Effect of Particle Characteristics on the Rheological Properties of Polypropylene (PP) Nanocomposites

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Abstract – **Polymer nanocomposites are a new class of materials, in which nanoscale particulates are finely dispersed within the matrices. The properties of polymer nanocomposites depend greatly on the chemistry of the polymer matrices, the nature of the nanofillers, and the dispersion of particles in the polymer matrix. The aim of this study was to investigate the effect of filler type, size and applied surface coating on the flow and mechanical properties of Polypropylene (PP) nanocomposites. To this end, four different types of nanoparticle were used for the preparation of different PP/ nanocomposites using melt compounding method and unmodified PP polymer as a matrix. Scanning Electron Microscopy (SEM) was used to evaluate the dispersion quality of nanoparticles. The Melt Flow Index (MFI) of the filled PP composites was determined to evaluate the Rheological properties of PP nanocomposites. The results show that a homogeneous dispersion of nanoparticles can be achieved by coating the nanoparticles with fatty acids. Results also show that, due to the lubricating/plasticizing effect induced by the coupling agent, the PP filled with coated nanoparticles has improved processability compared to PP filled uncoated nanoparticles.**

Index Terms— **nanocomposites, nanoparticle, melt compounding, polypropylene, rheological properties.**

I. INTRODUCTION

Polypropylene (PP) is a semicrystalline thermoplastic polymer that has been widely used because of its attractive combination of good processability, mechanical properties, chemical resistance, and low cost. However, owing to its low modulus, high notch sensitivity, and poor impact resistance, especially under extreme conditions such as low temperatures or high strain rates, the usefulness of PP as an engineering thermoplastic is still limited.

Blending PP with rubber is an efficient way to increase its toughness, but one drawback of rubber toughening is the significant loss of both tensile strength and stiffness of PP [1]. Incorporation of particulate mineral fillers, on the other hand, enhances stiffness but reduces the strength and toughness of PP.

The challenge of obtaining an ideal balance between stiffness, toughness and processability has prompted considerable interest. Polymer nanocomposites comprise a new class of materials in which nanoscale particulates are finely dispersed within the matrices. In comparison with neat polymers and microparticulate composites, these materials have been reported to exhibit markedly improved properties [2-5].

The large interfacial area of the nanosized fillers in a polymer nanocomposite helps to influence the properties of the nanocomposite to a great extent, even at rather low filler loading [6]. In order to achieve the optimum properties, it is generally believed that a homogeneous dispersion of the particles in the polymer matrix is a prerequisite. The presence of loosely agglomerated nanoparticles results in failure of the nanocomposites without approaching the desirable properties.

From a practical point of view a homogeneous dispersion of nanoparticles is very difficult to achieve, mainly because nanoparticles with high surface energy agglomerate easily. Thus, polymer nanocomposites are very difficult to make by the use of processing techniques common to conventional plastics because the shear force during compounding is not sufficient to overcome the strong agglomeration tendency of nanoparticles. Surface modification of these nanoparticles with fatty acid becomes a key issue to break the agglomerated nanoparticles and produce nanostructured composites [7].

The effect of fillers on flow and other properties of composites depends strongly on their shape, size and size distribution of the primary particles and their aggregates, surface characteristics, and degree of dispersion and distribution.

The size of the filler plays an important role for polymer composites. If, for example, the filler is very large then high filler loadings within the range of (20-40%) are required to achieve improved properties. High filler loadings, however, may adversely affect the processability.

The adhesion between the filler and the matrix is very important for PP composites. The two major factors, which determine the particle–particle interactions, are particle size and surface free energy [8].

Calcium carbonate ($CaCO_3$) and silicon dioxide (SiO_2) are inorganic materials that do not exhibit good adhesion to thermoplastic matrices. Therefore, the surface modification of filler particles with suitable coupling agent is often recommended to enhance the filler–particle dispersion into PP matrices to improve strong bonding with the matrix.

Although the effects of the filler particles' parameters, such as, type [9, 10], size [11] and surface function [12], on the mechanical properties of PP/$CaCO_3$ were extensively examined, the balance between these parameters on one hand and the mechanical properties and processability of the composites on the other hand are not yet fully understood. This paper therefore investigates the influence of the particles parameters on the processability of the composite.

II.   MATERIAL AND METHODS

PP homopolymer (Moplen – Himont, Italy) with molecular weight (Mw) =690 Kg/mole and polydispersity (PD) = 5.2 was used in this study. Nanosilica (15 nm) was obtained from Sigma-Aldrich. Four different types of precipitated calcium carbonate were kindly donated by Solvay. Material specifications are listed in Table 1.

The filler particles were dried by heating to 100 °C under vacuum for 6 h before melt compounding. Blending was carried out in a mechanical stirrer. The mixing temperature was 230 °C and the rotor speed was 60 rpm for 15 min. In a typical experiment, 4 g of PP was charged into the mixer and then anti-oxidant and the predetermined filler quantity were added. After mixing, the nanocomposites were grounded into powder.

The processability of the filled PP composites was determined with a CEAST melt-flow indexer according to a standard procedure. A load of 2.16 kg at 230 °C was used in the measurement.

TABLE 1. CHARACTERISTICS OF FILLER PARTICLES.

Code	Trade name	Specific surface (m^2/g)	Mean particle diameter (nm)
SiO_2	Silica	150	15
Uncoated CC0.07	SOCAL® 31	20	70
Uncoated CC0.25	SOCAL® P2	8	250
Coated CC0.07	SOCAL® 311	19	70
Coated CC0.1	SOCAL® U1S2	16	100

III.   RESULTS AND DISCUSSION

A.   Dispersion of filler nanoparticles

The main purpose of treatment of the filler is the reduction of the surface free energy, which results in a decrease of particle–particle interactions. Weaker interaction leads to a dramatic decrease in aggregation, improved dispersion, and better mechanical properties.

Figure 1 shows SEM micrographs of the fractured surfaces of the various PP/filler nanocomposites at a filler load of 20 %.

Figure 1 (a) shows that there are many large aggregated particles in the PP composites filled with SiO_2 nanoparticles. This is due to the high surface tension of SiO_2 (257.7 mJ/m^2) and the small particles size [13-14]. The particle aggregations were also observed in the case of the PP composites filled with uncoated CC0.07 (Figure 7.1 (b)) and uncoated CC0.25 (Figure 7.1 (c).

The size of the aggregated particles in all PP/$CaCO_3$ nanocomposites is smaller than that of the PP/SiO_2 nanocomposites. The lower surface tension of the $CaCO_3$ (207.9 mJ/m^2) compared to the SiO_2 allows the shear forces during compounding to break down all the large $CaCO_3$ aggregates.

Figure 1 (d) and (e) show SEM images of the fractured surface of PP filled with coated CC0.07 and coated CC0.1. Better dispersion with a lower degree of agglomeration of the filler was observed when the surface of the $CaCO_3$ particles was coated with a fatty acid.

When the fractured surfaces of the PP/filler nanocomposites with similar surface characteristics but with filler particles sizes are compared (CC0.07 and CC0.1), it is clear that the larger the particle size the less aggregation occurs. This is because larger filler particles have a lower surface tension compared to small filler particles.
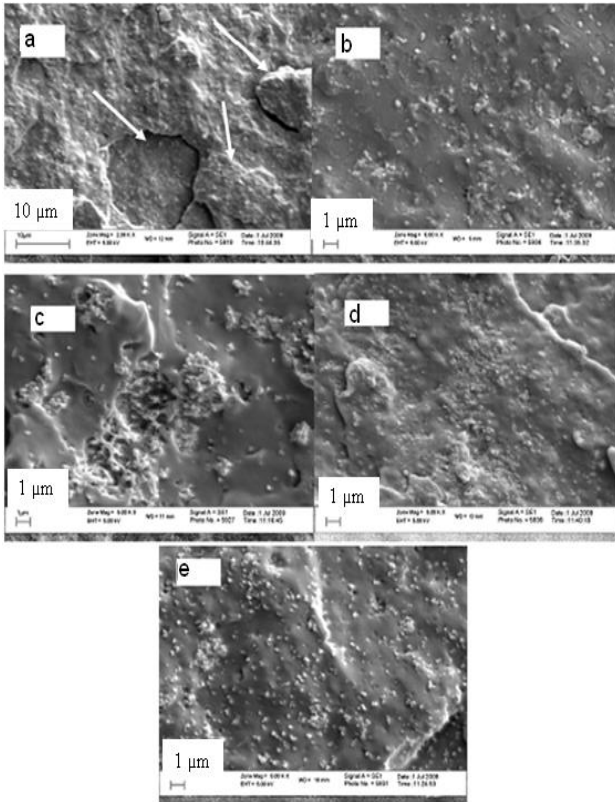
Figure 1. SEM images of fracture surfaces of various PP/filler nanocomposites with 20 % filler: a) untreated SiO_2 nanoparticle, b) uncoated CC0.07, c) uncoated CC0.25, d) coated CC0.07, and e) coated CC0.1.

B. Effect of filler type on flow behavior

In the thermoplastic processing industry, the MFI is an important parameter that is widely used to characterize the flow property of resins due to its ease of measurement. Generally, an increase in MFI value indicates better molecular motion between polymer chains.

The MFI values of various composites are shown in Figure 2. The MFI values for PP nanocomposites filled with SiO_2, coated CC0.07, uncoated CC0.07, and coated CC0.1 decrease with increasing filler content.

The incorporation of fillers hinders the flow of polymer and increases the viscosity of the polymer melt, thus a reduction of the MFI with increasing filler loading is expected. The MFI values of SiO_2 filled PP were lower than those of the neat PP and $CaCO_3$ filled PP nanocomposites.

When comparing the MFI values of the uncoated CC0.07 filled PP composites with those of the coated CC0.07 filled PP composites at all filler loading it is clear that the coated CC0.07 filled PP has improved processability compared to the uncoated CC0.07. This result was in agreement with the results of other related studies reported by several authors [16-18].
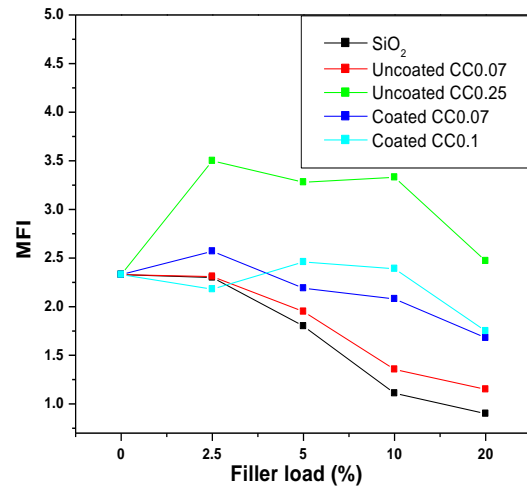

Figure 2. The effect of filler types and loading on the MFI values of PP nanocomposites.

This increase in melt flow might be as a results of the lubricating/plasticizing effect induced by the coupling agent. According to Han et al. [18] the reduction in melt viscosity with the presence of a coupling agent may result from the surface modification of the filler particles. Thus, under shear stresses, there could be far less frictional resistance to flow with treated filler particles than would be possible with untreated filler particles.

The MFI values for the PP composites filled with uncoated CC0.25 fillers, however, increased slightly compared to that of the pure PP. This trend agreed with the work of Ai Wah et al. [19], who reported an increase in MFI with the incorporation of filler into PP. Since this filler was uncoated, the lubricating effect is not possible and thus the possible reasons for this phenomenon could be molecular chain scission or change in PD.

IV. CONCLUSION

It has been shown that during the melt-mixing the filler type, size, and applied surface coating significantly influence the flow properties of filled PP. SEM studies revealed that better distribution with decreased agglomeration of the $CaCO_3$ particles within the PP matrix was found for the fatty acid coated fillers. Examination of the flow behavior of the various PP composites shows that the incorporation of the filler in PP adversely affected the processability. However, PP filled with coated filler show improvement in the processability compared to PP filled with uncoated filler. This effect was explained by the lubricating effect of the fatty acid.

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BIOGRAPHIES

Dr. Omar Sultan received his Ph.D. in polymer chemistry from University of Stellenbosch in 2010. After completion of his degree, he joined the Libyan Polymer Research Center, where he was a quality assurance consultant. Currently, Dr. Sultan is a lecturer and the head of the department of chemical engineering at Zawia University-Libya. His research interests is on the Structure-properties relationship in polyolefin's and Polymer nanocomposites