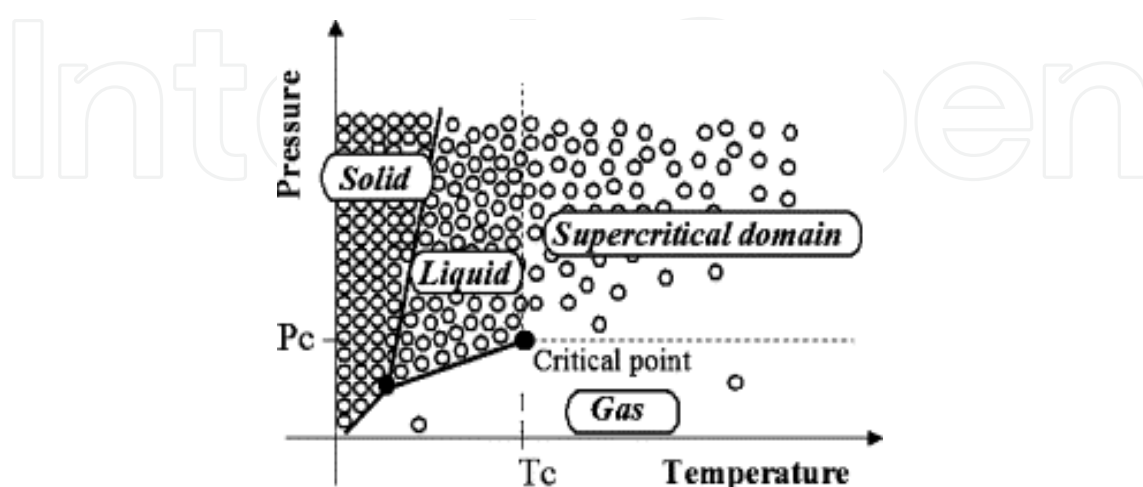


Fig. 3. A schematic representation of the microscopic behaviour of a pure fluid in the P-T plane phase diagram (Cansell et al., 2003)

Supercritical fluids are unique solvents with a wide range of interesting properties. Supercritical fluids have high diffusivities, similar to gas which allows them to effuse through solids, while also having liquid-like densities that allow them to act as effective solvents for many compounds. In addition, small changes in pressure and temperature greatly affect the density of a supercritical fluid and therefore many properties of SCF can be 'fine-tuned'. The unique properties of supercritical fluids allow them to be widely exploited in materials processing. The most promising developments are the processing of fine powders, core-shell particles, the processing and / or impregnation of aerogels, foams, surface modifications and the processing of polymers. (Cansell et al., 2003)

Among all the supercritical fluids, the use of  $\text{scCO}_2$  is the most desirable for polymer processing because of its environmental compatibility as well as the following properties:

- $\text{CO}_2$  has relatively easily accessible critical points of  $31.06^\circ\text{C}$  and 1070 psi (7.38 MPa) (Hyatt, 1984)
- The density of  $\text{scCO}_2$  is easily tunable (Fig. 4). Therefore, the solvent strength and processes can be easily controlled
- $\text{CO}_2$  is non-combustible and non-toxic in contrast to most of the organic solvents suitable for supercritical applications
- It is also easily available because it occurs naturally as well as being the by-product of many industrial processes; therefore  $\text{CO}_2$  is relatively inexpensive
- As  $\text{CO}_2$  is a gas at ambient temperatures and pressures it can be easily removed, leaving no solvent residues in the processed material (Behles & Desimone, 2001)

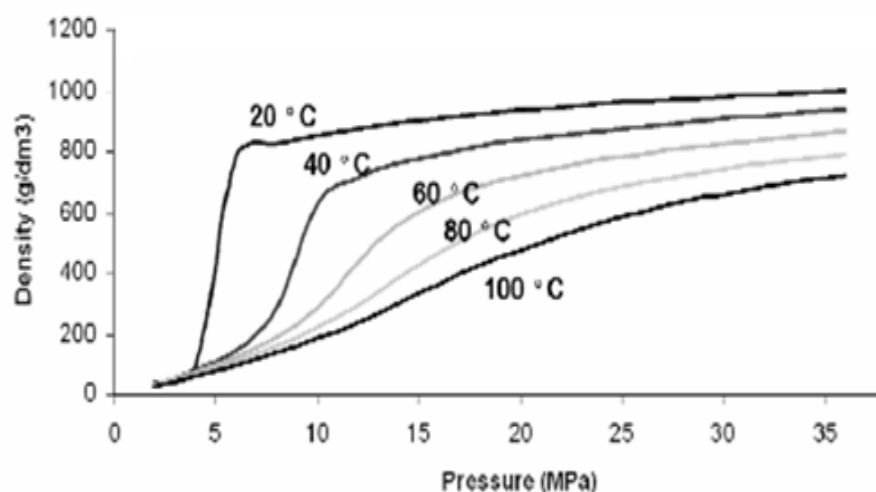


Fig. 4. The density of  $\text{CO}_2$  as a function of pressure for a range of temperatures

$\text{scCO}_2$  has found widespread application in industrial processes, including the extraction of metals or organic material, the decaffeination of green coffee beans, dry cleaning and degreasing, nano- and micro-particle formation, impregnation and dyeing, the processing and synthesis of polymers and composites, tissue engineering scaffolds, drug delivery, etc (Quirk et al., 2004; Hyde et al., 2001). The important fields most relevant to this Chapter are in the  $\text{scCO}_2$  processing of polymers and composites which will be discussed in greater detail below.



scCO<sub>2</sub> processing, as one of the new and cleaner processing methods for polymer nanocomposites, has recently received increasing attention. The solubility of polymers in scCO<sub>2</sub> is poor for many high molecular weight polymers. Table 1 gives a representative sample of the available literature data for the solubility of CO<sub>2</sub> in a variety of polymers. The low solubility is a result of the lower density of scCO<sub>2</sub> and the weak interaction between the CO<sub>2</sub> molecules and the non-polar groups of many polymers (Cansell et al., 2003). However, even for polymers which are not soluble in scCO<sub>2</sub>, the CO<sub>2</sub> is still able to permeate resulting in substantial and sometimes dramatic changes in the properties of these polymers. The permeation of scCO<sub>2</sub> into a polymer causes it to swell. Aided by their zero surface tension, the addition of scCO<sub>2</sub> into the polymer phase gives the chains a greater mobility. The CO<sub>2</sub> molecules act as lubricants, which reduces the chain-chain interactions as it increases the inter-chain distance and free volume of the polymer. This is called plasticization. The physical properties of the polymer are changed dramatically, including the depression of the glass transition temperature ( $T_g$ ), the lowering of interfacial tension and a reduction of the viscosity of the polymer melt. ScCO<sub>2</sub> may increase the crystallinity of the polymers because the polymer chains are given more freedom to align themselves into a more favourable order.

Polymer	Method <sup>a</sup>	Pressure [atm]	Temp. [°C]	Solubility
poly(methyl methacrylate)	GM-M	50	65	46 SCC/cm <sup>3</sup>
	GM-D	204	70	10.5 wt. %
polystyrene	GM-M	13.2	25	14.5 SCC/cm <sup>3</sup>
high-impact polystyrene	GM-D	204	70	0.5 wt. %
polycarbonate	GM-M	13.2	25	24 SCC/cm <sup>3</sup>
	GM-D	68	25	13 g/100g
poly(ethylene terephthalate)	GM-D	136	40	1.5 wt. %
poly(vinyl chloride)	GM-D	68	25	8 g/100g
	GM-D	136	40	0.1 wt. %
poly(vinyl acetate)	GM-D	54.4	25	29 g/100g
low density polyethylene	GM-D	68	40	0.2 wt. %
high density polyethylene	GM-D	68	40	0.1 wt. %
polypropylene	GM-D	68	40	0.1 wt. %
	GM-D	204	25	0.1 wt. %
	BM	73	160	1.59 g/100g
	BM	61.2	200	1.09 g/100g
Nylon 66	GM-D	68	40	1.8 wt. %
polyurethane	BM	136	40	2.2 wt. %
Teflon	GM-D	68	40	0.0 wt. %

<sup>a</sup>Method: GM-M, gravimetric method (microbalance); GM-D, gravimetric method (desorption); BM, barometric method. Units: SCC/cm<sup>3</sup>, cm<sup>3</sup>(STP)/cm<sup>3</sup> of polymer; g/100g, g of CO<sub>2</sub>/100g of polymer.

Table 1. The solubility of CO<sub>2</sub> in polymers (Tomasko et al., 2003)

Garcia-Leiner and Lesser (2004) have studied the use of  $scCO_2$  in the processing of a variety of polymers (s-PS, FEP, and PTFE) using a modified single-screw extruder with a  $CO_2$  injection (Fig. 5). The presence of  $CO_2$  significantly enhanced the processability of the polymer- $CO_2$  system by plasticization effect and the hydrostatic contribution. This presented an effective alternative to process intractable or high melt viscosity polymers.

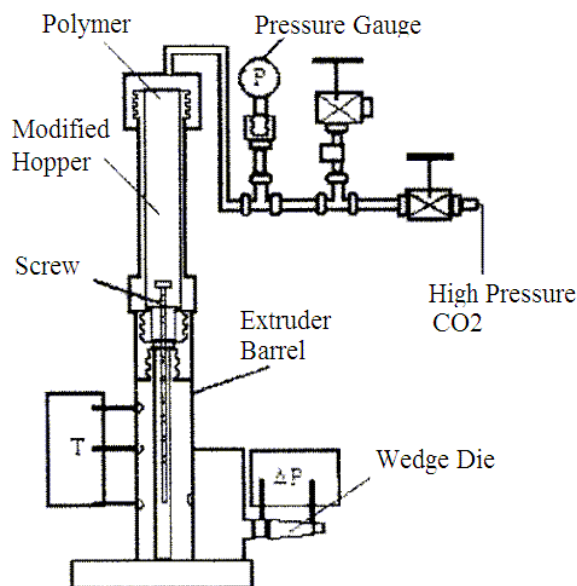


Fig. 5. Modified extrusion system for  $CO_2$ -assisted polymer processing (Garcia-Leiner & Lesser, 2004)

A wide range of opportunities have opened up for  $scCO_2$  that have an impact on the plastics industry (Tomasko et al., 2003). These include usages for extraction, foaming and impregnation. Extraction occurs merely by removing the soluble extractant material, such as any unreacted monomer, while leaving the insoluble substrate. Foaming occurs when rapid decompression forms gaseous  $CO_2$  inside the polymer, leaving the polymer in the form of a porous (micro) material. This is very important in supporting the growth of blood vessels and collagen fibres in the matrix of biodegradable polymers or when the final product is intended to be used as a catalyst. As for impregnation,  $CO_2$  can act as a transport medium facilitating the diffusion of monomers, initiators and molecules to impregnate a polymer, while the  $CO_2$  can be cleanly removed afterwards. A better dispersion of the molecules has been provided within the polymer matrix. Substances impregnated into polymers have included dyes, fragrances, drugs for controlled release, anti-microbial and anti-fungal agents, and nanoparticles (Kikic & Vecchione, 2003).

The effective dispersion of the fillers in the polymer matrix and the improvement of polymer-filler interactions are two key challenges in the field of polymer nanocomposites. The development of polymer processing technologies in  $scCO_2$  has enabled the synthesis of very complex polymer nanocomposites. Zerda et al. (2003) developed poly (methyl methacrylate) / montmorillonite composites via in-situ polymerization.  $ScCO_2$  was used as the reaction medium to distribute homogeneously the monomer and the initiator and allowing polymerization under lower viscosity conditions. The modulus of the nanocomposites increased 50% with 40 wt % of clay content. A significant improvement in physical properties has also been reported by Green et al. (2000) for  $scCO_2$  processed poly

(methyl methacrylate) / silicate nanocomposites, in which  $scCO_2$  acted as both a plasticizer for the polymer matrix and a carrier for the monomer. Polystyrene / clay has also been produced via in-situ polymerization by Li et al. (2006), where styrene monomer and initiator were directly intercalated into organomontmorillonite (OMMT) with the aid of  $scCO_2$ .

For PP nanocomposites, PP will become plasticized when treated with  $CO_2$ . Varma-Nair et al. (2003) have suggested that 1%  $CO_2$  could be dissolved in PP at 50 °C at 180 psi. Both decreases in  $T_m$  and  $T_c$  of PP in presence of  $CO_2$  have been reported in the literature (Varma-Nair et al., 2003; Garcia-Leiner & Lesser, 2003). Studies in PP have indicated improvements in the dispersion of nanofillers in the matrix via melt compounding in  $scCO_2$  (Garcia-Leiner & Lesser, 2003, Ma et al, 2007, Zhao & Huang, 2008). Zhao & Huang (2008) improved a twin-screw extruder with the aid of  $scCO_2$  for the preparation of PP / clay nanocomposites (see Fig. 6). A  $CO_2$  injection system was connected to the extruder and several kneading and reverse conveying elements were added to prevent  $CO_2$  from leaking. This continuous extrusion process of PP nanocomposites using  $scCO_2$  has set good examples for  $scCO_2$  usage in an industrial environment.

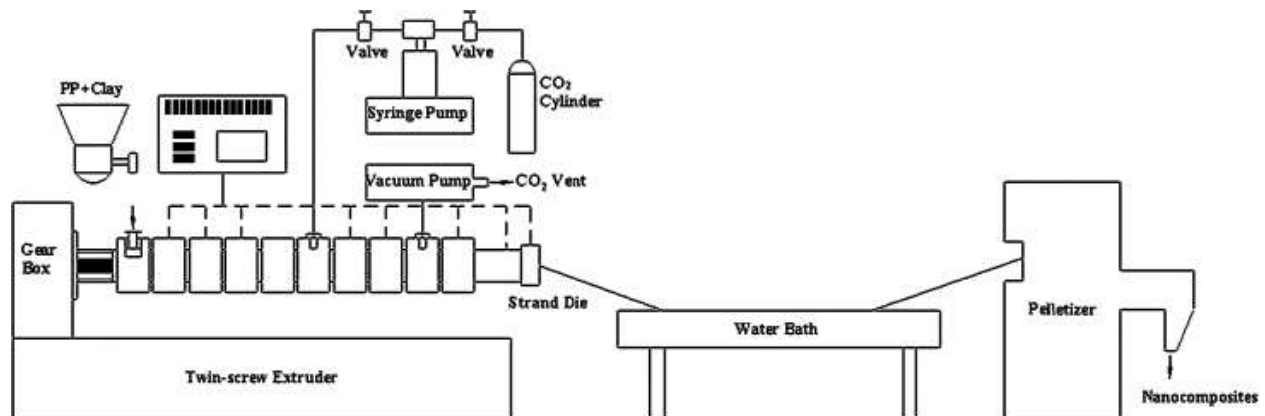


Fig. 6.  $scCO_2$  used in the extrusion process for the preparation of PP/ clay composites (Zhao & Huang, 2008)

## 5. Morphology and properties of PP nanocomposites

The preparation methods have crucial impact on the dispersion of the nanofillers and the final properties of the nanocomposites. In this section, the morphology of the PP nanocomposites and various nanocomposite properties will be discussed.

### 5.1 Morphology

Polymer-grafted CNTs were used in the study of Yang et al. (2008). They reported that PP-g-MWNTs were dispersed individually in the PP matrix at 1.5 wt%, but difficulty was found at higher CNT contents (Yang et al., 2008). Deng et al. (2010) reported that large bundles of MWNTs were present in their PP/MWNT samples using traditional melt compounding methods and better dispersions of MWNTs were observed for the HDPE coated MWNTs samples. The scanning electron microscopy (SEM) images of fracture surfaces of the nanocomposites are presented in Fig. 7. The HDPE coats the MWNTs and reduces the tendency of the nanotubes to aggregate and is partly miscible with the PP matrix. Ma et al.

(2010) studied the use of  $\text{scCO}_2$  to assist melt compounding of PP nanocomposites. The nanocomposites are prepared in an autoclave. The autoclave was filled with liquid  $\text{CO}_2$  and held at 2175 psi and 200 °C under stirring for 30 min. In their work, pristine MWNTs without HDPE coating were observed to exhibit good dispersion in the PP matrix under  $\text{scCO}_2$  assisted mixing (Fig. 7c). This indicates the great efficiency of  $\text{scCO}_2$  being a processing lubricant between the polymer chains enhancing the polymer diffusion.

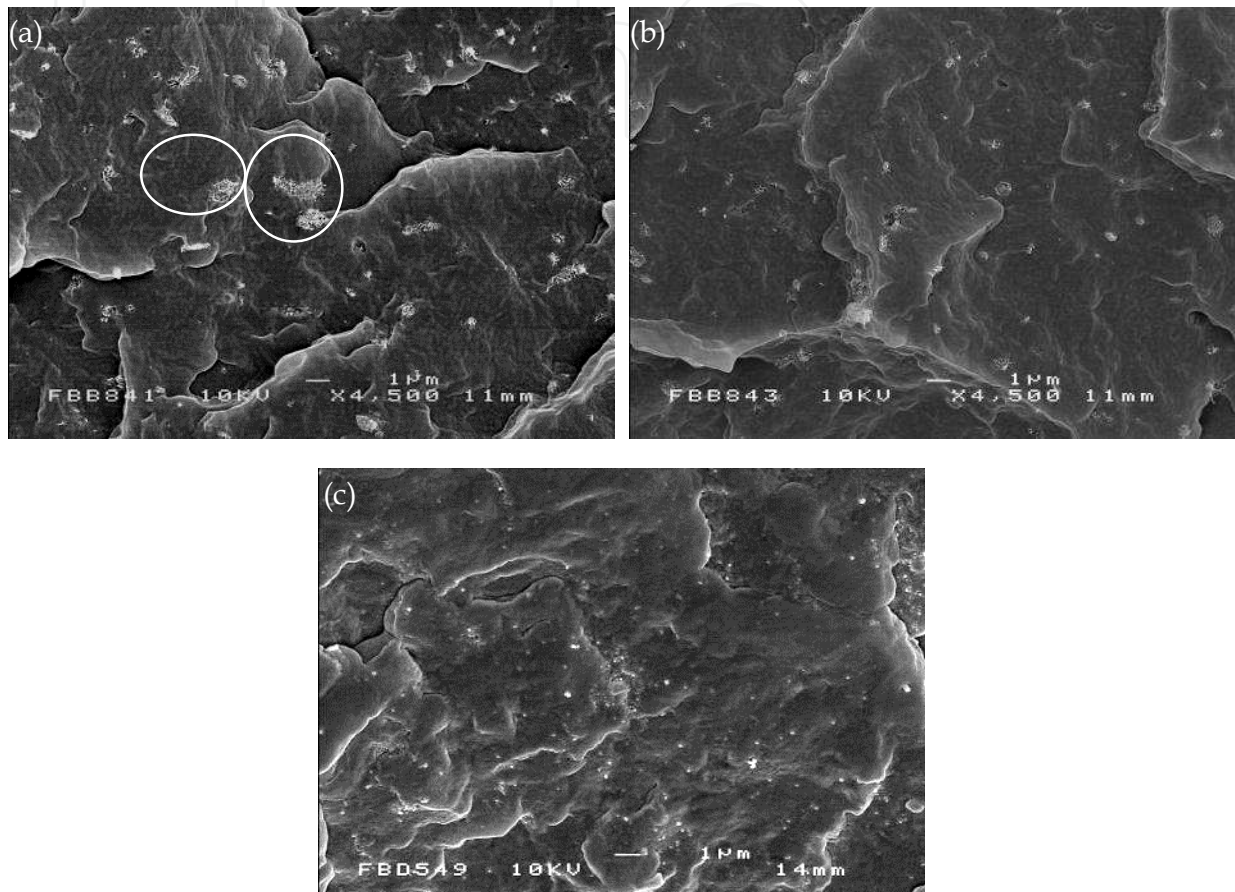


Fig. 7. SEM images of freeze-fractured samples of PP nanocomposites with 0.5 wt.% MWNT loading (a) melt-compounded MWNT (b) melt-compounded PP/coated MWNT (Deng et al., 2010) (c)  $\text{scCO}_2$  PP/MWNT (Ma et al., 2010)

In Zhao & Huang' (2008) work, a better dispersion of clays in PP matrix was also confirmed with  $\text{scCO}_2$  assisted mixing. Fig. 8 shows that the sample prepared with 2.5%  $\text{CO}_2$  has more uniform distributed clay and aggregations of clay are much thinner.

Ma et al. (2007) also reported a good dispersion of sepiolite clays in PP matrix with  $\text{scCO}_2$  assisted mixing. Without the use of any compatibilizer, the dispersion of sepiolite in the PP matrix improved significantly in the  $\text{scCO}_2$  assisted mixing compared to melt mixing. This indicates that compatibilizers such as PP-g-MA are not needed to achieve good dispersions in the case of  $\text{scCO}_2$  assisted processing of polyolefins. This is of particular relevance because the role of compatibilizers, such as PP-g-MA, is generally regarded as essential for the creation of well dispersed nanoclays composites based on polyolefins using traditional melt compounding methods.



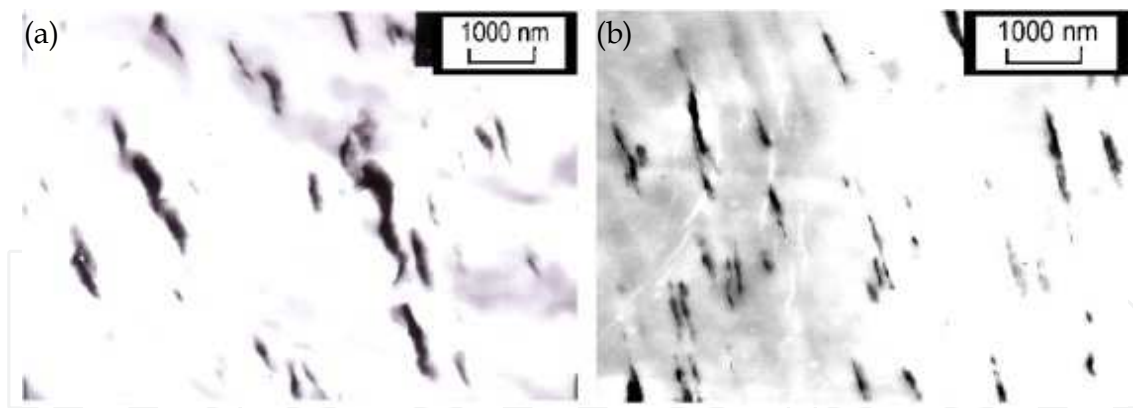


Fig. 8. TEM images of PP/clay nanocomposites prepared (a) without and (b) with 2.5% CO<sub>2</sub> (Zhao & Huang, 2008)

## 5.2 Mechanical properties

The mechanical properties including the tensile strength and Young's modulus of the PP nanocomposites can be significantly enhanced by the incorporation of nanofillers. Andrews et al. (2002) fabricated PP / MWNT composites by a shear mixer and found a modulus increase from 1.0 GPa to 2.4 GPa with a relatively high nanotube content of 12.5 wt%. However, this was at the expense of a reduction in yield stress from 30 MPa to 18 MPa. Similarly, Wang and Sheng (2005) found that the modulus of the PP nanocomposites increased from 788 MPa to 908 MPa by the addition of 7 wt% Attapulgite clay, but at the expense of a reduction in strength from 32 MPa to 26 MPa. Deng et al. (2010) investigated the effects of a HDPE coating onto MWNTs on the mechanical properties of PP / MWNT composites produced by melt compounding. A property increase from 1.42 GPa to 1.79 GPa for Young's modulus and from 34.5 MPa to 37.9 MPa for tensile strength, was achieved at relatively low loadings (0.5 wt%) of coated MWNTs.

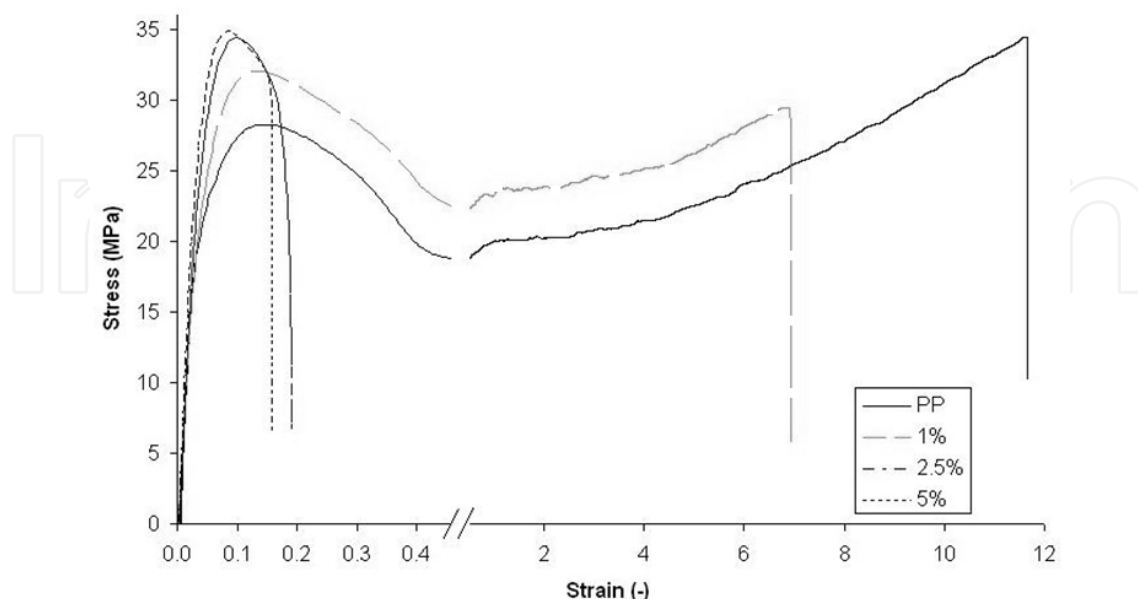


Fig. 9. Stress-strain curves of scCO<sub>2</sub> PP / sepiolite nanocomposites with different clay contents (Ma et al., 2007)



The elongation at break of the nanocomposites is often decreased. The increase of nanofiller content compromises the ductile nature of the PP matrix. Yielding followed by drawing still occurred in the 1 wt% sepiolite samples; while 2.5 wt% and 5 wt% sepiolite samples show brittle fractures at low strains (Fig. 9).

The effect on the modulus and yield stress of the  $\text{scCO}_2$  processed PP nanocomposites was studied for the addition of MWNTs and sepiolite clays (Ma et al., 2007 and 2010). The results were compared with traditional melt compounded nanocomposites.

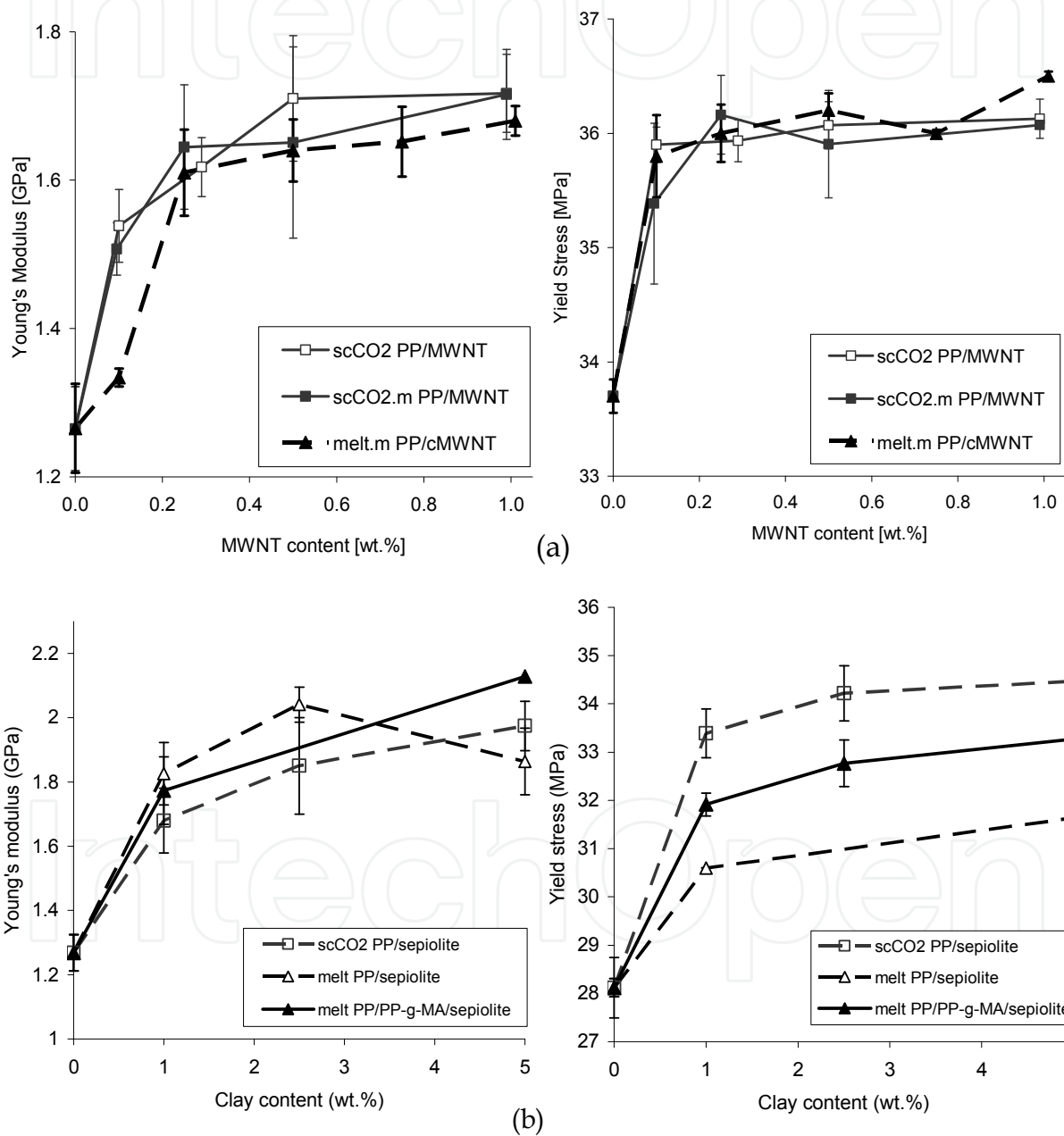


Fig. 10. The Young's modulus and yield stress of  $\text{scCO}_2$  processed and melt-compounded PP nanocomposites (a) PP / MWNT nanocomposites (b) PP / sepiolite nanocomposites. The label, melt.mPP/cMWNT, in the figure represents melt-compounded and masterbatch based HDPE-coated MWNT PP nanocomposites (Ma et al., 2007; Ma et al., 2010)

Increases of both properties were observed in all systems with the nanofiller content as expected. The melt-compounded and masterbatch based PP/coated MWNT composites show a continuous modulus increase up to 1.7 GPa by the addition of 1.0 wt% CNT loading (Fig. 10a). This is as a result of the de-aggregation of the MWNT bundles by the HDPE coating (Ma et al., 2010).  $\text{scCO}_2$  processed nanocomposites with pristine MWNTs also showed a competitive increase in Young's modulus. Furthermore, the use of masterbatch in the  $\text{scCO}_2$  assisted mixing method did not show much improvement in terms of Young's modulus. Similarly, increases in yield stress were observed for  $\text{scCO}_2$  PP / MWNT samples, with a significant 6 % increase at 0.1 wt% CNT loading followed by roughly constant values across the rest of the CNT loading range up to 1 wt% (Fig. 10a). The degree of reinforcement of pristine MWNTs is as good as for melt-compounded PP/coated MWNT composites. This indicates that  $\text{scCO}_2$  assisted mixing achieves a better dispersion of CNTs without the need for a HDPE coating. The enhanced mechanical properties are also benefited from the relatively low shear forces involved in  $\text{scCO}_2$  assisted mixing, which causes less nanotube breakage and damage.

In Ma et al.' (2007) work about PP/sepiolite nanocomposites, the Young's modulus of melt compounded PP nanocomposites (no PP-g-MA used as compatibilizer) shows a reduction at 5 wt% sepiolite loading (Fig. 10b). This corresponds to the aggregation of clay at higher loadings with the absence of PP-g-MA. This is in contrast to the analogous material with PP-g-MA, which shows a 68 % increase in modulus from 1 to 5 wt% clay content. The modulus for  $\text{scCO}_2$  processed PP nanocomposites without PP-g-MA shows a steady increase in modulus (by up to 56 % for 5 wt% sepiolite). In terms of yield stress,  $\text{scCO}_2$  processed PP nanocomposite without PP-g-MA shown the highest increase in yield stress of up to 23 % for 5 wt% sepiolite, which was benefited from the good dispersion of the sepiolite and also the benefit of preserving the clay fibre length when using  $\text{scCO}_2$  assisted mixing.

### 5.3 Characterization of PP

#### 5.3.1 Thermal behaviour

Nanofillers increase the crystallization temperature ( $T_c$ ) of PP. It has been observed for both CNT and clay nanocomposites (Ma et al., 2007; Bilotti et al., 2008; Lee et al., 2008). The nanofillers act as nucleating agents enabling PP to crystallize at a higher temperature during the cooling process. This increase in  $T_c$  is dependent on the nanofiller content, which suggests that higher loadings of nanofiller can provide higher nucleating efficiency. It has been reported that SWNTs are more effective nucleating agents than MWNTs, which provided larger increase in  $T_c$  (Miltner et al., 2008). Furthermore, pristine MWNTs also give a stronger nucleation effect than HDPE coated MWNTs, which suggests that the surface of the nucleating agents plays an important role in the crystallization process (Ma et al., 2010). It was also found that a more pronounced nucleating effect was observed for very low CNT loadings. Although nucleating agents significantly increase the number of nucleation sites, above certain loadings the introduction of more CNTs may hinder chain mobility and retard crystal growth.

Apart from the  $T_c$ , the crystallinity of PP has also been increased by the addition of nanofillers (Bilotti et al., 2008). The Young's modulus of the composites has been reported to increase with polymer matrix crystallinity in the work of Coleman et al. (Coleman et al., 2004). Similar results were also shown in other studies that changes in the crystallinity and the

crystalline morphology of the polymer matrix can have pronounced effects on the mechanical properties of nanocomposites (Bhattacharyya et al., 2003; Wang et al., 2007). Hence, the mechanical reinforcing effects observed are a combination of the modification of the PP matrix through increased crystallinity as well as true reinforcing effects from CNT fillers.

The effect of nanofillers on the melting temperature ( $T_m$ ) of PP is not clear. Yang et al. (2008) and Bikiaris et al. (2008) have observed an increase in  $T_m$ . Lee et al. (2008) has reported a decrease in  $T_m$  of PP. Other authors reported that  $T_m$  remains unchanged (Seo et al., 2005; Jin et al., 2009).

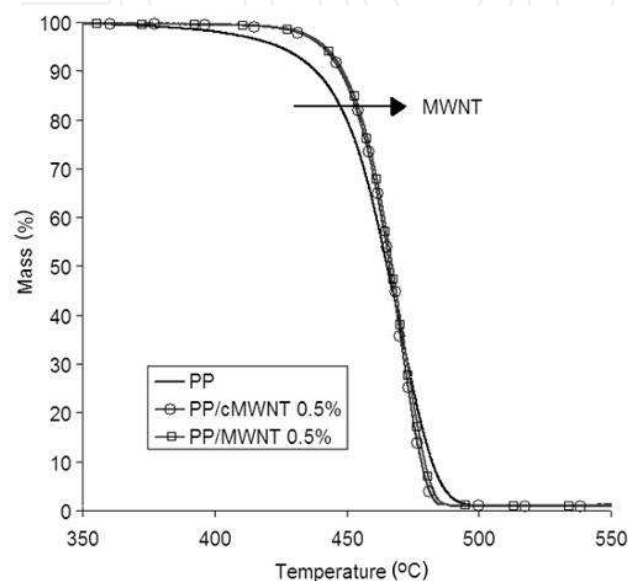


Fig. 11. The TGA of PP / MWNT nanocomposites processed using  $\text{scCO}_2$  assisted mixing, showing a slightly retarded thermal degradation of nanocomposites by the presence of MWNTs (Ma et al., 2010)

The thermal stability of PP is also slightly improved by the addition of the nanofillers. TGA shows that the thermal degradation of PP is retarded by the presence of CNTs (Fig. 11). PP / MWNT nanocomposites showed a higher onset decomposition temperature ( $T_{\text{onset}}$ ). The Reason is that the CNTs hinder the flux of degradation products and improves the heat dissipation within the composites (Huxtable et al., 2003). Seo & Park (2004) have observed a  $T_{\text{onset}}$  increase from 278 °C to 352 °C at the addition of 5 wt% of MWNTs. The effect of the clay surface modification on the thermal stability of PP has been studied by Tartaglione et al. on the melt-compounded PP / sepiolite composites (Tartaglione et al., 2008).

### 5.3.2 Microstructure of PP

PP can crystallize in three crystalline modifications: monoclinic ( $\alpha$ ), hexagonal ( $\beta$ ), and orthorhombic ( $\gamma$ ) (Bruckner et al., 1991). These phases can be examined by XRD. The XRD patterns for all the PP nanocomposites shows peaks corresponding to PP  $\alpha$ -phase at  $2\theta = 14, 17, 18.5, 21.5, 21.9$  and  $25.4^\circ$  for six major reflections: (110), (040), (130), (111), (041) and (060) plane, respectively. Most studies showed that only  $\alpha$  phase of PP was present in the PP nanocomposites and no other forms of PP crystallites were detected. This indicates that the addition of sepiolite does not affect the crystal modification of the final PP molecules

However, Wang & Sheng (2005) did report that the relative intensities of 040 peaks and 110 peaks can change (Fig. 12) and an increase in the  $I_{040} / I_{110}$  ratio was found. This preferential orientation of PP crystal growth has also been found with the addition of MWNTs and sepiolite clays (Ma et al., 2007 and 2010). Data of relative intensities are listed in Table 2. This increase indicates that the addition of sepiolite promotes a preferential orientation of PP crystals growing with (040) planes parallel to the sepiolite surface and the b-axis perpendicular to it (Ferrage et al., 2002; Wang & Sheng, 2005).

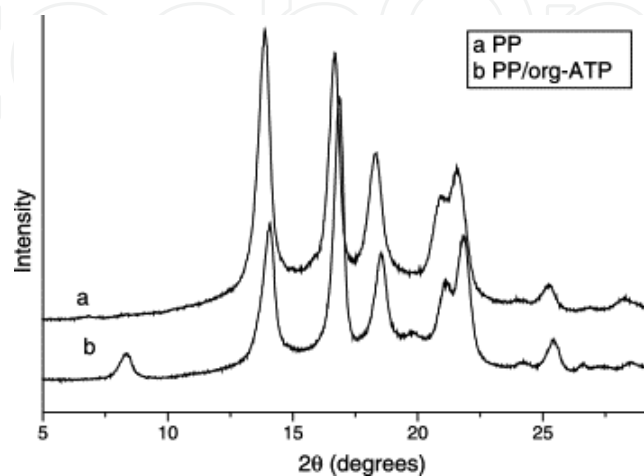


Fig. 12. XRD patterns of (a) PP and PP/org-ATP nanocomposites (Wang & Sheng, 2005)

Sepiolite [wt.%]	0	1	2.5	5
PP/sepiolite	0.80	2.41	2.40	2.24
PP/PP-g-MA/sepiolite	0.80	1.40	3.00	2.71

Table 2. Ratio of intensity between diffraction peaks of (040)<sub>a</sub> and (110)<sub>a</sub> in XRD patterns (Ma et al., 2007)

## 6. Conclusion

Researches on nanofillers such as CNTs and nanoclays reinforced PP nanocomposites have attracted wide attention. The properties of the nanocomposites can be significantly improved by the addition of nanofillers. The challenge in producing high performance PP nanocomposites is to achieve homogeneous dispersion of nanofillers thus obtaining efficient stress transfer. Among the nanocomposite preparation methods, *scCO*<sub>2</sub> assisted mixing is an interesting alternative to produce PP nanocomposites as it overcomes some of the issues in the traditional melt compounding process, such as high viscosities, high temperatures and high shear stresses involved, which can all lead to polymer degradation. The plasticization of *scCO*<sub>2</sub> could reduce the PP viscosity, decrease the  $T_m$  of the PP, and hence increase the processability of nanocomposites and improve the dispersion of nanofillers. *ScCO*<sub>2</sub> assisted mixing also benefits from a better preservation of nanotube or nanofibre lengths. Good nanofiller dispersion and mechanical properties were achieved without using the aid of compatibilizers such as PP-g-MA or polymer coated nanofillers, which are commonly used aiding the dispersion of nanofillers in the melt compounding process. This is all very encouraging from an economical point of view.

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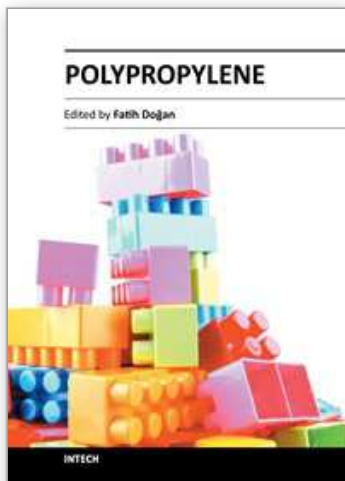
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