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The Effect of Calcium Carbonate Nanofiller on the Mechanical Properties and Crystallisation Behaviour of Polypropylene

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ABSTRACT: Polypropylene/calcium carbonate (PP/NPCC) nanocomposites were prepared using a co-rotating twin screw extruder at filler loadings of 5, 10 and 15 weight %. The impact strength and modulus of PP showed some improvement with the incorporation of the nanofiller while the tensile strength deteriorated. SEM photomicrographs showed evidence of NPCC agglomeration within the PP matrix, indicating that the level of shear stress generated during melt compounding was far from adequate to break-up the nanofiller. WAXD results showed the appearance of β-phase PP in the nanocomposites with 10 and 15 weight % NPCC. The influence of NPCC filler on the crystallisation behaviour of PP were also investigated using a DSC. Incorporation of NPCC shifted the crystallisation exotherms of PP towards higher temperatures, indicating that the nanofiller has acted as a nucleating agent for PP. The reduced values of half crystallisation times also implied that the introduction of NPCC has accelerated the crystallisation rate of PP.

Keywords: polypropylene, nano-sized calcium carbonate, nanocomposites, crystallisation

1.0 INTRODUCTION

Polypropylene (PP) is a versatile material widely used for automotive components, home appliances and industrial applications. To meet demanding engineering and structural specifications, PP is seldom used in its pristine state and is often transformed into composites by the inclusion of fillers or reinforcements. Introduction of fillers or reinforcements into PP often alters the crystalline structure and morphology of PP and consequently result in property changes [1].

Lately, many nanometer sized fillers have been commercially produced and they represent a new class of alternative fillers for polymers. Among the promising nanofillers which have stirred much interest among researchers include organoclay, nano silica, carbon nanotube and nano calcium carbonate. Studies have shown that the large surface area possess by these nanofillers promotes better interfacial interactions with the polymer matrix compared to conventional micrometer size particles, leading to better property enhancement [2-5].

However, the high adsorption surface energies associated with these nanofillers caused them to have a strong tendency to form agglomerates and aggregates [6]. Enhancement in the envisaged properties, such as impact performance, can only be realised if the nanoparticles are able to be homogeneously dispersed throughout the host polymer. The factors that have been found to influence the dispersion of the nanofillers during melt compounding include the mixing technique and parameters employed, the type of surface modification performed on the nanofiller and the addition of suitable coupling agents during compounding [7,8].

There have been many studies using nano calcium carbonate ($CaCO_3$) to enhance the properties of polymers. Among the techniques employed to disperse the nanofiller include in-situ polymerization, melt mixing using internal mixers and melt compounding using twin screw extruders. In situ-polymerization technique has been used for PVC and PET, while melt mixing and melt compounding appeared to be the preferred method for PP.

Xie et al [5] successfully synthesized PVC/$CaCO_3$ nanocomposites via in-situ polymerization technique with a filler loading of 2.5, 5.0 and 7.5 wt. %. Their studies found that the toughness and stiffness of PVC were simultaneously improved with the addition of 44 nm-sized $CaCO_3$ filler. A uniform filler dispersion was obtained using the technique employed and they concluded that the toughening effect observed was attributed to the debonding/voiding of the nano $CaCO_3$ particles and the deformation of the matrix material surrounding the nanoparticles.

Di Lorenzo et al [4] successfully polymerized poly(ethylene terephthalate) (PET) with coated and uncoated calcium carbonate particles of 40-80 nm in size. They found that stearic acid coated $CaCO_3$ resulted in a stronger polymer-filler interactions compared to the uncoated grade. The strong interfacial adhesion between the phases resulted in a significant increase in the glass transition temperature (14°C shift) and melting temperature (8°C shift) of the nanocomposites.

Nanocomposites of PP with 44 nm-sized $CaCO_3$ were prepared via melt mixing in a Haake mixer by Chan et al [3] using various mixing time (15, 30 and 45 minutes) with filler loadings of 4.8, 9.2 and 13.2 vol. %. Overall, good dispersion was obtained resulting in a significant increase in modulus with only a slight lowering of the tensile strength. The impact strength of the PP nanocomposites (mixing time of 30 minutes) increases with filler content reaching a maximum of 128 J/m at a filler content of 9.2 vol.% (The pristine PP used has an impact strength of 55.2 J/m). Their DSC results also indicated that the nano $CaCO_3$ are very effective nucleating agent for PP.

The present work aims to prepare nanocomposites using a stearic acid coated calcium carbonate (NPCC) nanofiller and PP as the host polymer. The melt compounding technique using a co-rotationg twin screw extruder is employed to disperse the nanofiller. The mechanical properties of the nanocomposites are evaluated using impact, flexural and tensile test, while the crystallisation behaviour are analysed using DSC and WAXD techniques.

2.0 EXPERIMENTAL

2.1 Materials and Sample Preparation

The grade of PP used was Titanpro 6331 produced by Titan Polymers Malaysia Sdn. Bhd. The homoploymer PP has a density of 0.899 g/cm^3 and a melt flow rate of 14 g/10 minutes (2.16kg at 230°C). The stearic acid coated nano calcium carbonate used was NPCC 201 supplied by NanoMaterials Pty. Ltd. The PP/NPCC samples were compounded in a Berstoff co-rotating twin-screw extruder (L/D = 33) with a temperature profile of 180°C to 200°C and a screw speed of 150 r.p.m. NPCC powder was added into the molten PP via a secondary side feeder at 5, 10 and 15 wt. % loadings. The nanocomposites were compounded twice to ensure homogeneous mixing and the palletised extrudates were injection moulded into ISO multi-purpose test specimens using an Arburg 75-tonne injection moulding machine at 190°C melt temperature and 30°C mould temperature.

2.2 Filler Dispersion Analysis

The NPCC powder was dispersed in isopropyl alcohol (IPA) and placed in an ultrasonic bath to ensure fine dispersion. Two to three drops were then placed on a filter paper and the NPCC particles were observed under a Philips Technie Transmission Electron Microscope (TEM) at 120 KV. The average primary particle size of the NPCC was then determined from the TEM photomicrograph.

The phase morphology of the nanocomposites was examined using a Hitachi S-2500 Scanning Electron Microscope (SEM). The surfaces of impact-fracture specimens were coated with gold prior to examination under the electron beam. An operating voltage of 10 kV and a magnification of 5,000 times were used. The average size of the dispersed NPCC filler was measured on the photomicrographs using the Roentec ScanVision software.

2.3 Mechanical Properties Evaluation

Tensile strength and elongation at break was determined using an Instron 5556 Universal Testing Machine (UTM) in accordance to ISO-527-1 at a crosshead speed of 50 mm/minute while tensile modulus was measured using an Instron 5582 UTM attached with a clip-on extensiometer at a crosshead speed of 1 mm/minute. Flexural properties were also measured using Instron 5556 UTM in accordance to ISO 178 at a crosshead speed of 2 mm/minute. The notched Izod impact strength was determined using a CEAST Resil Impactor according to ISO 180 at an ambient temperature of 25°C.

All test specimens were conditioned in accordance to ISO 291 at 25 ± 2°C and 55 ± 5% Relative Humidity for at least 16 hours before being tested. For the tensile and impact properties, ten specimens were tested while five specimens were evaluated for the flexural properties.

2.4 Crystallisation Studies

The crystallisation behaviour of the NPCC filled PP were studied using a Mettler Toledo Differential Scanning Calorimeter (DSC 822e), which has been calibrated using an indium standard reference material. The analysis was conducted in accordance with ISO 11357-7 Plastics - Differential Scanning Calorimetry (DSC) - Part 7: Determination of Crystallisation Kinetics. About 4 ± 0.5 mg of specimen obtained from injection moulded specimens were placed in an aluminium crucible and heated from 25°C to 200°C at a heating rate of 10°C per minute and held at that end temperature for 5 minutes. The reason for this first thermal cycle is to remove the crystalline elements of the specimen that could modify the crystallisation kinetics of the specimen. The specimens were than cooled at five different cooling rates viz. 2,4,6,8, and 10°C per minute to 30°C below the final crystallisation temperature of the specimens (between 50-90°C). The exothermic crystallisation curves were then obtained for the analysis.

The x-ray diffraction (XRD) experiments were performed using a Rigaku Diffractometer with Cu Ka radiation (30 mA and 50 kV) from 5 theta to 80 theta at scanning speed of 2^{o}/minute on injection moulded samples which have been surface polished using silicone carbide.

3.0 RESULTS AND DISCUSSION

3.1 Dispersion of NPCC in the PP Matrix

Figure 1 shows the TEM photomicrograph of the nanofiller used in this study. The average primary particle size the stearic acid coated NPCC filler was measured to be about 50 nm. Figure 2 (a-c) illustrates the morphology of the impact-fractured surface of the PP/NPCC nanocomposites at 5, 10 and 15 wt. % filler loadings. The dispersion of the NPCC in the PP matrix was observed to be relatively poor as a large number of filler aggregates whose dimension were much higher than those of the isolated particles could clearly be observed on the SEM photomicrographs.

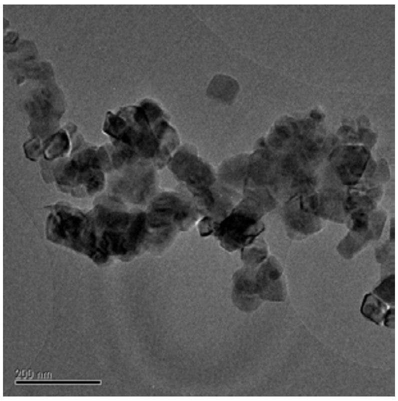

Figure 1: TEM photomicrograph of the NPCC used in this study

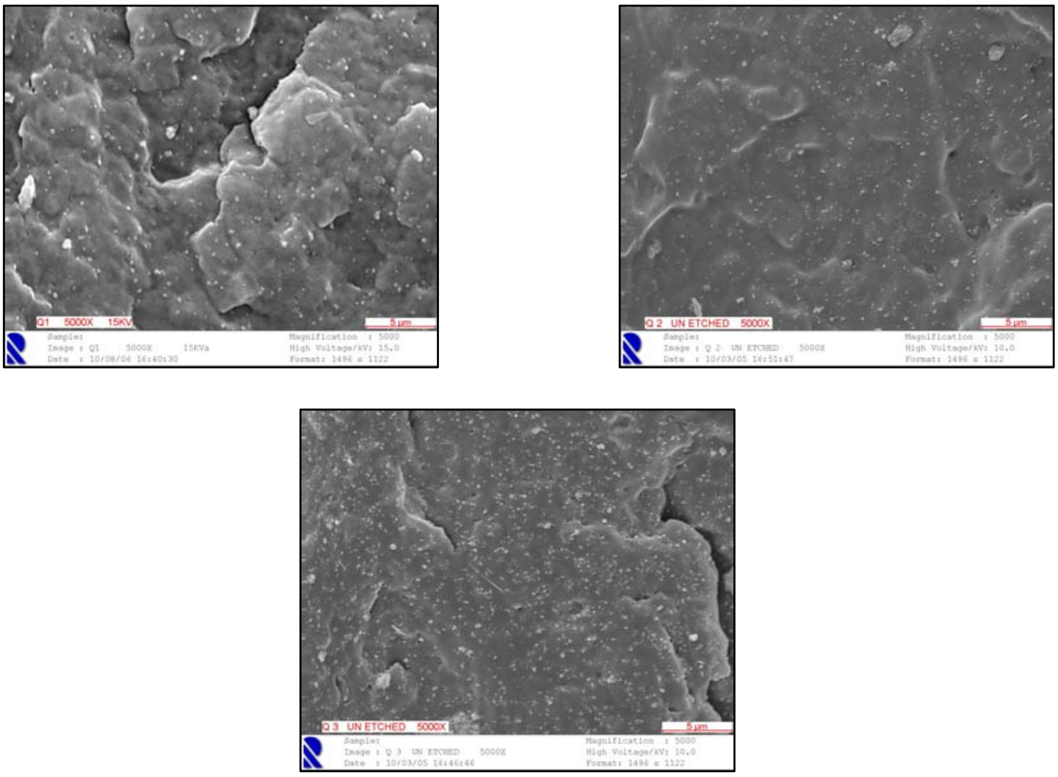

Figure 2: SEM photomicrographs of (a) 95PP/5NPCC, (b) 90PP/10NPCC and (c) 85PP/15NPCC

As tabulated in Table 1, the average size of the NPCC at 5 wt. % was measured to be about 0.25 μm while at 10 and 15 wt. %, the average NPCC size was found to be about 0.18 μm. Although the NPCC used in this work was a nanofiller, but when blended with PP using the technique described above and without the presence of any coupling agent, the NPCC showed strong tendency to form aggregates and could not be dispersed uniformly on a nanoscale.

Table 1: Average size of NPCC particles in the PP nanocomposites

SampleComposition (PP/NPCC)	Average Size of NPCC, μm
95/5	0.25±0.09
90/10	0.18±0.13
95/15	0.18±0.07

3.2 Mechanical Properties of the Nanocomposites

The effect of NPCC on the tensile and flexural modulus of PP is illustrated in Figure 3. As expected, addition of the NPCC increased the stiffness of the PP gradually with increasing filler content. The tensile modulus of PP was enhanced by about 40% while the flexural modulus was increased by about 30% compared to the neat PP with the addition of 15 wt. % of NPCC.

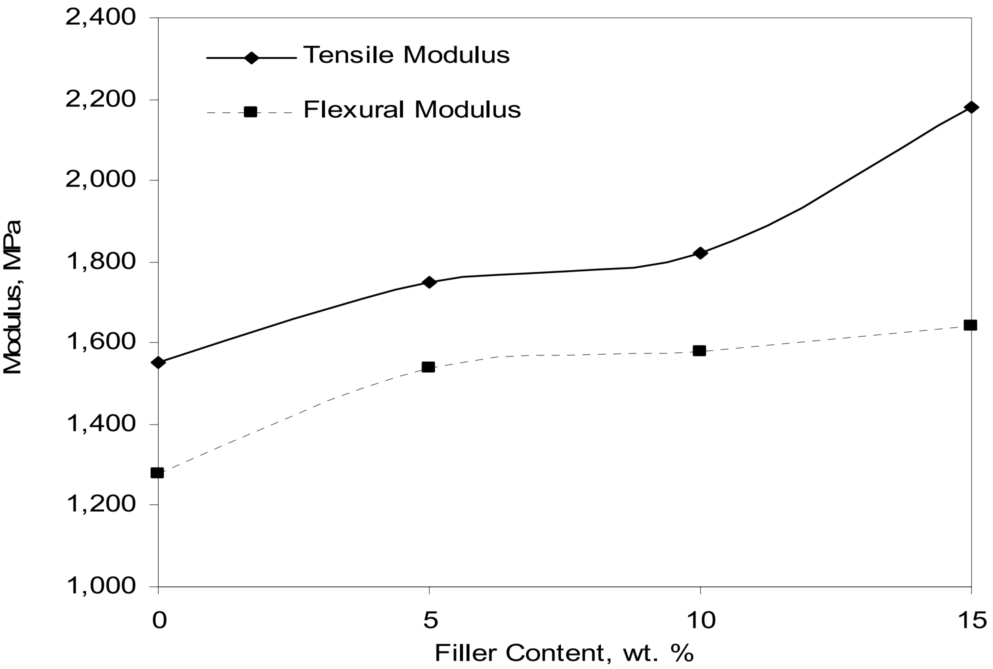

Figure 3: Effect of NPCC on the Modulus of PP

An equation which is commonly used to predict the modulus of composites containing a certain amount of spherical fillers developed by Guth and Gold [7,9] is as follow:

$$E = E_m [1+2.5\phi +14.1\phi^2] \qquad (1)$$

where E is the Young's modulus of the composite, E_m is the matrix Young's modulus and ϕ is the volume fraction of the filler. It has been reported that equation (1) is only applicable to composites filled with a certain amount of spherical fillers. If the filler concentration is higher than 10 vol. %, the modulus increases much more rapidly than equation (1) would predict, attributed to the formation of a network by the spherical filler chains [10].

The modulus of particle-filled composites may also be predicted using the following two equations [3,7]:

$$E_c = E_p\phi_p + E_f\phi_f \quad (2)$$

$$E_c = \frac{E_pE_f}{E_p\phi_f + E_f\phi_p} \quad (3)$$

where E_c is the modulus of the composites, E_p and E_f are the moduli of the polymer matrix and the filler respectively, ϕ_p and ϕ_f are the volume fraction of the polymer and filler respectively. Equation (2) is appropriate when strong adhesion exist between the filler and the polymer and the filler has a large aspect ratio and equation (3) is applicable to rigid spherical particles.

Figure 4 illustrates the experimental and calculated modulus based on the above equations. It can be seen from the plots that the experimental moduli of the nanocomposites agree quite well with equation 1 and 3 up till a filler content of 10 wt.%. Equation 2 was found to be the most inaccurate to predict the moduli of the nanocomposites, indicating that the law of mixtures is invalid in this case as the equation is only applicable when the filler has a large aspect ratio and there is a strong bonding between the host matrix and the filler.

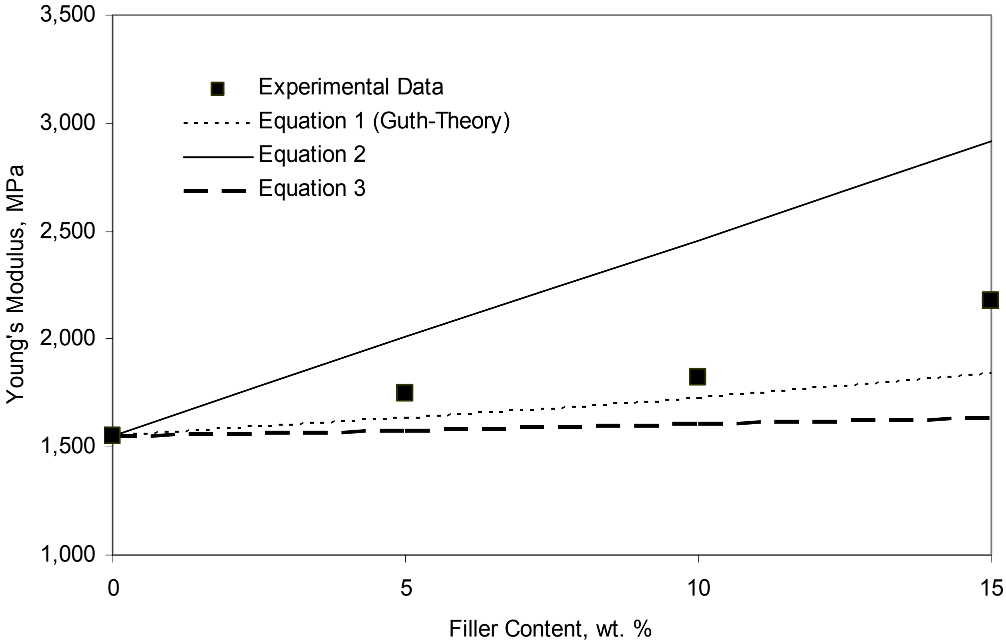

Figure 4. The calculated (theoretical) and measured (experimental) moduli of PP/NPCC nanocomposites as a function of filler content.
[Note: The modulus of NPCC is taken as 26 GPa]

The effect of NPCC on the tensile strength and elongation at break of PP is shown in Figure 5. It can be seen that both the tensile strength and elongation at break decreases with increasing amount of NPCC. Compared to neat PP, the maximum drop in tensile strength was about 11% at 15 wt. % NPCC loading. According to Liang [11], the strength of particulate-filled polymer composites depends, to a great extent, on the interfacial adhesion between the matrix and the filler which will facilitate the transfer of a small section of stress to the filler particle during deformation. In this study, no coupling agent has been added into the PP/NPCC nanocomposites and in the absence of any coupling agent, the interfacial adhesion between the PP matrix and the NPCC have obviously not been improved.

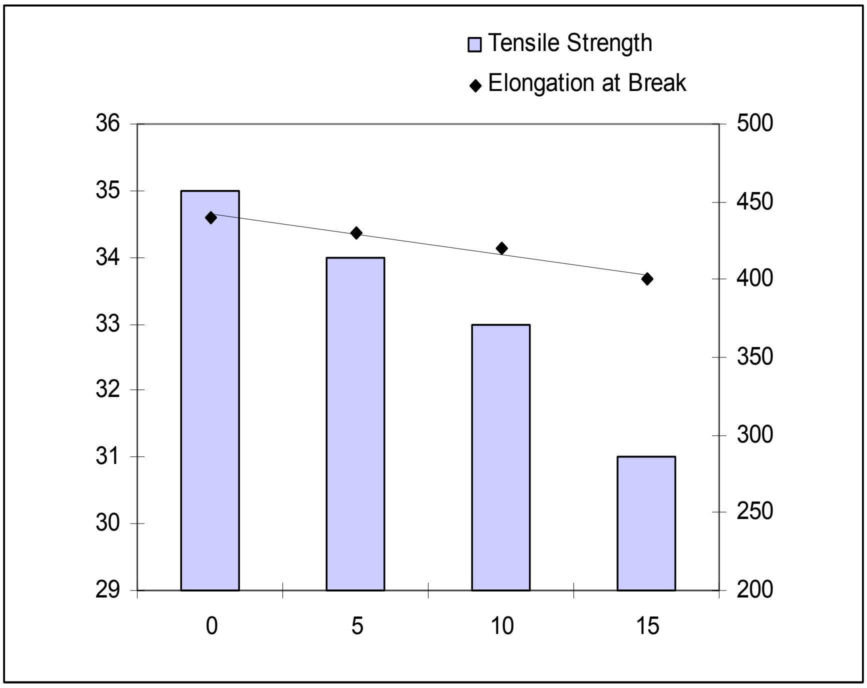

Figure 5: Effect of NPCC on the Tensile Strength and Elongation at Break of PP

Figure 6 presents the effect of NPCC on the notched Izod impact strength of PP. Results show that the impact strength of PP increased sharply with the addition of 5 and 10 wt. % of PP. Addition of 15 wt. % of NPCC did not bring about any further improvement to the impact strength. The deterioration in impact strength is most probably related to the presence of agglomerates at higher filler concentration as observed in the SEM photomicrographs described earlier.

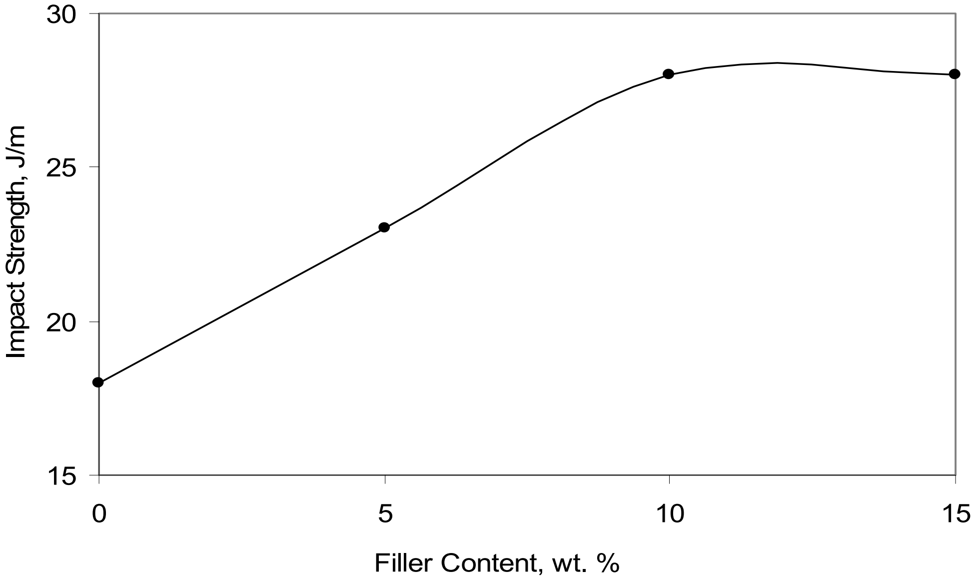

Figure 6: Effect of NPCC on the Impact Strength of PP

3.3 Crystallisation Behaviour of the Nanocomposites

The crystallisation exotherms of PP and PP filled with 5, 10 and 15 wt. % NPCC at various cooling rates are presented in Figure 7 (a-d). For all samples, increasing the cooling rates shifted the exothermic crystallisation curves towards lower temperatures. At slow cooling rates, there is sufficient time to activate nuclei at higher temperatures, while at faster cooling rates, the activation of nuclei occurs at lower temperatures. Hence, crystallisation is initiated at higher temperatures at slower cooling rates, and vice versa [4].

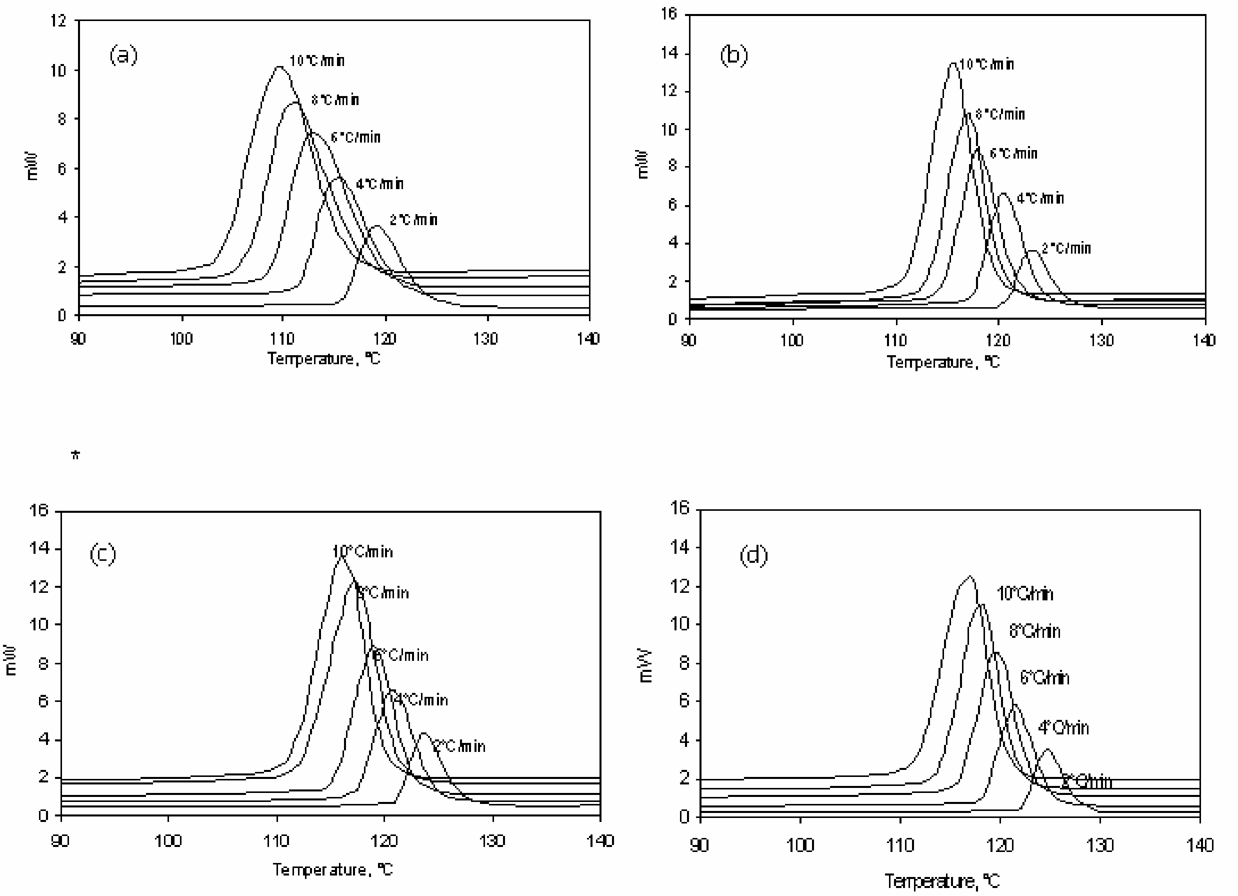

Figure 7: Effect of cooling rates on the DSC crystallsation exotherms of (a) 100% PP (b) 95% PP/5% NPCC (c) 90% PP/10% NPCC and (d) 85% PP/15 % NPCC

The influence of NPCC on the dynamic crystallisation of PP at selected cooling rates of 2°C per minute and 10°C per minute is shown in Figure 8 (a-b). Similar trends were observed for samples cooled at 4°C, 6°C and 8°C per minute. At all cooling rates studied, addition of NPCC produced narrower exotherms with steeper onset of crystallisation. Presence of NPCC has possibly provided high number of nuclei which induced a large amount of crystallites to grow simultaneously. The large quantity of nuclei present produced a steep beginning of the exothermic peak and crystallisation is completed in a relatively shorter time.

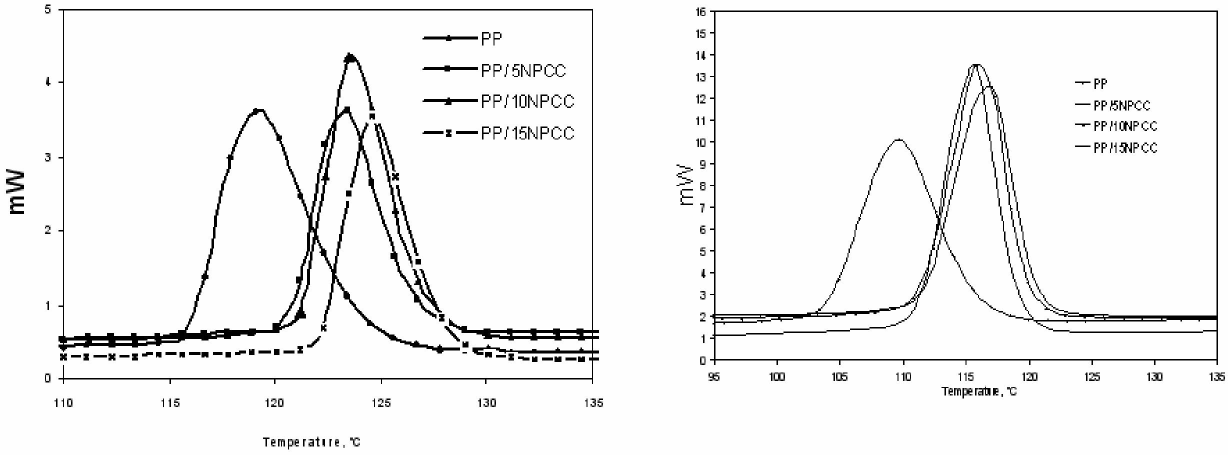

Figure 8: Effect of NPCC on the crystallization exotherms of PP at (a) 2°C/minute and (b) 10°C/minute cooling rates.

The NPCC added into the PP had also induced crystallisation to occur at higher temperatures, resulting in higher peak crystallization temperature (T_{pc}) at all cooling rates studied. The results of T_{pc} are given in Table 2, and the average difference between the T_{pc} of the nanocomposites and that of the neat PP was found to be about 4 to 7°C.

Table 2: Effect of NPCC on the peak crystallisation temperature of PP at various cooling rates

Sample (a)	Peak Crystallization Temperature, T_{pc} (°C) (b)				
	2°C/minute	4°C/minute	6°C/minute	8°C/minute	10°C/minute
PP	119	115	113	111	110
PP/5 wt.% NPCC	123	120	118	117	116
PP/10 wt.% NPCC	124	121	119	117	116
PP/15 wt.% NPCC	125	122	120	118	117

The $t_{0.5}$, which represents the time to reach the maximum rate of heat flow and corresponds to the change over to a slower kinetic process due to impingement of adjacent spherulites, also decreased with increasing cooling rates and filler content (see Table 3). The average $t_{0.5}$ (taken at the five different cooling rates) for PP was found to be 2.3 minutes while those filled with 5, 10 and 15 wt. % NPCC were found to be 1.7, 1.8 and 1.6 minutes respectively.

Table 3: Half-crystallisation time ($t_{0.5}$) of the nanocomposites at various NPCC content and at various cooling rates.

Sample	Half- crystallization time, $T_{0.5}$				
	2°C/minute	4°C/minute	6°C/minute	8°C/minute	10°C/minute
PP	5.4	2.2	1.5	1.3	0.9
PP/5 wt.% NPCC	3.7	1.9	1.2	1.1	0.8
PP/10 wt.% NPCC	4.2	1.8	1.2	1.0	0.8
PP/15 wt.% NPCC	4.2	1.5	0.9	0.8	0.8

Table 4 shows the results for the enthalpy of crystallization of PP at various cooling rates and at different NPCC loadings. Overall, increasing the cooling rate caused a decreased in the enthalpy of crystallisation for each sample. At slow cooling rates, bigger crystals are formed, resulting in high crystallinity, while at slow cooling rates, many nuclei are formed, creating smaller crystals. At any specified cooling rates, there was also a decrease in the enthalpy of crystallisation with increasing NPCC content. The observed reduction in the enthalpy crystallisation is probably attributed to the lesser PP content in the PP/NPCC nanocomposites available for crystallisation.

Table 4: Enthalpy of crystallisation of the nanocomposites at various NPCC content and at various cooling rates.

Sample	Enthalpy of Crystallization (ΔH_c) Jg^{-1}				
	2°C/minute	4°C/minute	6°C/minute	8°C/minute	10°C/minute
PP	108	90	89	81	76
PP/5 wt.% NPCC	84	82	81	76	81
PP/10 wt.% NPCC	88	75	66	83	76
PP/15 wt.% NPCC	75	68	68	65	77

Figure 10 shows the WAXD patters of neat PP and PP/NPCC nanocomposites. Neat PP shows five distinct crystalline peaks at diffraction angles (2-theta) of 13.1, 16.7, 18.4, 21.5 and 25.4°, which corresponds to crystal planes of (110), (040), (130), (111) and (131) respectively. The above peaks are typical crystal form of α-PP [7,12]. In comparison to the neat PP, the nanocomposites filled with 10 and 15 wt. % of NPCC displayed a new diffraction peak at a diffraction angle of 16.1° corresponding to the (300) crystal plane of β-PP. It has been reported that β-PP has greater toughness than α-PP, and this agrees with the higher impact strength displayed by the PP/NPCC nanocomposites compared to the pristine PP.

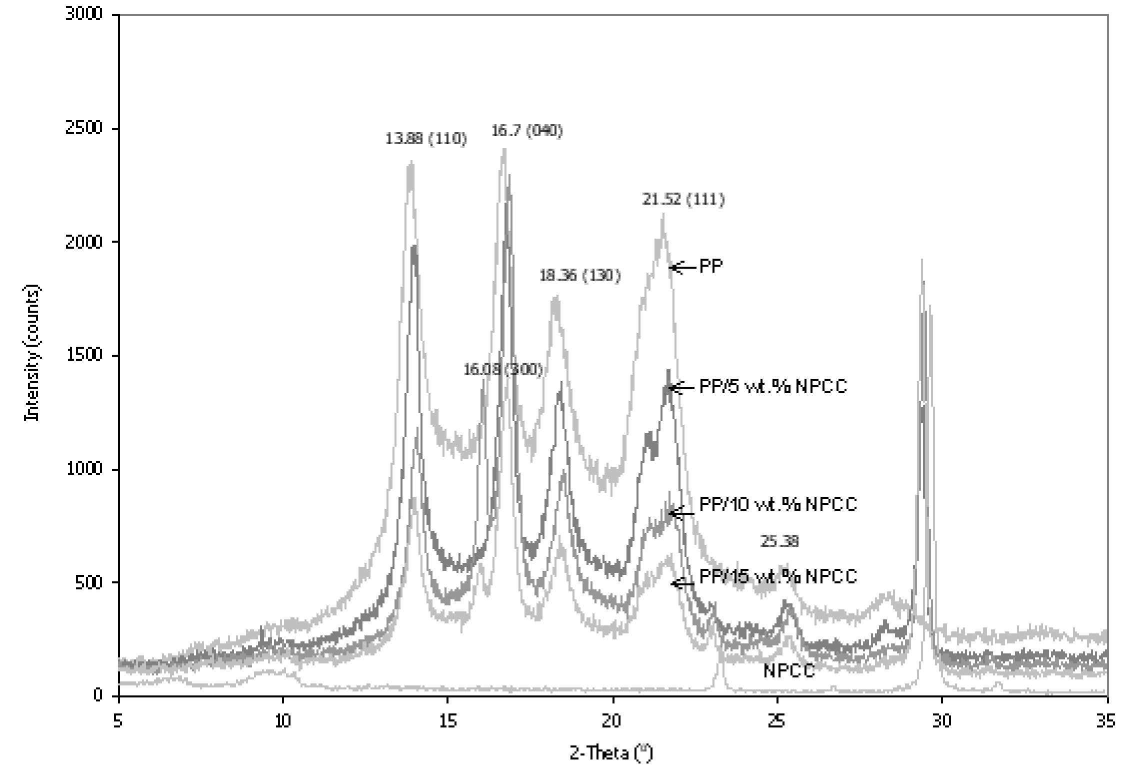

Figure 10: X-ray diffractions of PP and PP/NPCC nanocomposites

4.0 CONCLUSION

Addition of calcium carbonate nanofiller have resulted in some improvement in the mechanical properties of PP, namely the modulus and impact strength despite the rather poor dispersion of the NPCC within the PP matrix observed from the SEM photomicrographs. The tensile strength and elongation at break of PP was slightly reduced with the incorporation of the nanofiller. Presence of NPCC has also induced the crystallization of PP to start at a much earlier temperature, indicating that the nanofiller has played its role as a nucleating agent for PP.

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