Journal of Macromolecular Science, Part A

In situ Polypropylene Nanocomposites: Gas-Phase Polymerization of Propylene in the Presence of Nanofillers using Nanosilica-Supported-Zirconocene Catalyst

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In situ Polypropylene Nanocomposites: Gas-Phase Polymerization of Propylene in the Presence of Nanofillers using Nanosilica-Supported-Zirconocene Catalyst

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This work concentrates on using the gas-phase polymerization technique for the production of highly loaded nanocomposites. Filler loading levels near the vicinity of 40 wt% have been obtained using different nanofillers. Three different in situ Polypropylene (PP) nanocomposites, i.e., Cloisite-20A filled polypropylene (CFPP), Kaolin filled polypropylene (KFPP) and nanosilica filled polypropylene (SFPP) have been prepared by gas-phase polymerization. The catalyst used is Nanosilica-Supported-Zirconocene. The fillers used are Closite-20A, Kaolin and nanosilica, respectively. These were pre-treated with MAO (Methylaluminoxane) to inhibit their deactivating action on the catalyst because of the presence of either acidic or basic groups on their surfaces; in this way MAO acts as a co-catalyst for the three polymerization reactions being discussed. Significantly higher molecular weight polypropylene was formed with nanosilica as the filler. The melting temperature and enthalpy is also observed to be comparatively higher in this case. However, in the case of other fillers, the molecular weights, as well as melting points, are comparatively lower. With the catalyst used, a mixture of crystalline and amorphous polypropylene was observed to form. Comparatively lesser amounts of crystalline polypropylene are also observed.

Keywords gas phase polymerization, methylaluminoxane, nanocomposites, nanosilica-supported-zirconocene

Introduction

Typically, inorganic materials such as mica, talc, etc. are used as inorganic fillers to improve the mechanical properties of pure polymeric resins. Particularly, for incorporating such inorganic materials in the case of polyolefin resins, the melt blending method has been found to be very productive. However, since the inorganic particles are incompatible with polyolefin resins, the melt blending method results in an agglomeration of particles rather than uniform dispersion. To improve the properties of these composites, various techniques have been cited in earlier several literatures (1–7), (for example, chemical modification of the filler surface by functional silanes and titanate esters and encapsulation

of filler with polymeric resin). The polymerization-filling technique (PFT) invented by Howard et al. (8) has drawn much attention by polymer and materials scientists working in the field of polyolefin nanocomposites. PFT consists of attaching a Ziegler-Natta type catalyst onto the surface of an inorganic filler so that the olefin monomer can be polymerized from the filler surface. This provides high filler loading capability to the polymer, at the same time maintaining appreciable mechanical properties in the final nanocomposite. Research led by a team headed by Robert Jerome (9–11) has focused on the development of nanocomposites, especially polyethylene, by adopting the aforementioned technique.

The discovery of *metallocene catalysts* (12) by Sinn and Kaminsky is a remarkable revolution in the history of polymer industry. The syntheses of most of the metallocene catalysts are based on Zirconium, Hafnium or Titanium. Kaminsky et al. are the first to show how the treatment of filler surfaces with metallocene-based catalysts can be used in the production of polyolefin nanocomposites (13, 14). Much of the current research related to this area is directed towards the development of "*in situ*" nanocomposites of olefins by polymerizing them with metallocenes in the presence of surface treated fillers in the slurry phase. Tsutsui et al. (15) have investigated the gas phase polymerization of propylene using a solid catalyst complex obtained from $Et[Ind]_2ZrCl_2$ and Methylalumin-oxane (MAO) with NaCl as the dispersion medium. Recently, Weiss et al. (16) has used Zirconocene-Supported-on-Montmorillonite as a catalyst for propylene polymerization. This catalyst has also been reported as having appreciably high activity.

The present work is focused on the development of in situ polypropylene nanocom-posites using a Nanosilica-Supported-Zirconocene catalyst by the "gas phase polymeriz-ation technique". One noteworthy observation is that the gas phase polymerization technique is a highly preferred method for the large scale industrial production of polyo-lefins. This is due to two reasons. Firstly, in most of the slurry-phase techniques there is always a requirement of large volumes of solvents. Secondly, in the case of slurry-phase methods, after the final product has been obtained, there is always a need of purification because there remains a possibility of traces of solvents remaining in the product.

These two demerits of slurry-phase methods can be eliminated by the gas-phase polymerization techniques.

Experimental

Materials

Zirconium tetrachloride, sodium cyclopetadienide and toluene were received from Sigma Aldrich Chemicals. Nanosilica (NS) was obtained from the Department of Chemistry, IIT Kharagpur, India; it was prepared by the sol-gel method. The particle size of nanosilica was in the range of 25 nm-35 nm and the surface area was 360 m^2/g. Organically modified clay with dimethyl dehydrogenated tallow alkyl ammonium, Cloisite-20A, was obtained from Southern Clay Products (USA). Kaolin clay was received from C.D. Pharmaceuticals, India. The co-catalyst, 10 wt% Methylaluminoxane (MAO) in toluene, was obtained from Crompton GmbH/Bergkamen. Ultra high purity polymerization grade propylene gas was obtained from BOC India Ltd., used as received. Nanosilica and aforementioned clays are employed as nano- and micro- fillers to generate *in situ* nanocomposites of polypropylene. These nanocomposites were prepared using Nano-silica-Supported-Zirconocene catalyst by the gas phase polymerization of propylene.

Preparation of Nanosilica-Supported-Zirconocene Catalyst

Nanosilica-Supported-Zirconocene catalyst was prepared using a slightly modified procedure from the literature (17). 4 g of nanosilica and 1.052 g of zirconium tetrachloride were manually mixed in a crucible kept inside a glove box. Throughout the mixing, an inert atmosphere of nitrogen was maintained inside the glove box. The crucible was then heated at 300°C for 30 min in a high temperature muffle furnace. During this heat treatment period, the zirconium tetrachloride sublimed over the nanosilica surface. The crucible was then taken out from the furnace and was allowed to cool down to room temperature under vacuum. Nanosilica-Supported-Zirconium was thus obtained. 1 g of this Nanosilica-Supported-Zirconium was suspended in 30 ml of dry toluene. To the resulting suspension, gram equivalents of sodium cyclopetntadienide were added. The resulting suspension was then stirred at 100°C for 1 h. The solid part was then filtered and dried in vacuum. Thus, finally, Nanosilica-Supported-Zirconocene was obtained.

MAO Treatment of Fillers

The fillers, nanosilica and Kaolin, were heated at 800°C for 8 h and the filler, cloisite-20A, was heated at 200°C for 8 h. Each of the fillers mentioned above was modified with MAO using the same procedure which goes as follows. 10 g of the dried nanofiller was suspended in 100 ml of dry toluene. To the resulting suspension, 5 ml of MAO was added and stirred for 5 h at room temperature. Supernatant toluene was removed using the help of a syringe. The solid part was dried in vacuum for 2 h at 150°C. The resultant MAO treated nanofiller was immediately transferred into a dried 2l stainless steel reactor (from Parr Instruments).

Propylene Polymerization

Three different polymerizations were conducted in presence of the MAO treated fillers described in the *MAO Treatment of Fillers* section. The products obtained were Closite-20A filled polypropylene (CFPP), Kaolin filled polypropylene (KFPP) and nanosilica filled polypropylene (SFPP). These were synthesized by gas phase polymerization of propylene using Naosilica-Supported-Zirconocene catalyst in the presence of the respective MAO-treated-nanofillers. Propylene polymerization was conducted in a 2l stainless steel reactor. The reactor was first dried by heating it up to 120°C under vacuum for 1 h and then cooled to 70°C under nitrogen flow. 10 g of previously vacuum dried MAO-treated-nanofiller was added into the reactor. 0.039 g of Nanosilica-Supported-Zirconocene was added into the reactor through a Teflon capillary under nitrogen flow and the mass was stirred for 15 min at 70°C. Thereafter, 5 ml of MAO was injected into the reactor; then the entire mass was stirred for 5 min. at 70°C. For a uniform polymerization of propylene, a continuous flow of propylene gas was maintained through the bottom of the reactor at 8 bar pressure. The polymerization was carried out for 5 h at a constant temperature of 70°C. Polymerization was stopped by releasing the pressure and cooling down the reactor to the room temperature. The solid mass of the composite formed in the reactor was then collected and dried at 100°C for 1 h under vacuum. The dried composite samples were used for further characterization.

In this paper, CEPP represents polypropylene extracted from the surface of CFPP. Similarly, KEPP and SEPP represent polypropylene extracted from KFPP and SFPP, respectively.

Characterization of the Polypropylene Nanocomposites

Fourier Transform Infrared Spectroscopy (FTIR). Fourier transform infrared spectroscopy experiments were done on the powder samples of polypropylene nanocomposites and extracted polypropylene using a NEXUS 870 FTIR (Thermo Nicolet) in a humidity-free atmosphere, at room temperature, with $4 \, cm^{-1}$ resolution and 32 scan signal average. Spectra were taken from $400 \, cm^{-1}$ to $4600 \, cm^{-1}$ in the transmission mode using a DTG TEC detector. The FTIR data are presented in this paper without any correction or modification.

Wide-angle X-ray Diffraction Study. This study was performed using the Philips—PW 1840, X-ray diffractometer with a copper target (Cu-K) at a scanning rate of 0.050 2 θ/s., chart speed $10 \, mm/2\theta$, range 5000 c/s and 0.2 mm slit aperture with the operational voltage and current being 40 kV with 20 mA, respectively. This was done to assess distribution of various phases present in the synthesized polypropylene nanocomposites.

Thermogravimetric (TG) and Differential Scanning Calorimetric (DSC) Studies. Thermal stability studies were performed on the nanocomposites using a TGA V 50 1A Dupont 2100 thermogravimetric analyzer in presence of nitrogen in the temperature range of 50°C to 700°C and at a heating rate of 10°C/min. Differential scanning calorimetric studies were carried out in an inert atmosphere of nitrogen with a TA DSC Q1000 V7.0—Differential Scanning Calorimeter. The data has been reported for the second heating from 55°C to 200°C at 10°C/min.

Scanning Electron Microscopy (SEM). Scanning Electron Microscopic analysis was done using a JEOL JSM-5800 SEM. This was done to analyze the morphology of the synthesized polypropylene nanocomposites. For this, the surfaces of the samples were first coated with gold by auto-sputtering.

Results and Discussion

Catalyst Preparation

Nanosilica supported catalyst was prepared in two steps according to the procedure described in the literature (17). In the first step, zirconium tetrachloride was sublimated on the nanosilica surface. In the second step, nanosilica supported zirconium was functionalized with sodium cyclopentadienide. The possible chemical reactions of step one and step two are shown in Scheme 1. The zirconium content in the supported catalyst was measured by the inductively coupled plasma technique and was found to be 0.858×10^{-4} mol [Zr] per gram of the Nanosilica-Supported-Zirconocene catalyst.

### Filler Treatment and Propylene Polymerization

Conventionally, the use of Ziegler-Natta catalysts in the polymerization-filling technique consists of anchoring the catalyst directly onto the filler surface followed by its activation with a co-catalyst before starting the olefin polymerization. In the present work, we have prepared a Zirconocene catalyst directly supported on the nanosilica surface. The

Step 1.

Step 2.
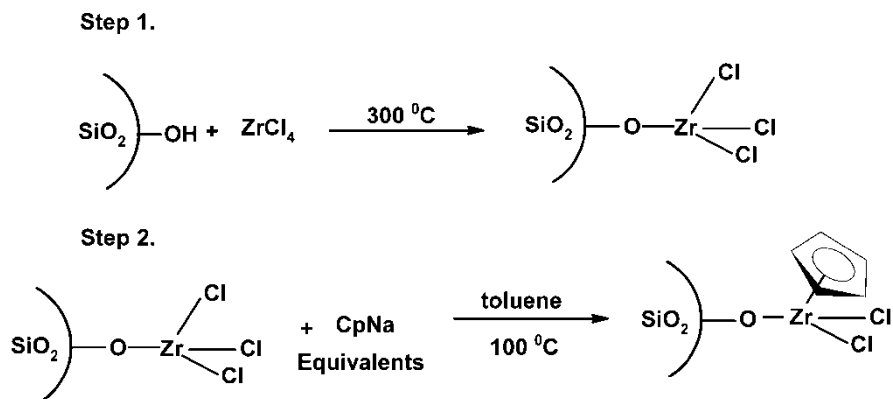
Scheme 1. Catalyst preparation.

nanofillers described in the *MAO Treatment of Fillers* section were pre-reacted with MAO in order to minimize the deactivation effects of their surfaces on metallocene catalyst activity. It should be noted that if this is not done, then the polymerization yield of polypropylene will get hampered substantially. The Al-Me bonds of MAO can react with the hydroxyl groups available on the surface of acidic fillers (Nanosilica and Kaolin) leading to the formation of an Al-O covalent bond. The occurrence of this reaction is experimentally supported by the concomitant release of methane as a volatile product. Scheme 2 shows the possible interactions of surface silanol groups of fillers and MAO during the surface treatment of fillers by MAO. Polymerizations of propylene in the gas phase in the presence of MAO-treated-nanofillers were performed at 70°C using the prepared Nanosilica-Supported-Zirconocene catalyst (described earlier in the text). The molar ratio of MAO (Al) and Zr in all the polymerizations was the same (Al/Zr = 500).

The typical results of gas phase polymerization are listed in Table 1. It can be clearly observed that the activity of the Nanosilica-Supported-Zirconocene catalyst is higher in the presence of MAO-treated-nanosilica for propylene polymerization. Also, high molecular weight is observed for SEPP.
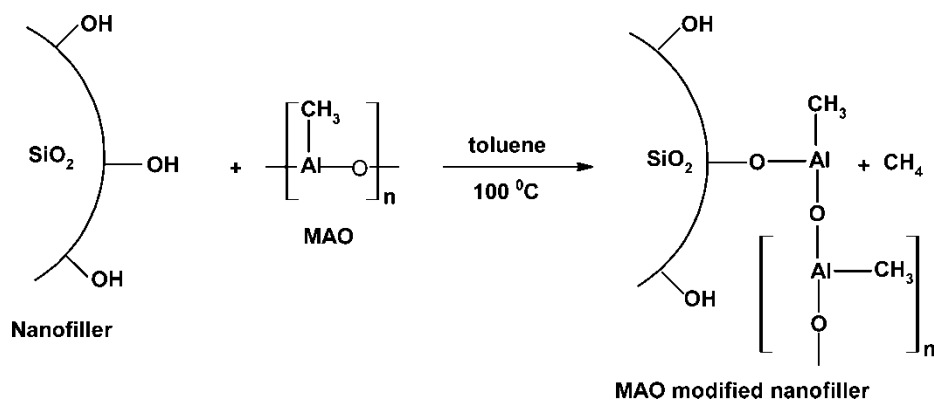
Scheme 2. Reaction between nanofiller and MAO.

Table 1
Polymerization results

	In situ polypropylene nanocomposites		
	CFPP	KFPP	SFPP
Nanosilica-Supported-Zirconocene catalyst (mmol)	0.034	0.034	0.034
MAO treated nanofiller (g)	10	10	10
Total MAO (mmol)	17	17	17
[Al]/[Zr]	500	500	500
Activity (Kg/mol. Zr)	411 ± 3	441 ± 5	470 ± 4
Nanofiller abundance (%)	41	40	38
Viscosity molecular weight, $M_v \times 10^{-4}(g/mol)^a$	6.90	3.80	19.40

[a]Viscosity molecular weight of extracted polypropylene measured at 30°C in Benzene solvent.

FTIR Study

Figure 1 shows the IR spectra of the dried composite samples collected from the reactor. All the composite samples show a strong absorption band in the range of $2900\,cm^{-1}$ to $2962\,cm^{-1}$ (corresponding to –C-H symmetric stretching) and a strong IR band at $1378\,cm^{-1}$ (corresponding to –C-H deformation of tertiary carbon). The occurrence of all these IR bands indicates that polypropylene has been formed in the presence of nanofillers (*MAO Treatment of Fillers* section) during the polymerization.

Figure 2 shows the IR spectra of polypropylene extracted from the respective polypropylene nanocomposites. Polypropylene extracted from SFPP, i.e., SEPP shows a higher and intense IR peak with respect to CEPP and KEPP (corresponding to $2900\,cm^{-1}$–$2962\,cm^{-1}$ for –C-H symmetric stretching and corresponding to $1378\,cm^{-1}$ for –C-H deformation of tertiary carbon). This further supports reasonably high molecular weight for SEPP than that of CEPP and KEPP (seen in Table 1).

WAXD Study

Figure 3 shows the X-ray diffractograms of nanosilica and Kaolin, both heated at 800°C for 8 h, and Cloisite-20A, heated at 200°C for 8 h. All the fillers show sharp and intense crystalline peaks. Figure 4 shows the X-ray diffractograms of CFPP, KFPP and SFPP. It is observed from the Figure 4 that a decrease in intensity of crystalline peaks of the respective fillers is observed in the case of all the synthesized polypropylene nanocomposites. This decrease in intensity of peaks can be attributed to the presence of two phases in the synthesized polypropylene nanocomposites. Also, in all the synthesized polypropylene nanocomposites, from Figure 4, it can be observed that relatively higher intensity peaks are observed at $2\theta = 14°$, $16.8°$, $18.5°$ and $21.7°$. These peaks correspond to the α—crystalline phases of polypropylene. From this observation, it can be concluded that the polypropylene formed with Nanosilica-Supported-Zirconocene catalyst in the presence of the nanofillers is a mixture of α—crystalline and amorphous polypropylene. In the gas phase polymerization of propylene with solid zirconocene catalyst, Tsutsui et. al. (15) also observed the formation of α—crystalline polypropylene.
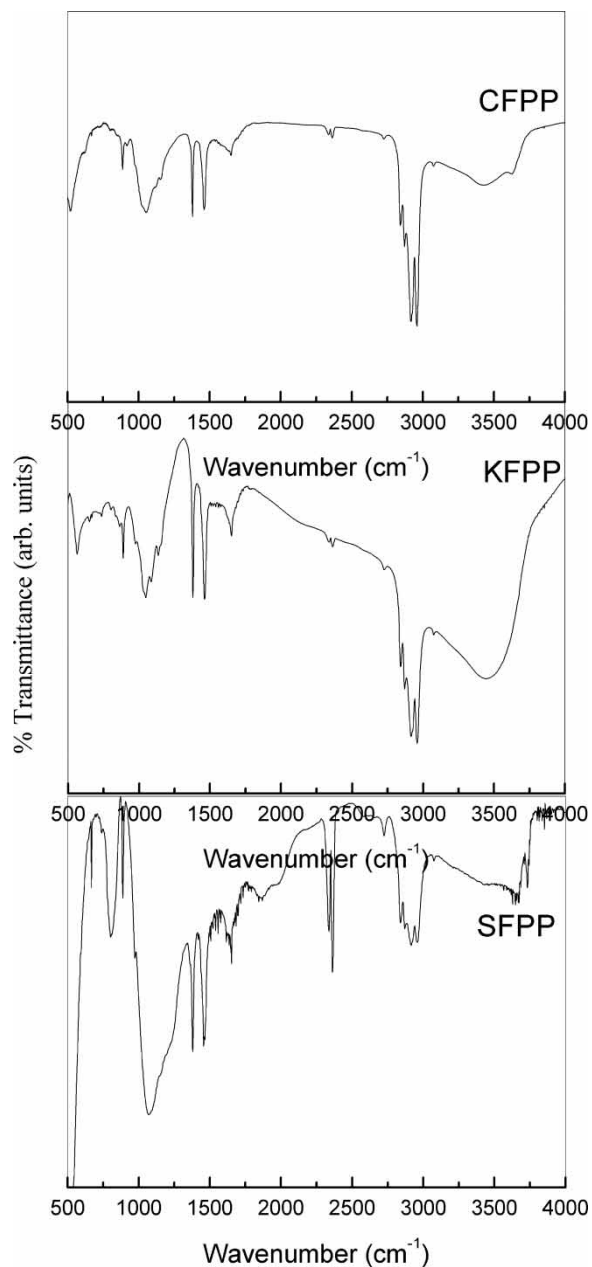
Figure 1. IR spectra of *in situ* polypropylene nanocomposites.

TGA and DSC Study

Thermogravimetric analysis was carried out on the synthesized polypropylene nanocomposites using a thermogravimetric analyzer (TGA V50 1A Dupont 2100). TGA curves are shown in Figure 5 and the corresponding parameters are listed in Table 2. It is observed that the decomposition temperature (temperature at 5% wt loss) is around 36°C higher
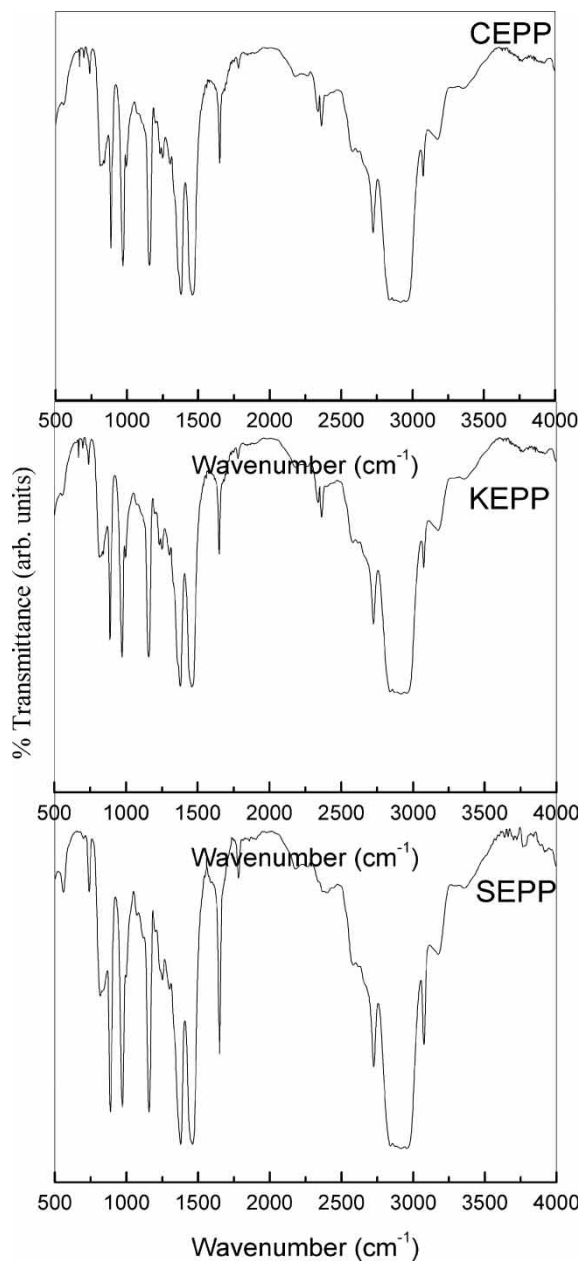
Figure 2. IR spectra of extracted polypropylenes from the respective nanocomposites.

for SFPP (200°C) with respect to CFPP (164°C) and 30°C higher with respect to KFPP (170°C). The weight percent of fillers in the synthesized polypropylene nanocomposites are calculated from the residual weight of the composites at 700°C (from the TGA curves of Figure 5). The residual weight percent for SFPP at 700°C also supports the higher activity of Nanosilica-Supported-Zirconocene for propylene polymerization in presence of MAO treated nanosilica.
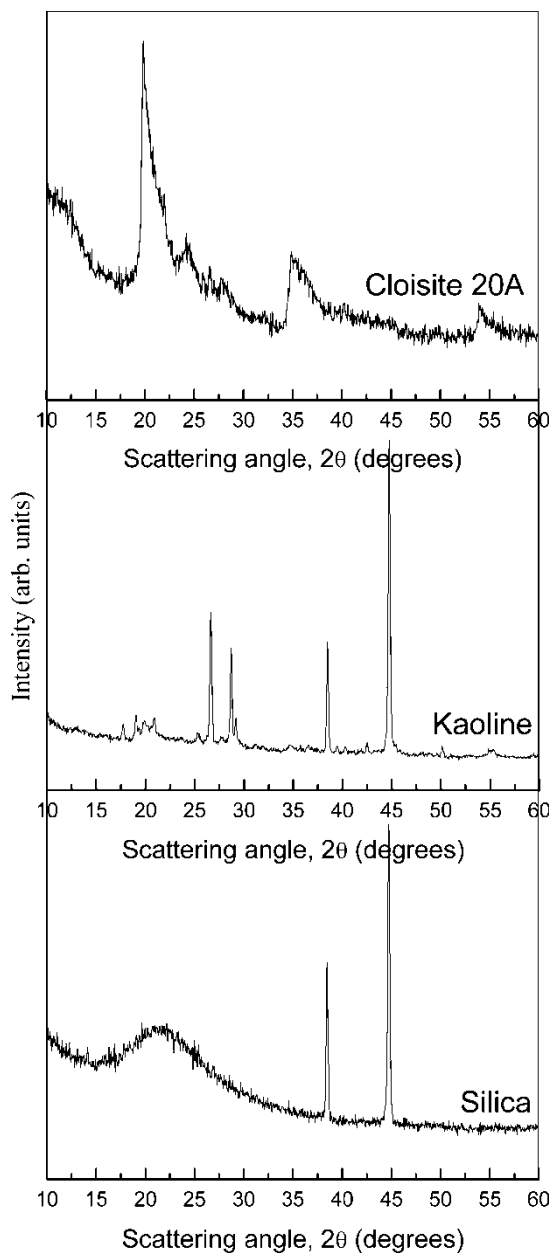
Figure 3. X-ray diffractograms of nanofillers.

CFPP, KFPP and SFPP dried at 100°C for 1 h have been analyzed by DSC. Figure 6 shows the DSC melting thermograms of CFPP, KFPP and SFPP. Melting temperature and melting enthalpy of synthesized polypropylene nanocomposites are listed in Table 2. For SFPP, higher melting temperature and melting enthalpy are observed than those for CFPP and KFPP. The degree of crystallinity of the composites
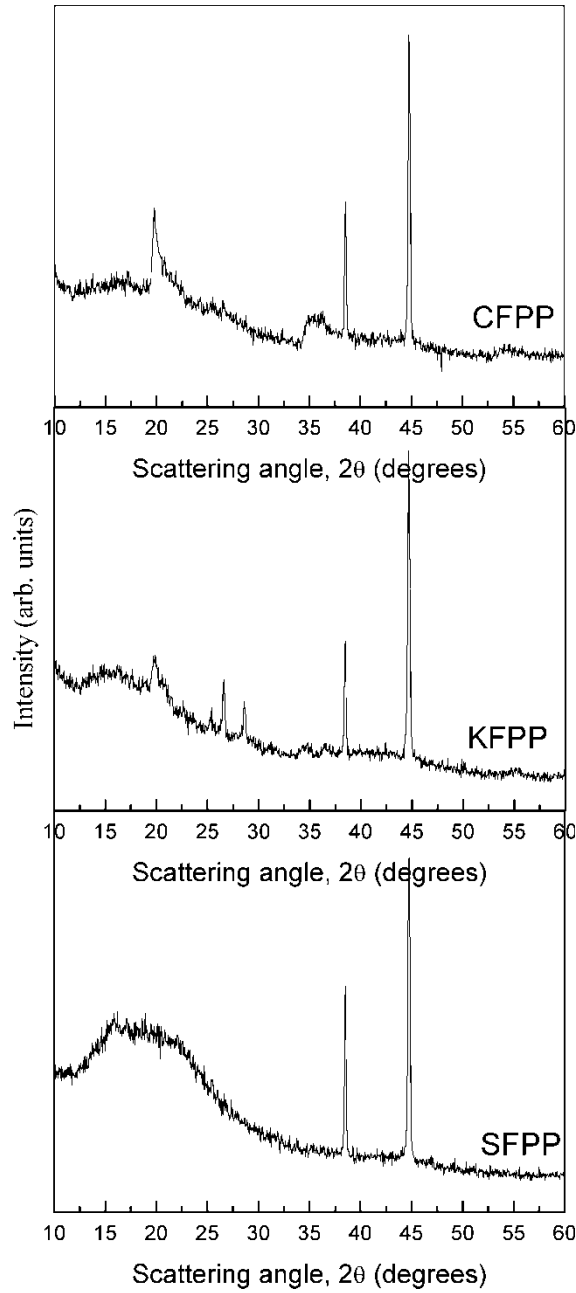
Figure 4. X-ray diffractograms of *in situ* polypropylene nanocomposites.

has been measured using the formula given bellow (18) and the typical values are listed in Table 2.

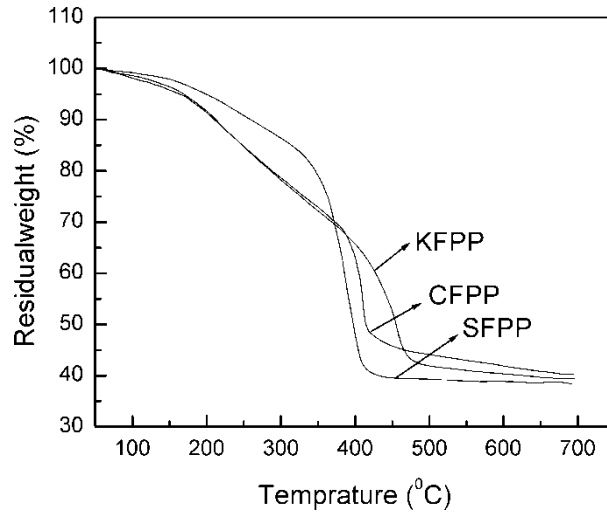$$x = \frac{\Delta H_m}{\Delta H_0 \times \frac{m_p}{m_c}} \times 100\%$$

Figure 5. TGA curves of *in situ* polypropylene nanocomposites.

Table 2
TG and DSC results

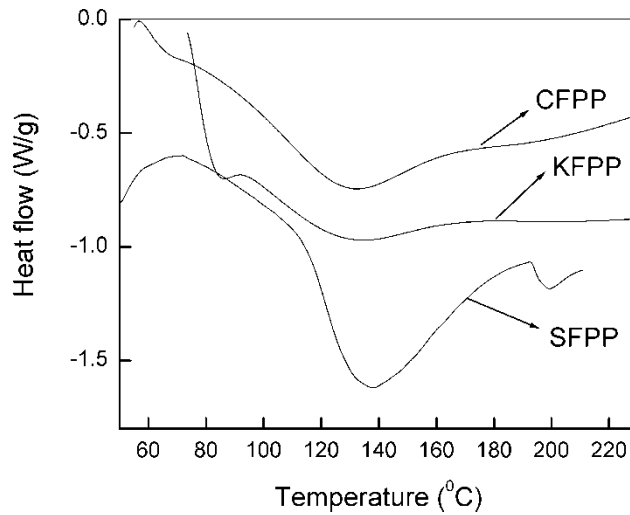| In situ polypropylene nanocomposite	5% weight loss temperature (°C)	Filler content (%) (measured)	Melting temperature (°C)	Melting enthalpy (J/g)	Crystallinity (%)
CFPP	164	40	132	27.9	22.2
KFPP	170	39	134	25.2	19.7
SFPP	200	38	138	30.0	23.2

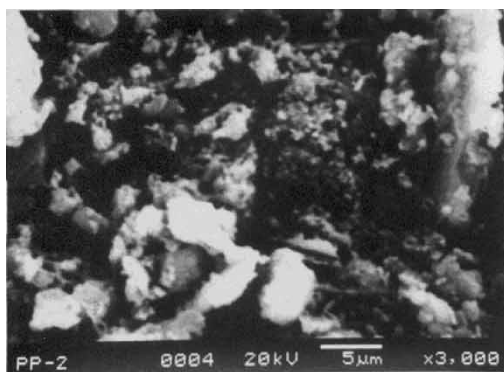**Figure 6.** DSC curves of *in situ* polypropylene nanocomposites.

where,

x = % degree of crystallinity of polypropylene nanocomposite

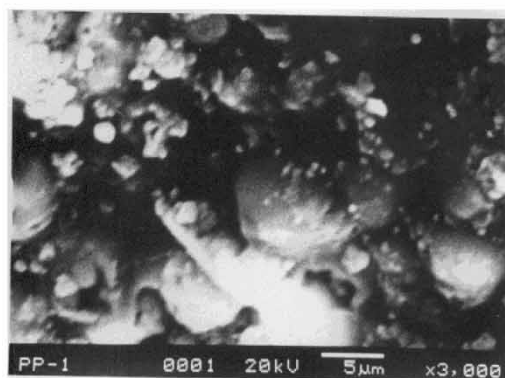ΔH_m = melting enthalpy (J/g) of polypropylene nanocomposite

ΔH_0 = melting enthalpy (209 J/g) of 100% crystalline polypropylene (19)
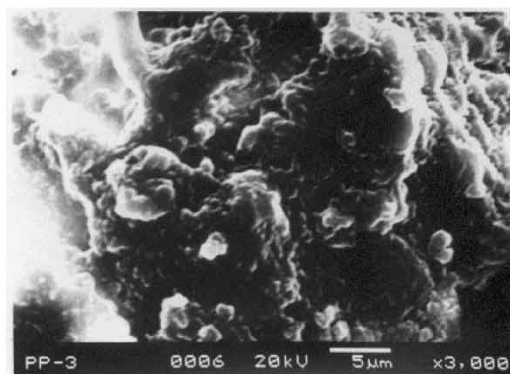
m_p = mass (g) of polypropylene in the nanocomposite

m_c = mass (g) of the polypropylene nanocomposite

Figure 7. SEM micrographs of *in situ* polypropylene nanocomposites.

Morphology of the Composites—SEM Study

The morphology of the synthesized polypropylene nanocomposites has been observed by a scanning electron microscope. We have studied the effect of different types of fillers in this gas phase polymerization process and the SEM photographs we have shown are those of composites surfaces after cryofracture. SEM micrographs for the CFPP, KFPP and SFPP are shown in Figure 7. It can be observed that the morphology of the synthesized polypropylene nanocomposites are completely different from one another depending on the filler size and their agglomeration and also on the location of polypropylene moieties. All the nanocomposites show a mixed type of morphology consisting of a growth of polymer chains on the filler surface and clay platelet particles. In case of CFPP, cloisite-20A platelets coexist with typical PP particles. In the case of KFPP, a thin polymer layer growth on the Kaolin platelets can be easily visualized. The SEM micro graph for SFPP is completely different from the other two nanocomposites. It can be seen that deposition of PP layer on silica surface and confirms that MAO has reacted with the surface and drives the propylene polymerization from the surface. In most of the regions a thin layer of polypropylene has covered almost all of the silica particles. A growth of polymer particles can also be observed from the micrograph for SFPP.

Conclusions

In situ polymerization of propylene in presence of MAO treated nanofillers using Nano-silica-Supported-Zirconocene by the gas phase polymerization technique has been successfully carried out to develop polypropylene nanocomposites. In the case of SFPP, from the IR study and polymerization results, it has been found that a high molecular weight polypropylene was formed. The yield of polypropylene in this case was also high. The XRD study shows that most of the polypropylene content in the developed nanocomposites is a mixture of α—crystalline and amorphous in nature. The DSC study shows that SFPP has a higher melting temperature and melting enthalpy than CFPP and KFPP. TGA study indicates SFPP has higher thermal stability than CFPP and KFPP. Finally, SEM micrographs confirm that the polypropylene content is formed on the filler surfaces.

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