Synthesis of Nano-Composites Material Using in-Situ Polymerization

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Abstract:

Synthesis of nano-composites material namely polypropylene-silica nano-composites were investigated. Interested results were obtained for insertion silica nano-particle in polypropylene using in-situ polymerization with methyl-aluminoxane (MAO) activated metallocene catalyst in the presence of the metallocene catalyst. Different amounts of the MAO modified silica were added to the activated catalyst which, in turn leads to nano-composites with different silica loads. C2 symmetric ansa metallocene, ethylene-bis(indenyl) zirconium dichloride (EI), was used in this study. The effect of addition MAO modified silica and polymerization temperature on the catalyst activity in the in-situ polymerization was investigated. The morphology, crystallization behaviors and crystallization degree of the

synthesized nano-composites were also investigated. Promising results were obtained and showed that nano-composites with improved properties and retention of the high activity of the metallocene catalyst could be prepared via in-situ polymerization.

***Keywords*:** nano-composites; nano-composites morphology; in-situ polymerization.

1. INTRODUCTION:

It is well known that nanotechnology is widely considered as a major area that will undergo great technological progress in the future. In materials category as polymer nano-composites, it is regarded as a radical alternative to conventional filled polymers or polymer blends, and new classes of materials will be available with improved properties. Nano-composites can be simply described as multi-constituent materials that consist of reinforcing where the length scale of the nano-particles is in nanometer, such as nano-silica, embedded in a rigid polymer matrix [1]. The potential applications of the nano-particles in different areas of polymer composites is due to their characteristic large external surface area and their functionality [2-4].

The area of nano-silica filled polypropylene (PP) is attractive in the field of polymer composites. This is because of the unique properties resulting from the nano-scale microstructure of the silica particles. Mechanical and optical properties of these composites can be significantly improved by adding a very low filler content, provided that the nano-silica is well interacted with the polymer matrix and distributed homogenously [5-8].

There are basically three methods that can be used to produce the filled polymer; melt mixing, solution blending, and in-Situ polymerization [9]. In-Situ polymerization has been considered to be the most effective method for the preparation of PP nano-composites with homogeneous dispersion of particles in PP matrix [8]. Furthermore there is evidence that the in-Situ polymerization of monomers in the presence of nano-fillers is a useful approach for achieving a more homogeneous distribution of inorganic nano-particles, due to the close contact of polymer and filler during synthesis [10-12].

Metallocene catalysts activated by methylaluminoxane (MAO) show very high activity in propylene polymerization and produce PP with a narrow molecular weight distribution [13-14]. It has been found that silica is a very useful catalyst support, with improved catalytic activity after immobilization of the homogeneous catalysts [15-17]. The nature of the support and the method used for supporting the metallocene influence the catalytic activity, the final properties of the polymer, and especially the polymer particle morphology and molecular weight distribution [18-19].

The morphology of polypropylene particles of systems supported on microsilica has been widely studied, and it depends strongly on the form of the SiO_2 support used [19-21]. But there are few reports in the literature in which the final polypropylene particle morphology is studied with the incorporations of nanoparticles [20].The incorporation on nanoparticles in the polymerization reactions has the advantage that the nanoparticles can be distributed in the polymer generating a polymer nanocomposite by in-Situ polymerization [21]. Trujillo et al. [22] investigated the effect of the preparation method on the behavior of polyethylene/carbon nano-tubes

nano-composites. They found that lamellae produced within the in-situ polymerized high density polyethylene (HDPE) nano-composite are thicker than those produced in pure HDPE or in physical blends prepared by melt mixing of HDPE. To the best of our knowledge to date there is no report in the open literature that addresses the effect of the preparation methods with regards to polypropylene-silica nano-composites. The overall objective of this study is therefore to determine, and compare, the characteristics of the PP/silica nano-composites prepared by in-situ polymerization.

2. EXPERIMENTAL:

2.1. Materials:

Propylene (99.95%), Nano-silica (15 nm), ethylene bis(1-indenyl)zirconium dichloride (rac-Et(Ind)$_2$ZrCl$_2$) (EI) were obtained from Sigma-Aldrich and used as received. The co-catalyst methylaluminoxane (MAO) was also purchased from Sigma-Aldrich and used in 10 wt% solution of toluene. Toluene was dried by refluxing over sodium/benzophenone, distilled under a nitrogen atmosphere, and then stored over 4 A^o molecular sieves.

2.2. Nano-silica treatment:

All air- and moisture-sensitive compounds (e.g., catalyst and cocatalyst) were handled using standard Schlenk techniques, or in a glovebox, under a deoxygenated and dry argon atmosphere. The nano-silica was heated to 250 °C under vacuum for 12 h prior to use. Nano-silica (1 g) was suspended in toluene (5 mL) in a Schlenk tube. A predetermined quantity of MAO (1.5, 3.0 and 6.0 mL) was added and the mixture stirred for 24 h at 60 °C. After cooling, it was washed with toluene (5×10 mL).

2.3. *In-Situ propylene polymerization:*

The polymerization reactions were carried out in a 300 mL stainless steel autoclave. The reactor was charged with toluene (30 mL), followed by the addition of the activated catalyst (EI = 2.2 X 10^{-6} mole; Al/Zr = 2000) and the required amount of treated nano-silica (see Table 1). The reactor was heated to the desired temperature and propylene (6 g) was then introduced. The reactants were stirred at desired temperature for 1 hour. In order to terminate the polymerization reaction the reactor was first vented and cooled, and then acidic methanol (10% HCl) was added. The resulting polymer was filtered off, washed with methanol and then with acetone, and finally dried at 60 °C under reduced pressure. As temperature plays a vital role in polymerization a series of polymerizations was performed at different temperature in order to determine the temperature at which the best activity is obtained, which was at 60 °C as seen in Figure (1).
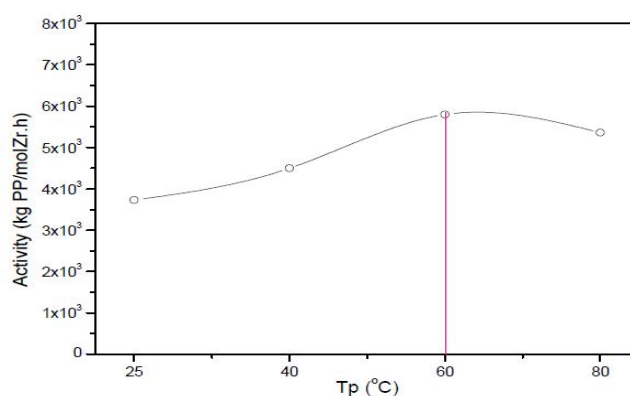

Figure (1): Effect of temperature of polymerization (Tp) on the activity of the in-Situ polymerizations MAO-filler 300 mg and time 60 min

2.4. Characterization of nano-composites:

Thermogravimetric analyses (TGA) were carried out using a TGA-50 SHIMADZU thermogravimetric instrument, with a TA-50 WSI thermal analyzer connected to a computer. Samples (10-15 mg) were degraded in a nitrogen atmosphere. The flow rate was 50 ml/min, and the heating rate 20 °C/min.

Transmission electron microscopy (TEM) experiments were performed using a JEOL 200 CX instrument. Prior to analysis, samples of the nano-composites were stained with OsO_4, then embedded in epoxy resin and cured for 24 h at 60ºC. The embedded samples were then cut into slices of a nominal thickness of 100 nm, using an ultra-microtome with a diamond knife on a Reichert Ultracut S ultra microtome at room temperature

A Zeiss Axiolap polarized optical microscope with a high resolution digital camera was used to examine the effect of the nano-silica on the crystal structure of the composites.

Differential scanning calorimetry (DSC) analyses of composites were carried out with a TA Instruments Q100 DSC system. Polymer samples of 1.0 to 5.0 mg were heated in aluminum pans to 220 °C and then cooled to room temperature at rate of 10 °C /min, then heated again to 220 °C at the same rate.

3. RESULT AND DISCUSSION :

3.1. *Activity of the catalyst:*

A challenging aspect related to the in-Situ polymerization of olefins is the decline in the catalyst activity due to the deactivation of the active sites by the filler surface. Therefore, considerable effort has been made in this study to obtain catalyst activity comparable to that of a homogenous catalyst. Tables 1 give the polymerization conditions used and the effects of the initial quantity of MAO-filler on the nano-filler load in the obtained nano-composites and on the subsequent thermal properties of the nano-composites prepared by in-Situ polymerization. From the table one can see that at low filler feed there is an increase in the activity of the in-Situ polymerization compared to the homogeneous polymerization. This is explained by differences in monomer diffusion. Due to the presence of the filler, a PP with low crystallinity was obtained by the in-Situ polymerization. This allows the monomer to reach the active site, resulting in high activity. On the other hand, the restriction of the monomer diffusion, due to the high crystallinity of the PP, results in low polymerization activity.

Table (1): Effect of the MAO treated nano-silica loading on the activity of the catalyst and on the melting temperature (T_m) properties of the resulting nano-composites:

Run	SiO_2(mg) a	Activity (kg PP/molZr.h)	SiO_2% *	T_m (°C)
1	0	7125	0	149
2	100	7625	1.3	149
3	200	7800	2.7	149
4	500	7390	6.8	149
5	1000	7060	14.0	148

* Determined by TGA.

The addition of SiO_2-MAO has no effect on the catalyst activity of up to 200 mg SiO_2, but above this load the activity diminishes. The effect of the initial silica load on the catalyst activity above this critical load is attributed to an increase in the chance of the deactivation of the catalyst by the silica surface and to a change in the relative concentration of the catalyst in the polymerization phases [19, 28]. Hence, by knowing the load of the MAO on the nano-silica it is possible to control the final silica load in the nano-composite, provided that all the other polymerization conditions remain constant.

The effect of the initial quantity of MAO used to treat the nano-silica on the polymerization activity was investigated. Increasing the initial amount of MAO from 1.5 to 6.0 ml (2.23 mmole to 8.9 mmole) MAO per 1 g silica led to Al percentages of about 3.4% and 4.1% in the silica surface, respectively, as determined by energy dispersive X-ray analysis (EDX) analysis. A small increase in the amount of Al in the silica surface, from

3.4% to 4.1%, led to a slight decrease in the polymerization activity, as can be seen in Figure 1. Some authors have reported decreases in catalyst activity with an increase in the amount of co-catalyst in homogenous polymerization [23-25]. According to Chien et al. [26] the decrease in activity when using very large amounts of MAO might be attributed to excessive complexation of MAO to active sites.

The amount of MAO used during the polymerization reactions was similar in all the reaction. The only difference was the amount of MAO attached to the silica. An increase in the amount of attached MAO to the silica surface will increase the chance of the catalyst coordinating with the MAO on the silica surface. Thus catalyst attached to the silica will exhibit lower productivity than that of the homogenous catalyst [19, 27].

3.2. Morphology of nano-composites:

Various analytical techniques were used to determine the distribution and dispersion of the nano-silica in the composites. Optical microscopy (OM) was used to study the effect of the nano-silica particles on the crystal structure of the polymer, compared with the pure polymer. The crystal morphologies of both pure PP and polypropylene-silica nano-composites are shown in Figure 2. The pure PP displayed larger and fewer spherulites compared with PP/silica nano-composite having similar microstructure (Figure PP). From these results, one can deduce that the silica nano-particles in the nano-composite, regardless the preparation method, have a nucleation effect which leads to an increase in the quantity of spherulites.
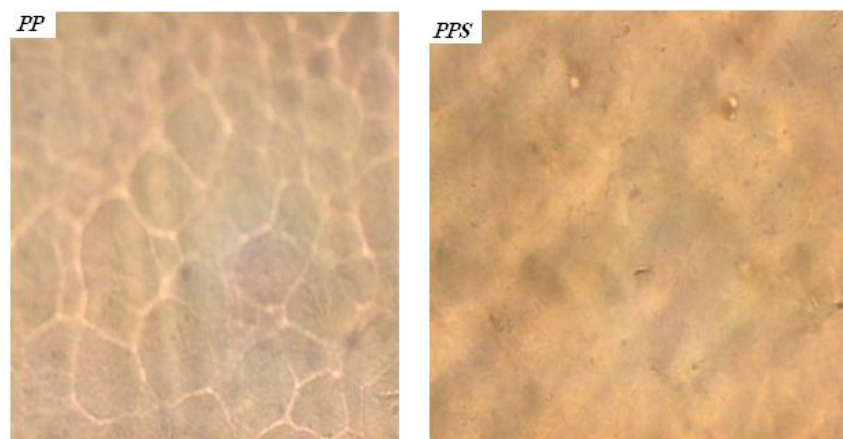
Figure (2): Images of polarized optical for (PP) pure polypropylene and (PPS) a polypropylene-silica nano-composite film, pressed at 210 °C. Magnification 10^3.

High-resolution TEM images are useful for the characterization of nano-composites, a particular to study the dispersion of nano-fillers in the polymer matrix. Figure 3 shows TEM micrographs of various PP/silica nano-composites. The dark spots in the images are related to the silica particles, while the bright rigion is related to the polypropylene matrices. The low resolution image of Figure 3 (A) shows that the nano-silica appears as a bunch of spherical-like particles, indicating the agglomeration of the primary particles. A possible reason for this is the strong interaction between this type of nano-particles [29]. From the high resolution images of nano-composites one can see that it was possible to separate the individual nano-particles via in-Situ polymerization (Figure 3(B)).

Figure 3 shows a TEM micrograph of nano-composites in which the primary particles and aggregates can be clearly seen. The average diameters of the primary particles are in the range of 20 to 50 nm. The extremely small particles naturally result in a large specific surface area, ranging from

approximately 50 m2/g to 400 m2/g. The size of the surface area is easily illustrated if one considers that approximately 20 g of nano-composites (average primary particle size is 30 nm) has the same surface area as a football field.

Nano-silica consists entirely of amorphous silicon dioxide. Crystallization only occurs after heat treatment. Nano-silica is nearly insoluble in water. It is also insoluble in acids. It does, however, dissolve in strong alkaline media to form silicates [30].
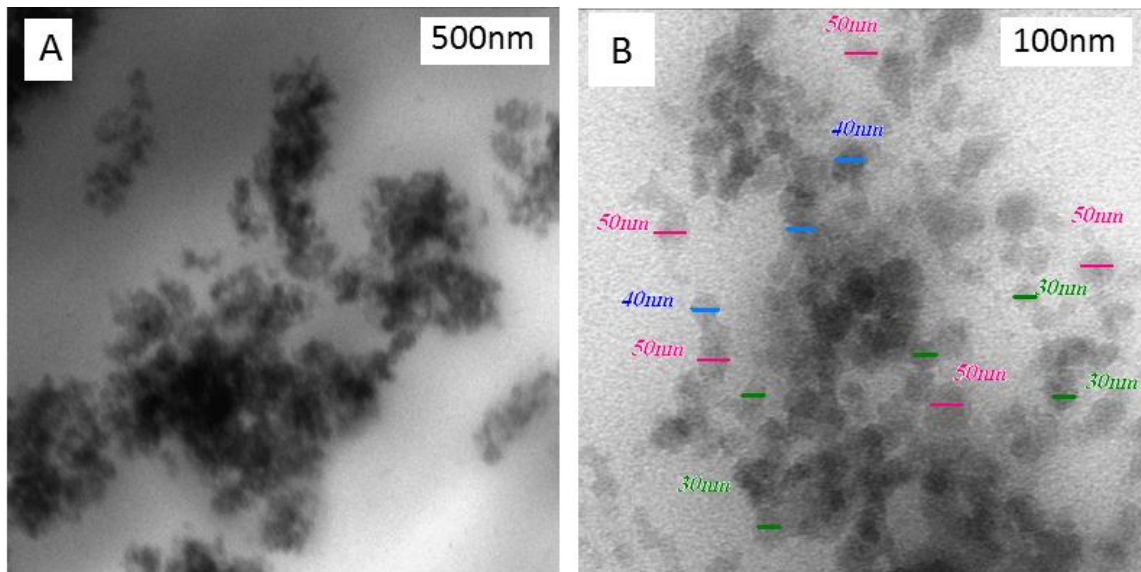

Figure (3): TEM micrographs of PP/silica nano-composites at different magnifications.

The particle size is determent from the TEM images see Figure (3) and particle size distributions of the nano-silicas is constructed and illustrated in Figure (4). The maximum value of the distribution as seen from

Figure (4) is 40 nm, which represents the average diameter of the Nano-silica particles in this study.
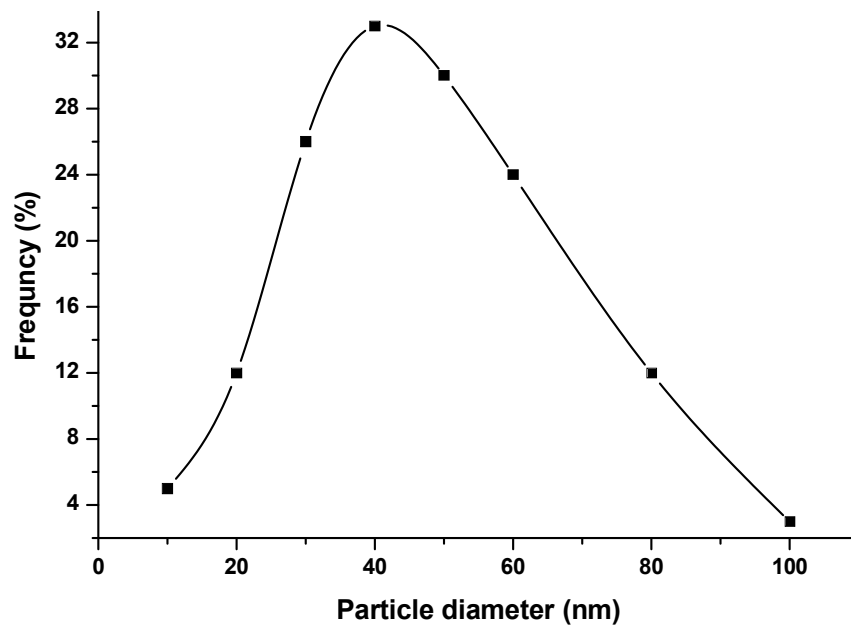

Figure (4): Particle size distributions of the nanosilicas in the PP/silica nano-composites.

3.3. *Crystallization temperatures and the crystallization degree (enthalpy of melting):*

The crystallization temperatures and the enthalpy of melting, as a function of the nano-silica load of the nano-composites prepared by in-Situ polymerization using different SiO_2 percentage are shown in Figure (5). There is a significant increase in the crystallization temperature (Tc) of the in-Situ prepared polymers as the nano-silica load increase from 0 to 5%. The increase in the crystallization temperature is attributed to two reasons; the

first one is the increase in silica content in the nano-composites leads to more numbers of spherulites, where the silica acts as nucleating agent. This results in many small spherulites and thus higher crystallization temperature. The second reason is that in the in-Situ prepared nano-composites the chains produced by the supported catalyst that are in direct contact with the silica surface, which resulting in an increased nucleating ability of the silica surface as the content of silica increases in the same polymer chain.
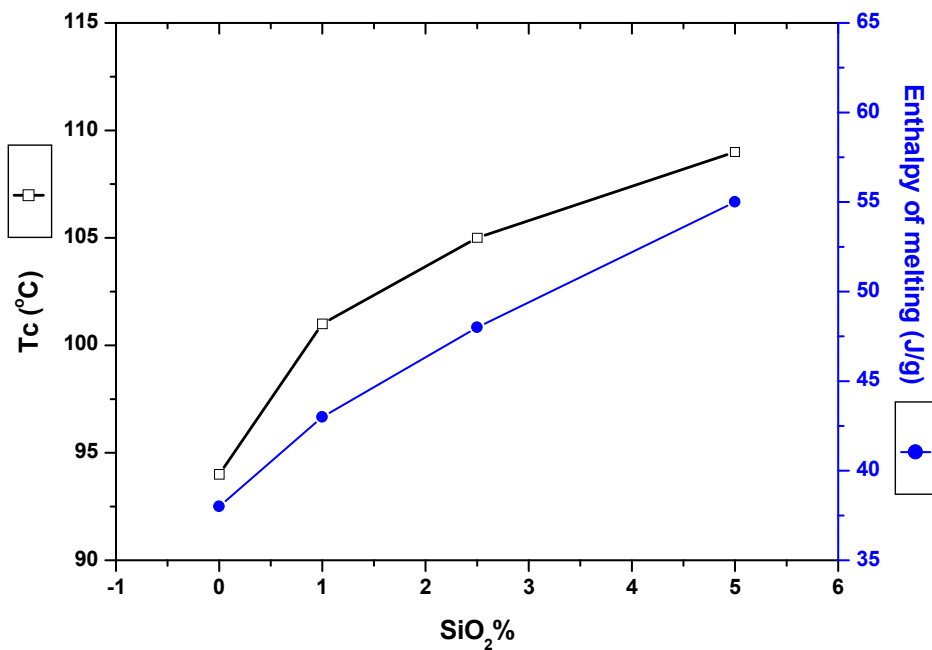

Figure (5): Crystallization temperature (Tc) and the enthalpy of melting as a function of nano-silica load (%).

Figure (5) also shows that the change in the crystallization degree, which is presented by the enthalpy of melting, as a function of the nano-silica load. There is a significant increase in the enthalpy of melting which means more crystal is formed as the nano-silica load increase from 0 to 5%.

This is as a result of the increasing numbers of spherulites as the nano-silica load increase.

4. CONCLUSION:

The syntheses of polypropylene-silica nano-composites were successfully carried out via in-Situ polymerization in which different quantities of MAO treated fillers were reacted with pre-activated catalyst solution. The effect of the addition of MAO-filler on the polymerization kinetics and consequently on PP matrix microstructure was investigated. It was also possible to predetermine the silica loading by controlling reaction conditions, specifically the load of the MAO on the nano-silica and the initial amount of SiO2-MAO. Changes in the in-Situ polymerization kinetics, compared to kinetics of homogeneous polymerization, were observed. Therefore, the microstructure of the polymer matrix was also influenced by the presence of nano-fillers in the polymerization media. TEM and OM analyses provided evidence that the silica is well distributed in the in-Situ prepared nano-composites. All composites have improved crystallization behavior and thermal oxidation stability than the pure polypropylene.

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