

# POLYPROPYLENE/SiO<sub>2</sub> NANOCOMPOSITES WITH IMPROVED MECHANICAL PROPERTIES

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**Abstract.** Polypropylene-SiO<sub>2</sub> nanocomposites were synthesized using twin-screw extruders. The properties of the nanocomposites were studied using two different inorganic fillers: colloidal (sol) and powder silica nanoparticles. Reinforcing and toughening effects of the nanoparticles on the polymer matrix were found at a loading of 4.5 wt.%, which is lower than for most particulate filled composites. The use of silica nanoparticles led to different microstructure when compared with that of the pure polymer. Addition of colloidal silica to the polymer matrix produced good filler dispersion while the use of powder silica resulted in aggregated silica particles in the polymer matrix. There was no noticeable improvement of the mechanical properties when powder silica was added to the pure polymer. On the contrary, the presence of silica-sol nano-particles in the polymer matrix led to an increase of both Young modulus and impact strength, from 1.2 GPa to 1.6 GPa and from 3.4 kJ/m<sup>2</sup> to 5.7 kJ/m<sup>2</sup> respectively.

## 1. INTRODUCTION

The problem of rendering composite polymer materials more impact-resistant without decreasing the material's modulus of elasticity has been attracting the attention of many polymer and materials scientists. Some advantages of using polymers are found in their easy processing and light-weight. During processing, high particle loadings result in end products with much higher weight than that of the pure polymers. Therefore a composite with improved properties at low particle concentration is desired. Nanostructured materials often exhibit combinations of physical and mechanical properties that are not superseded by conventional materials. For example, by decreasing the particle size of silica

from the micrometer to the nanometer domain, a change in strength, elongation at break, modulus and yield stress was observed in polyurethane and nylon [1,2]. Polypropylene (PP) is one of the fastest growing turnover polymers to date [3]. One of the difficulties regarding the use of inorganic nanoparticles in PP is their dispersion quality. This is due to the hydrophobic nature of PP, which gives rise to a significant problem in enhancing the adhesion between the 'hydrophilic' filler and the matrix [4] creating poor bond strength between the polymer matrix and filler. This problem has been overcome by tailoring the affinity between the inorganic material and the organic polymer by for example *in-situ* polymerisation, employment of silane coupling agents [5,6] and other strategies [7,8]. The

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studies have shown an improvement in properties of thermoplastics when silica has been chemically modified when compared with unmodified silica [9,10]. For PP, low silica concentrations (< 5 vol.%) led to an improvement of the mechanical properties [11-14]. Comparisons were however, based on an inhomogeneous dispersion of the unmodified silica with a homogeneous dispersion of the modified silica. Poorly dispersed inorganic fillers in the polymer matrix generally do not lead to an improvement of the material properties. The presence of inorganic fillers affects the crystallization behaviour of the polymer when the particles act as nucleation sites. It has been reported that the modification of the filler surface can influence the effect of the filler on the crystallization behaviour [15]. It is not evident if the improvement of the properties is due to the change of the stress around the fillers, a significant nucleation effect or both. In order to minimise external effects, introduced by the chemical bond formed between filler and polymer, we have chosen for filler material that does not have a direct chemical interaction with the polymer matrix.

In this article, the preparation of new PP-silica composites that show enhanced mechanical properties is described. The effort was focused on obtaining well-dispersed nanoparticles without using modifiers. The motivation to obtain good dispersion stemmed from the observation that if any properties are to be further improved then the distribution of the inorganic filler particles in the polymer matrix has to be as homogeneous as possible by using a filler size of diameter  $\leq 30$  nm. Two different inorganic nanoparticles were used: colloidal (abbreviated: Col) and powder silica (abbreviated: MOX). The particle content was kept constant at 4.5 wt.% as it has been already demonstrated that at low filling ratios an improvement in the elastic modulus and impact resistance is achieved [12,13]. The nanocomposites contained primary filler particles with a diameter less than 30 nm. The composites were prepared using a twin screw extruder where unmodified colloidal nanosized silica particles are used. The system led to better modulus values compared to the systems in which modified silica was added. Four samples of each composition were tested; the average values obtained for the different parameters are presented. Furthermore, the effect of the inorganic filler on the thermal behaviour of the PP was studied by means of Differential Scanning Calorimetry (DSC).

## 2. EXPERIMENTAL

### 2.1. Materials

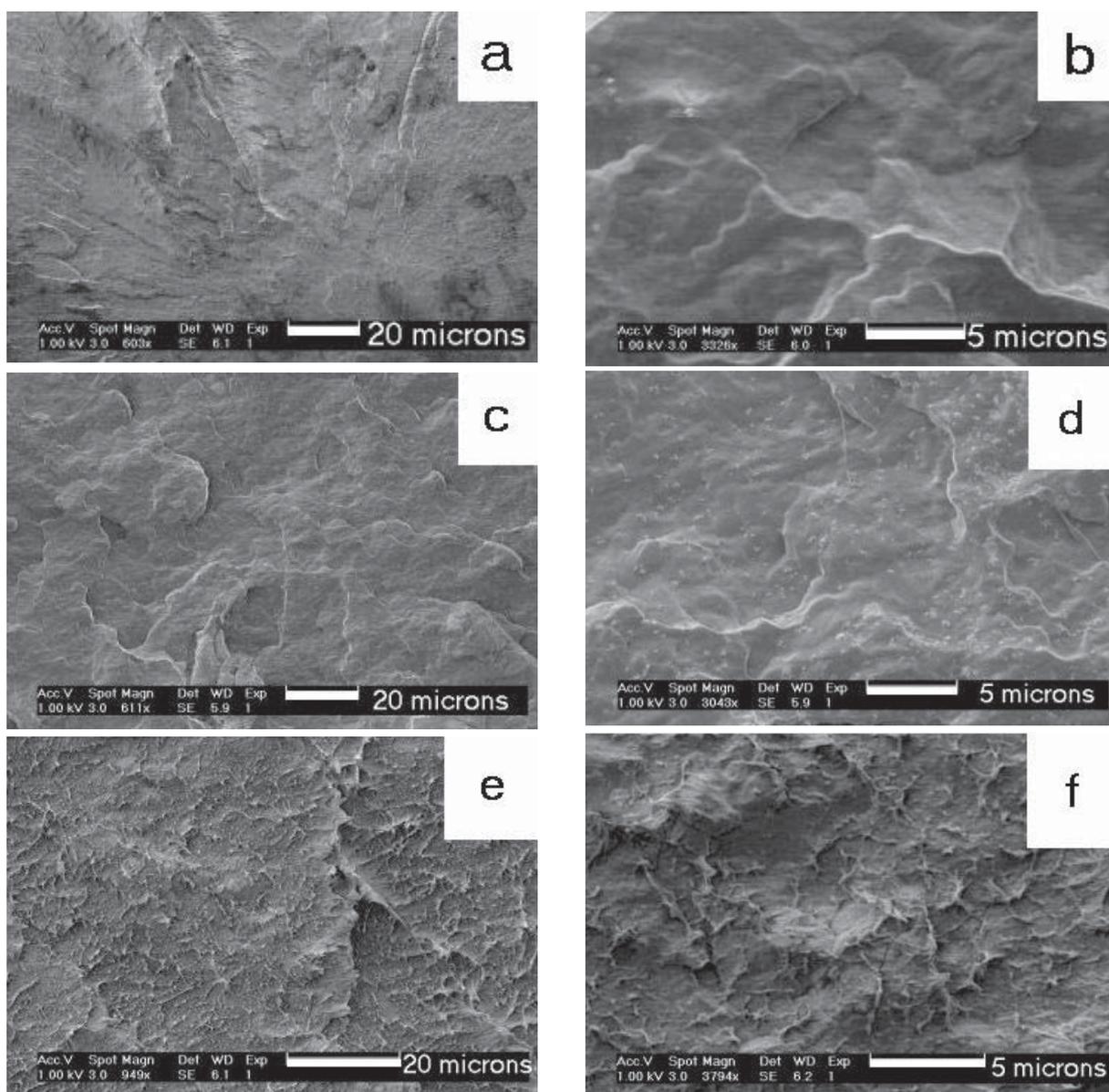
The polypropylene used was Stamylan PP 17M10 ( $M_w = 280,000$  g/mol) provided by DSM. Silica nanoparticles were generously provided by Nissan Chemicals (Japan) under the brand name Snowtex™ as an acidified aqueous sol with particle sizes 10-20 nm. Silica Aerosil MOX-80 powder (Degussa chemicals) was obtained with an average primary particle size of 30 nm. Pure PP samples were labeled PP, composites with powdered silica aerosil PP-MOX and composites with colloidal silica Snowtex PP-Col.

### 2.2. Processing

Mixing of MOX silica with PP was performed with a 25 mm co-rotating ZSK 25 twin-screw extruder. The temperature of the extruder was 185-200 °C, the rotation speed of the screws was 150 rpm and the length of the extruder was 1050 mm. The silica powder was fed to the polymer melt by a side feeder situated directly behind the melting zone. The material flux was optimised to get the highest torque of the extruder in order to achieve a proper particle dispersion. The extruded material was cooled directly at the exit of the extruder in water and the material strings were subsequently palletised. The compounding of the Col nanocomposite was performed feeding the colloidal silica in a high-pressure reaction zone. The process was developed on a ZSK-30 twin-screw extruder. The pressure in the mixing zone was significantly higher than the vapor pressure of the water and the pressure drop (passage of the melt through the left handed elements) was faster than the destabilizing foam forming process. The pressure drop prevented fluctuations and instabilities to occur in throughput. The screw needs to be designed with a reaction-zone for mixing the polymer/silica. A dynamic seal of 8 blister-discs increases the pressure level in the reaction-zone and resulted in a stable process.

### 2.3. Sample preparation and mechanical tests

The materials were compression moulded between brass plates and aluminum foil into a mould of 50x75x5 mm<sup>3</sup>. The temperature was kept at 220 °C during molding. The polymer pellets were melted under atmospheric pressure and subsequently the



**Fig. 1.** SEM images of fractured samples (a, b) PP, (c, d) PP-MOX and (e, f) PP-Col.

pressure was increased stepwise to a maximum pressure of approx 500 kPa. Tensile strength tests on dumb-bell shaped specimens were performed on a Zwick Z1020 tensile testing machine, at a constant strain rate of  $10^{-2} \text{ s}^{-1}$ . Notched Izod-impact tests were performed according to ASTM-D 256.

#### 2.4. Characterization

Quantitative XRF was used to determine the amount (as wt.%) silica present in each bulk sample. Analysis was performed on a Philips PW 1480/10 fluorometer (Eindhoven, The Netherlands). The heat of

fusion ( $\Delta H$ ) was measured for all samples with DSC in a standar mode on a Perkin Elmer Pyris series 1 DSC and TA-instrument Q-series in modulated mode were used for studying the thermal behavior of modified PP and nanocomposites synthesized. Heating and cooling scans at  $10 \text{ }^{\circ}\text{C}/\text{min}$  over the temperature range from  $-60$  to  $250 \text{ }^{\circ}\text{C}$  were performed in the standard mode, while  $2 \text{ }^{\circ}\text{C}/\text{min}$  was used during measurement in the modulated mode (to distinguish the effect of recrystallization during melting). Size Exclusion Chromatography (SEC) was used to determine the  $M_w$ ,  $M_n$  and intrinsic viscosity ( $\eta$ ). Scan-

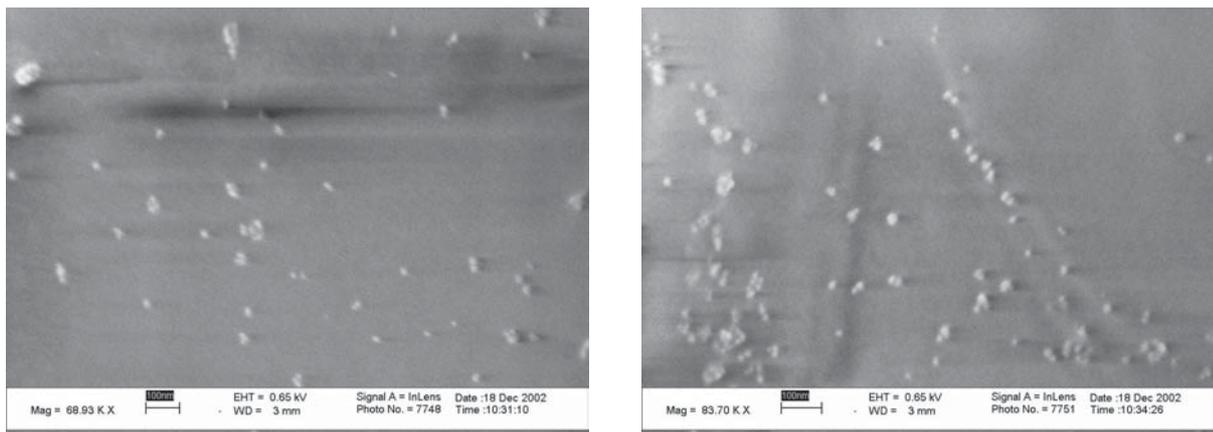


Fig. 2. SEM images PP-Col samples.

ning Electron Microscopy (Philips XL 30 SEM) was used to determine the dispersion of the silica in the polymer. Fracture surfaces after the Izod-impact test were used for morphology characterization to study the dispersion and fracture behaviour.

### 3. RESULTS AND DISCUSSION

Figs. 1a-1f show the morphology of fractured samples of PP (a,b) PP-MOX (c,d) and PP-Col (e,f). The morphology was studied after the processing experiment post-mortem. Figs. 1a and 1b show SEM micrograph of a fracture surface of the pure polymer. Small (micro) aggregates of silica can be observed in Figs. 1c and 1d. No visible particle agglomerates were observed at this magnification in the composites containing colloidal silica (Figs. 1e and 1f). This was taken as an indication that the silica remained not aggregated, i.e. in the nano domain < 30 nm. A picture of a non-fractured sample of PP-Col was taken at higher magnification (Fig. 2). Well-dispersed particles appear distinguishable from the matrix for the colloidal silica composite. This is in accordance with Figs. 1e and 1f where the particle size is below the resolution limit.

The degree of crystallinity of the composites was calculated from the DSC thermographs using the heat of fusion of 209 J/g for 100% crystalline PP [16], and is mentioned in Table 1.

Fig. 3 shows the thermographs measured during heating of the pure sample and the nanocomposites. It was observed that the melting point of the samples was clearly affected by the presence of silica nanoparticles. The heating thermogram of the pure polymer exhibited its first endothermic melting peak at about 145 °C, followed by a second

larger endothermic peak at 165 °C, which is likely due to the melting of the  $\alpha$ -form that is the most common crystal phase of iPP. The  $\gamma$ -phase is not usually observed as a separate phase, but (co) crystallizes with and within the  $\alpha$  phase spherulites [17]. The small peak below 150 °C is due to the presence of the  $\beta$ -phase.

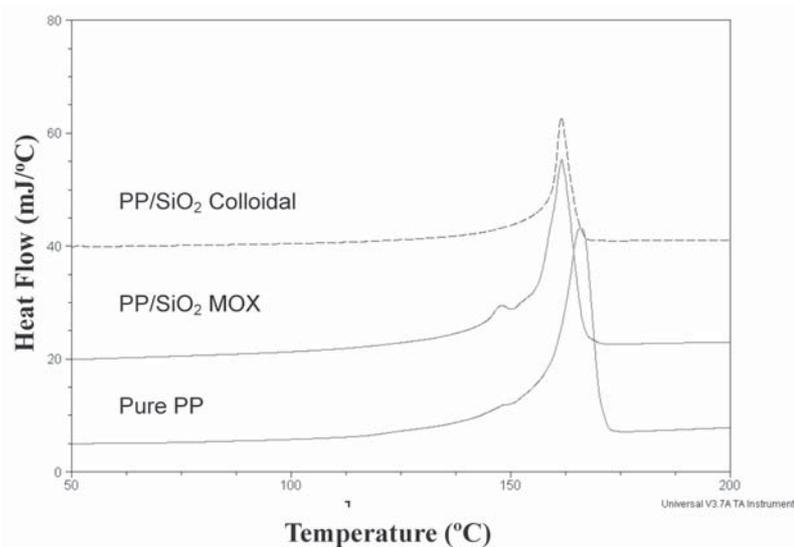
It is interesting to note that the onset of the first endothermic peak is the lowest (in comparison with the other two samples), indicating the beginning of the melting of the metastable  $\beta$ -form. In general, the  $\beta$ -form, which is thermodynamically less stable, melts at lower temperatures and recrystallize as

Table 1. DSC data of the samples.

Sample	Heat of fusion, J/g	$W_{c,x}$ , %
Pure PP (Pellets)	100.5	48
PP MOX silica powder	100.9	50
PP with silica colloid	90.5	45

Table 2. Molecular structure parameters of PP and PP/SiO<sub>2</sub> nanocomposites as obtained from SEC-triple molecular weight measurements in kg/mole and  $[\eta]$  in dl/g.

Sample	$M_n$	$M_w$	$[\eta]$
Pure PP (Pellets)	67	280	1.49
PP with silica colloid	59	245	1.38
PP MOX silica powder	61	260	1.43



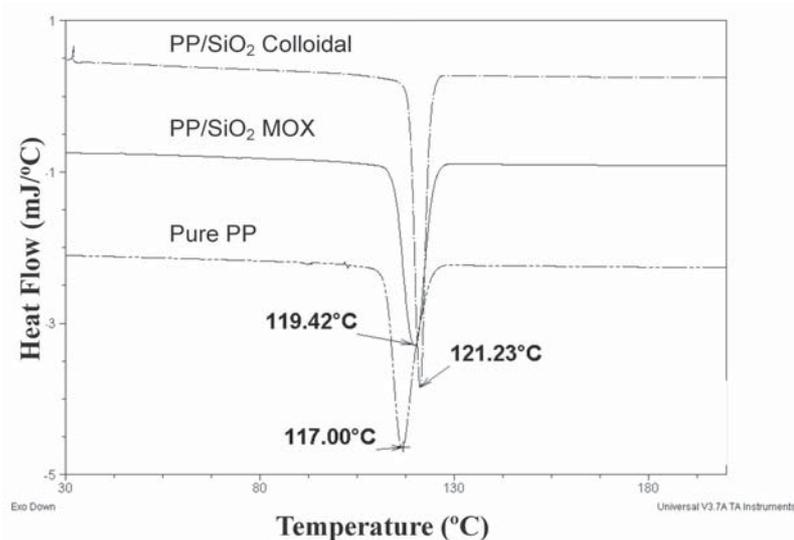
**Fig. 3.** DSC thermogram of samples. From top to bottom: PP-Col, PPMOX and PP. (Graphs are displayed vertically).

the stable  $\alpha$ -form [18]. The shifting of  $T_m$  to lower temperatures upon addition of silica can probably be attributed to a decrease in lamellar thickness of the polymer crystals. Furthermore, the PP-Col nanocomposite showed a narrower and sharper peak than that of PP-MOX composite indicating possibly better crystal formation.

The crystallization point of the samples is shown in Fig. 4. PP displays an exotherm (crystallization point) with a main peak at 117 °C. A crystallinity value of 48% was calculated from the measure-

ments of the melting enthalpy. PP-MOX showed a peak at 119 °C, from which a crystallinity of 50% was calculated. Addition of colloidal silica increased the crystallization point to 121 °C, and resulted in a degree of crystallinity of 45%. The significantly narrower peak of PP-Col confirms a more uniform crystal formation than when using MOX.

The number average molecular weight ( $M_n$ ) and weight average molecular weight, ( $M_w$ ) of PP, PP-MOX and PP-Col samples are shown in Table 2. Upon addition of colloidal silica, the polymer intrin-



**Fig. 3.** Crystallization point of the samples. From top to bottom: 121 (PP-Col), 119 (PPMOX) and 117 (PP).

**Table 3.** Mechanical properties of the samples.

Sample	E-modulus,GPa	Max. Tensile Strength	Izod Impact Test, KJ/m <sup>2</sup>
Pure PP (Pellets)	1.2	33.1	3.44
PP MOX silica powder	1.5	34.4	4.17
PP with silica colloid	1.6	31.4	5.77

viscosity  $[\eta]$  and molecular weight ( $M_w$ ), obtained from SEC experiments, decreased. This is most likely related to the degree of crystallinity, which also slightly decreased from 48% to 45%. Upon addition of MOX silica, the molecular weight of the polymer decreased, but to a lesser extent than for the colloidal composite. In contrast, the degree of crystallinity slightly increased to 50%. Within experimental error, however, it can be concluded that regardless the type of nanosilica, both  $M_w$ ,  $M_n$  and  $h$  decreased whereas the crystallinity remained constant (Table 1). It has been reported [19] for isotactic polypropylene (iPP) that the degree of PP crystallinity was inversely related to the weight average molecular weight of the polymer. This is not the case for PP-MOX and PP-Col nanocomposites (Table 2).

Regarding the mechanical measurements, tensile stress experiments were performed at a strain rate of  $10^{-2} \text{ s}^{-1}$ . Samples of the pure polymer showed neck formation at the yield stress. The composite samples, in contrast, fractured before neck formation could start. For the weight percentage of filler used, the yield stress did not change significantly when compared to the pure polymer. A considerable increase in the yield stress has been reported for non-uniformly dispersed composites with 6 and 12 wt.% of filler having particles diameters in the 12 and 25 nm range [2, 14]. This has been attributed to the complex geometry of the aggregates that leads to a better stress transfer between polymer and filler than for a spherical filler shape [20]. In accordance with the rule-of-mixtures (which assumes simply the sum of properties of each component phase weighted by the volume fraction of that phase) for our system, a more significant difference for higher filled nanocomposites is expected. Debonding of the filler particles plays also a role during the applied tensile stress, but for small particles debonding is more difficult to occur.

While the influence of the filler particles on the tensile stress test is rather limited, the influence on the Izod impact strength is significant. The addition of colloidal particles led to 68% higher impact

strength than the pure polymer matrix (see Table 3). This suggests that for a nanocomposite subject to impact loading, the interfacial regions are able to resist crack propagation more effectively than the polymer matrix. This can be explained as follows [21]: The use of rigid inorganic filler particles in a polymer matrix under tension will cause stress concentrations followed by debonding and shear yielding. Due to the formation during crazing of an interconnected network of voids, which are traversed by small fibrils, yielding and crazing are found to be deformation mechanisms in polypropylene [22,23]. Obviously the higher is the resistance to separation between matrix and filler, the higher are the stresses that can be applied to the specimen before the separation takes place. For large particles (100 nm) matrix de-wetting will create voids that immediately begin to grow destroying the integrity of the composite. The void size however, is determined by the filler particle size. The smaller the particles the smaller will be the resulting voids. If the adhesion strength is higher than cohesion forces of the matrix (i.e. good adhesion), then the stress ( $\sigma$ ) to break the specimen will be controlled by the stress concentration in the vicinity of the filler particles. If the resistance to separation is low (poor adhesion), voids will be formed already under low stresses, but this situation might not be damaging the structural integrity of the specimen. Such voids will be responsible for a pseudo-plastic behaviour of the polymer [21]. In case of good adhesion between phases, stress concentration near the particle is independent of their size. In case of poor adhesion between phases, the moment at which the matrix actually separates from the particles depend on the particle size due to subsequent debonding sequence (void forming) that would lead to the specimen failure. Hence, large-sized particles are undesirable when the adhesion between matrix and filler is poor.

#### 4. CONCLUSIONS

The influence of silica nanoparticles on PP was studied using two different inorganic fillers with particle size  $\leq 30$  nm. As a basis for comparison, not chemically modified silica with lower bond strength between filler and polymer matrix was used. The filler dispersion state within the matrix varied from unaggregated particles to aggregates of different shape (even though silica particles were in the same diameter range). Colloidal silica nanoparticles added to PP showed good dispersion of the inorganic filler into the polymer matrix, whereas the addition of powder nanosilica particles showed a good dispersion of aggregates into the PP as seen from the fracture surfaces. Upon addition of silica, an improvement of the elastic modulus of ca. 30% was obtained. The yield stress at this filler percentage was found not to be too sensitive to the dispersion state. Nevertheless, it seemed that the dispersed particles slightly decreased the yield stress. A significant improvement was found in the toughness by performing Izod-impact tests. Regardless of the kind of inorganic filler, an increase in the fracture toughness of the material was obtained. An enhancement of 68% was measured with the colloidal silica particles. Furthermore, addition of colloidal particles decreased the melting point of the PP and the heat of fusion whereas the differences with the pure polymer were much less pronounced for the MOX composite.

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