



Influence of Particle Size and Bound polymer on the Mechanical and Rheological Properties of Polypropylene/Inorganic Powder Composites

S. Djellali ^{a*}, L. Djahnit ^a, H. Ferkous ^b

^a Laboratory of Physical Chemistry of High Polymers, Faculty of Technology, University Ferhat Abbas1, 19000, Setif, Algeria.

^b Department of Technology, University of Skikda, Skikda, Algeria.

ARTICLE INFO

Article history:

Received: 04 December 2019

Revised: 27 January 2020

Accepted: 23 February 2020

Published: 26 February 2020

Keywords:

Reinforcement

Interphase

Bound polymer

Polypropylene

Calcium carbonate.

ABSTRACT

Composites based on polypropylene and calcium carbonate powder were prepared in melt by varying the filler percentage (0-50 wt%) and size (0-180 μm). The effects of filler content and size on mechanical and rheological properties of PP/CaCO₃ composites as well as the matrix/filler interface were evaluated. The results showed that Shore D hardness of PP/CaCO₃ composites is slightly affected by the variation of particles size of the filler. However, the Izod impact strength of the composites decreased remarkably with the increase in the filler content and particle size. The characterization of polymer/filler interphase revealed the presence of a bound polymer layer on calcium carbonate surface which persisted even after a prolonged extraction in xylene. In addition, the amount of polypropylene chains adsorbed on filler surface is greater for small size particles than for large particles.

© 2020 mbmscience.com. All rights reserved.

Introduction

A composite material is generally composed of matrix (polymers, metals, ceramics, etc.) in which a filler or reinforcement (fibers, particles, etc.) is dispersed. Despite the original purpose to reduce cost, a judicious selection of the fillers, having different properties to polymers, can produce composite materials with enhanced properties for a given use. In some cases, particulate fillers are essential to develop acceptable properties of the matrix for most applications such as modulus and heat distortion temperature [1, 2]. Polymers and polymer-based composites are extensively used in various applications such as aircrafts, civilian structures, marine structures, oil and gas platforms, electronic packaging and encapsulations, satellite devices, and recently as smart materials [3-7]. Reinforced polymers are now offering a better alternative to carbon steel due to their lightness (about 30% to 70% lighter than carbon steel), their stealth capability and more importantly, their fatigue accumulation which is 4 to 7 orders of magnitude slower than in metals [8, 9]. Within polymer-based composites, the matrix and the filler particles are constantly in interaction resulting in the forma-

tion of an interphase having a specific thickness and properties (Fig.1) [10]. This interfacial interaction, which varies from strong to weak depending on the affinity matrix- filler, governed almost all the properties of the resulting composite [11].

The amount of adsorbed polymer, called “bound polymer” (Fig. 2), is primarily a function of the available surface area, surface characteristics of the filler, available reactive sites on the polymer backbone and finally processing conditions which cause the formation of primary bonding between the polymer molecules and filler particles [13].

Because filler particles size and shape are critical factors in the processing and final properties of polymer composites, the present study was devoted to the investigation of the effect of filler particle size on mechanical properties (hardness, impact toughness) and viscosity of composites based on polypropylene and calcium carbonate. The analysis of the interphase at the boundary matrix/filler was also conducted. Polypropylene (PP) was used as matrix because of its low price and its useful properties like excellent chemical resistance, high heat distortion temperature, transparency, flame resistance, dimensional stability and its great capacity to accommodate with several filler types [14, 15].

✉ * Corresponding author: Souad Djellali
souad.djellali@univ-setif.dz

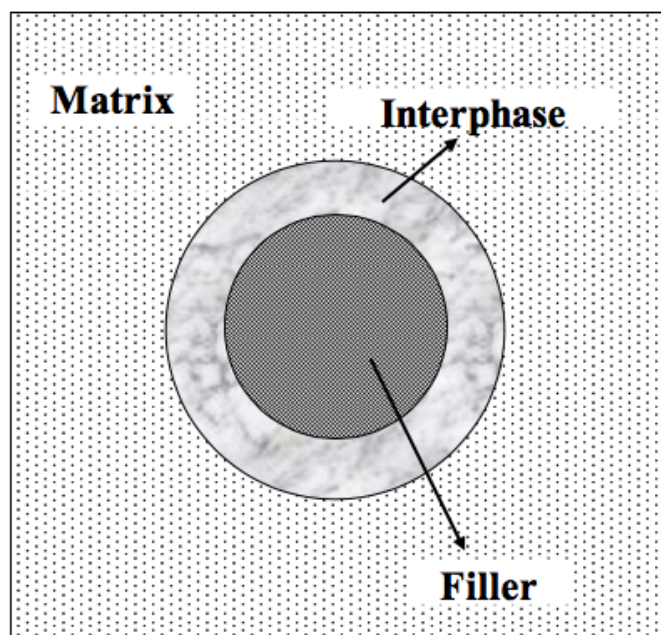


Fig. 1. Interphase polymer/filler in polymeric composites [4].

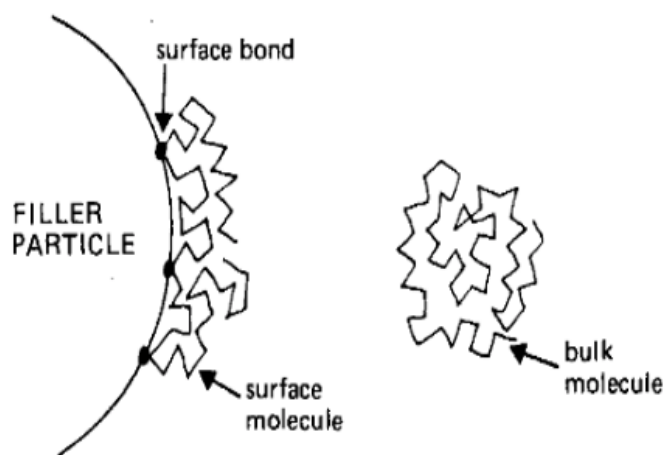


Fig. 2. Representation of a polymer chain bound to a filler particle surface and a polymer chain in the bulk (not bound) [12].

Experimental

Materials

The matrix used in this study is a homopolymer polypropylene (STAMYLAN P 17M10) with a MFI of 4.5 (190 °C, 2.16 Kg) and a melting temperature of 165.6 °C. The filler is calcium carbonate (CALCILIT®) with particles size distribution varying in the range 0–180 µm. The most important characteristics of this filler are given in Table 1.

Table 1. Characteristics of Calcium carbonate (CaCO₃).

Trade name	Particle size (µm)	Density	Specific surface area (m ² /g)	Humidity (%)
Calcilit® G	< 180	1.2	0.5	< 0.3

Four ranges of filler particle sizes were obtained by mean of a sieve shaker type RETSCH®. Sieving was carried out during 1 hour at a speed of 60 tr/s using various sieve sizes (180 µm, 125 µm, 63 µm, 45 µm and 32 µm). Tables 2 and 3 give details on these particles and samples compounding.

Table 2. Filler codes according to particle size (Sieve hole).

Size range (µm)	32–45	45–63	63–125	125–180
Code	S32	S45	S63	S125

Sample preparation

Different compositions were used to prepare polypropylene–CaCO₃ composites. For each particle size range, five weight fractions, ranging from 10 to 50%, were chosen (Table 3). Prior to mixing, calcium carbonate was dried overnight at the oven at a temperature of 120 °C.

The composites were prepared in melt using a single screw extruder (Brabender Type 19/25D) with die temperature of 190 °C. The temperatures of the three different zones of the extruder were (in order): 170 °C, 180 °C and 190 °C. Samples for hardness test and impact test were prepared by compression molding at 190 °C using a hydraulic press type Davenport 25TC.

Hardness test

Hardness of elaborated materials was evaluated on smooth and uniform surfaces using a SHORE D hardness durometer according to ASTM D2240 (DIN 53/505). Each formulation was tested at different areas and the hardness was determined as the mean value of six measures.

Impact test

Izod impact tests on unnotched and notched rectangular test bars were carried out using CEAST RESIL impact tester according to ASTM D256. The impact machine is equipped with a pendulum hammer of 7.5 joules. Ten samples were tested for each composition and the average value is reported. All the tests were performed at ambient temperature.

Table 3. PP–CaCO₃ Composites composition.

PP (wt%)	100	90	80	70	60	50
PP (vol%)	100	92.23	84.06	75.47	66.42	56.87
CaCO ₃ (wt%)	0	10	20	30	40	50
CaCO ₃ (vol%)	0	7.77	15.94	24.53	33.58	43.13

Izod impact strength (acU), expressed in kilojoules per meter square, is calculated using the following equation (1).

$$a_{cU} = \frac{W}{h \cdot b} \times 10^3 \quad (1)$$

with :

W [J] : Energy absorbed by the sample at the fracture;

h [mm] : sample thickness;

b [mm] : sample width.

Melt flow index (MFI)

MFI measurements of PP/CaCO₃ composites were performed using a melt indexer (MELT Flow Rate Apparatus) according to ASTM 1232 (2.16 kg/190 °C). For each formulation, at least 6 extrudates were cut at regular intervals and weighed; the average value is then reported.

The melt flow index is obtained using the equation (2).

$$MFI (190^\circ C) = \frac{600 \cdot m}{t} \quad (2)$$

Where :

MFI : Melt Flow Index [g/10 mn]

m : Mass extruded [g].

t : Time required to the extrusion of the mass m [s].

Filler/polymer interactions

Small amounts of PP/CaCO₃ composites prepared with the smallest filler particle size (range S32) and the widest one (range S125) were analyzed. Samples of filled polypropylene were extracted in boiling xylene for 8 hours using a soxhlet to dissolve the polymer not bound to the filler. The remaining material (filler/bound polymer) was dried at 100°C under vacuum for 24 hours, cooled to room temperature in a desiccator then weighted. Polymer concentration in each composition was then determined by incineration the polymer at 500°C in furnace.

Results and discussions

Shore D Hardness

The effect of CaCO₃ particle sizes and content on the hardness (Shore D) of polypropylene/calcium carbonate composites is shown in Fig. 3. The hardness values of the various compositions of PP (filled and unfilled) exhibit little changes when the filler is added. However, the enhancement of the hardness observed with increasing filler content is more important for large particles than for small particles. This improvement can be attributed to the hardness of the filler itself and to the fact that the particles of the filler may act as nucleation centers for PP chains during the crystallization process, leading to an increase in the number of spherulites [16] which provide to the polymer matrix a higher surface stiffness.

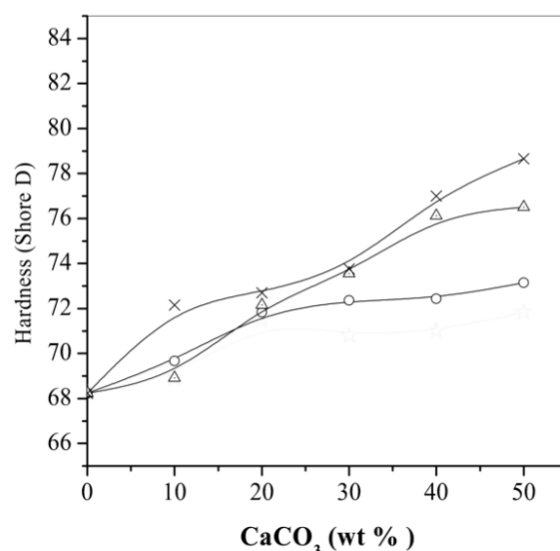


Fig. 3. Variation of Shore D hardness of PP-CaCO₃ composites with content and particle size of CaCO₃. S32 (■); S45 (●); S63 (▲); S125 (▼)

Impact strength

The variations of Izod impact strength of the unnotched and notched specimens of PP-CaCO₃ composites as a function of the filler content and particle size are illustrated in Fig. 4 and 5. It is observed that the strength of these particulate–polymer composites depend strongly on the particle size and particle loading [17,18]. For unnotched composites bars (Fig. 4), a little improvement of strength is noticed for low concentrations of the filler, up to 20 wt%, for all ranges of filler sizes, followed by a decrease when the filler contents increase. This observation is in agreement with results of some authors [19] who stated an improvement in the impact resistance for low concentrations of fillers, especially those characterized by very small particles. However, for notched specimens, the variation of PP-CaCO₃ composites resilience (Fig. 5) exhibits a different behavior. The strength of unfilled polypropylene decreases significantly after addition of the filler; however, smaller calcium carbonate particles provide higher strength of filled polypropylene composites at a given particle loading.

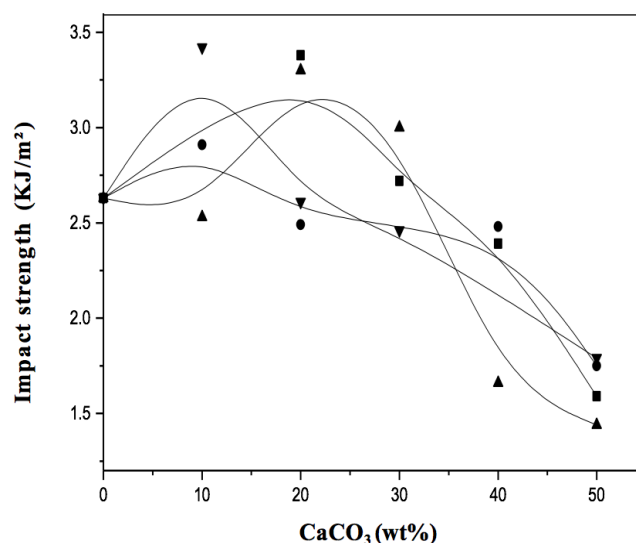


Fig. 4. Effects of particle size and content of the filler on the fracture toughness of unnotched PP/CaCO₃ composites. S32 (■); S45 (●); S63 (▲); S125 (▼)

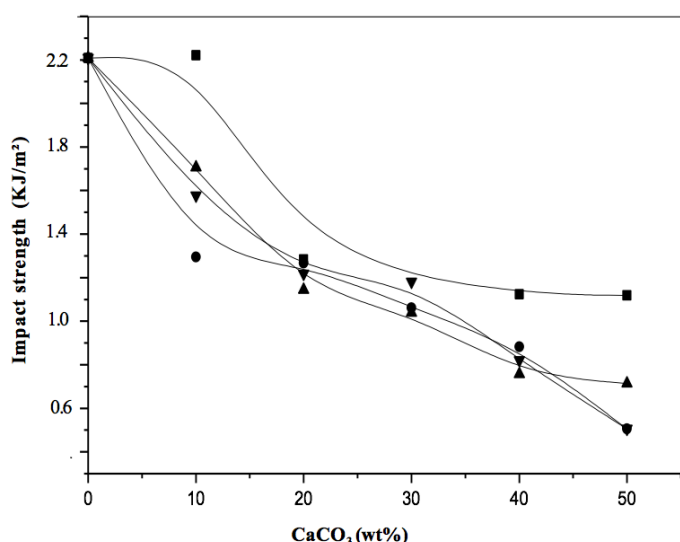


Fig. 5. Effects of particle size and content of the filler on the fracture toughness of notched PP-CaCO₃ composites. S32 (■); S45 (●); S63 (▲); S125 (▼)

The degradation of the impact strength of unnotched and notched samples of PP-CaCO₃ materials may be attributed to the mechanical properties of the filler, characterized by rigidity, high modulus of elasticity and almost no elongation which causes a weakening of the composite [20]. In addition, the interactions between polymer chains and particle surfaces restrict the macromolecular motion and hence the impact energy absorption, as compared to free polymer chains in the bulk (far from the particle surface) [21].

Melt flow index (MFI)

Results of the melt flow index (MFI) measurements of PP-CaCO₃ composites are reported in Fig. 6 which shows that MFI values of elaborated polypropylene composites decrease with increase in the concentration and particle size of the filler.

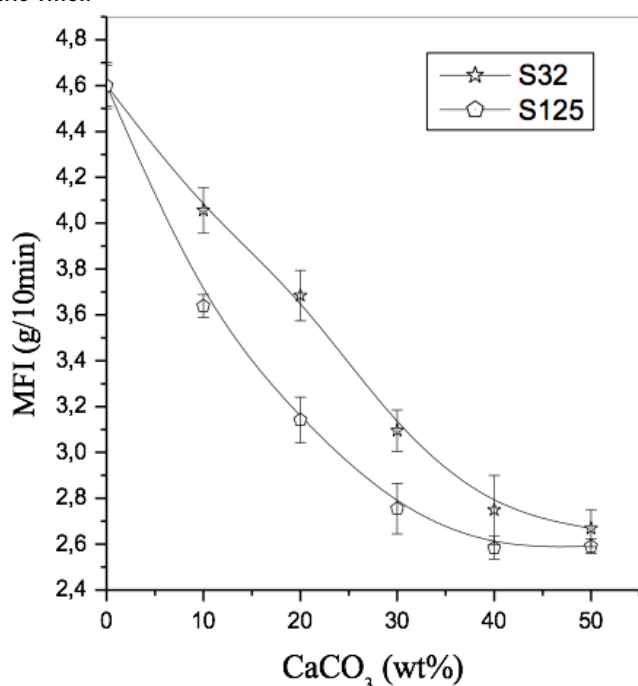


Fig. 6. Effect of calcium carbonate particle size and content on the melt flow index PP-CaCO₃ composites.

It is well known that the melt flow index varies inversely with the viscosity of polymers, so it may be concluded that the inclusion of fillers into PP matrix leads to an increase in the viscosity of the resulting composites. This result is attributed to the replacement of the matrix flexible chains with more rigid calcium carbonate particles which hinder the mobility of chain segments in the melt and consequently increased the value of the viscosity [22]. In addition, the melt flow index of PP-CaCO₃ exhibits more reduction with increase in particle size for a same content.

Interphase properties

A polymer-based composite is considered as a tri-phasic system consisting of a continuous phase (polymer), a dispersed phase (filler) and an interphase. The adsorption of polymer chains on the surface of the filler particle results in the creation of a “bound polymer layer” on the particle surface. This layer is insoluble even after prolonged extraction in a suitable solvent [23, 24]. In the present work, the properties of the interphase PP-CaCO₃ was evaluated through the determination of the effective concentration of the filler after mixing and the amount of adsorbed polymer chains on the filler surface resulting from the interactions at the boundary matrix/filler.

Effective filler content in composites

The composites prepared were incinerated in order to evaluate the effective percentage of the filler in the different samples and the mass losses of the filler during the mixing operation. The results are reported in Table 4 which reveals that the filler losses during the processing are not significant, except for higher concentrations. This step is important for the determination of the amount of the bound polymer.

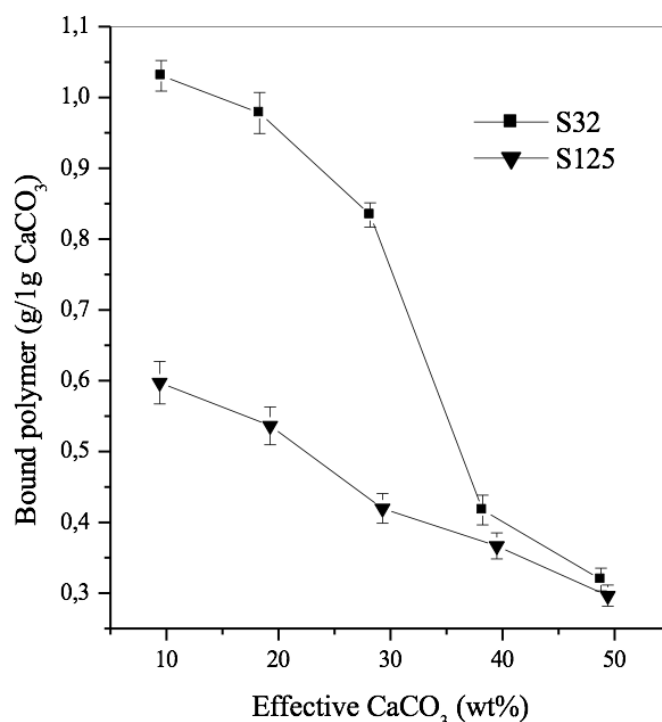


Fig. 7. Effect of calcium carbonate particle size and content on the bound polymer amount in PP-CaCO₃ composites.

Table 4. Effective content of calcium carbonate (remained in samples after incineration).

CaCO ₃ initial (wt%)	CaCO ₃ remained (wt%)	
	S32	S125
10	9.53 ± 0.05	9.39 ± 0.07
20	18.30 ± 0.07	19.26 ± 0.05
30	28.18 ± 0.03	29.29 ± 0.03
40	38.21 ± 0.9	39.48 ± 0.08
50	48.79 ± 0.1	49.40 ± 0.02

Bound polymer

Fig. 7 shows the variation of the amount of bound polymer as a function of the effective filler content. It is observed that the amount of bound polymer decreased with increasing filler concentration, indicating that the thickness of the bound polymer is higher when there is an excess of free polymer chains [25].

At elevated contents of the filler, important particle-particle contact leads to aggregation and therefore only a part of the surface area of the primary particles is available for polymer absorption [26]. Furthermore, the comparison of results obtained for S32 and S125, reveals that small amounts of the fine filler are capable to adsorb nearly 2 times the amount of polymer chains than the coarse filler for equal content. It is, hence, evident from the figure 7 that the bound polymer thickness is dependent on the concentration and the size of the filler. In general, the thickness of bound polymer layer formed on the filler particle surface is in order of nanometers and is resistant to dissolution even in a good solvent [27].

The formation of the bound polymer layer of polypropylene on calcium carbonate particles despite their incompatible behavior may be attributed to the presence of structural defects in the polymer and the possible formation of carboxyl groups on the polymer chains during mixing leading to chemical interactions at the boundary matrix/filler [25, 28].

Conclusion

Polypropylene–calcium carbonate powder composites were prepared and characterized by mechanical tests (hardness, impact), rheological test (MFI) and their interphase properties were investigated. From the results obtained, it can be concluded that the hardness of polypropylene was slightly improved when the filler is incorporated. In contrast, the impact strength and the melt flow index of PP were considerably affected by the content and particles size of the filler. Direct evidence of bound polymer layer formation was obtained after the extraction of the filled polymer with boiling xylene which gives an insolubilised fraction. The amount of the bound polymer deduced from this insoluble fraction was found to decrease significantly with increase in the filler content. In addition, the smaller the particle size the greater the bound polymer amount.

References

1. Rotheron, R., ed. Particulate-filled polymer composites. Rapra Publishing, Shawbury, 2003.
2. Fu, S. Y., Feng, X. Q., Lauke, B., Mai, Y. W. (2008). Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites. *Composites Part B: Engineering*, 39(6), 933–961.
3. Pendhari, S. S., Kant, T., Desai, Y. M. (2008). Application of polymer composites in civil construction: A general review. *Composite structures*, 84(2), 114–124.
4. Koniuszewska, A. G., Kaczmar, J. W. (2016). Application of polymer based composite materials in transportation. *Progress in Rubber, Plastics and Recycling Technology*, 32(1), 1.
5. Ngo, I.-L., Jeon, S., Byon, C. (2016). Thermal conductivity of transparent and flexible polymers containing fillers: A literature review. *International Journal of Heat and Mass Transfer*, 98, 219–226.
6. Liu, Y., Du, H., Liu, L., Leng, J. (2014). Shape memory polymers and their composites in aerospace applications: a review. *Smart Materials and Structures*, 23(2), 023001.
7. Charca, S., Shafiq, B., Just, F. (2009). Repeated slamming of sandwich composite panels on water. *Journal of Sandwich Structures & Materials*, 11(5), 409–424.
8. McGeorge, D.; Vredeveltdt, A. W. Mode I fracture toughness of secondary bonds of a novel CFRP hull structure”, In: Williams, J. G.; Pavan, A., editors. *Eur Struct Integrity Soc: Elsevier*; 2000. p. 83–96
9. Boyd, S. W., Blake, J. I. R., Shenoi, R. A., Kapadia, A. (2004). Integrity of hybrid steel-to-composite joints for marine application. *Proceedings of the Institution of Mechanical Engineers, Part M: Journal of Engineering for the Maritime Environment*, 218(4), 235–246.
10. Lipatov I. S., Lipatov, Yu. S., Polymer reinforcement, ChemTec Publishing, Toronto, 1995.
11. DeArmitt C., Rotheron R. (2017) Particulate Fillers, Selection, and Use in Polymer Composites. In: Rotheron R. (eds) *Fillers for Polymer Applications. Polymers and Polymeric Composites: A Reference Series*. Springer, Cham
12. Kendall, K., Sherliker, F. R. (1980). Effect of polymer molecular weight on colloidal reinforcement. *British Polymer Journal*, 12(3), 111–113.
13. Akay, G. (1990). Flow induced polymer-filler interactions: Bound polymer properties and bound polymer-free polymer phase separation and subsequent phase inversion during mixing. *Polymer Engineering and Science*, 30(21),

- 1361–1372.
14. Chacko, V. P., Farris, R. J., Karasz, F. E. (1983). Tensile properties of CaCO₃ filled polyethylenes. *Journal of applied polymer science*, 28(9), 2701–2713.
 15. Shubhra, Q. T., Alam, A., Quaiyyum, M. (2011). Mechanical properties of polypropylene composites. *Journal of Thermoplastic Composite Materials*, 26(3), 362–391.
 16. Long, Y., Shanks, R. A., Stachurski, Z. H. (1995). Kinetics of polymer crystallisation. *Progress in Polymer Science*, 20(4), 651–701.
 17. Lau, K. T., Gu, C., Hui, D. (2006). A critical review on nanotube and nanotube/nanoclay related polymer composite materials. *Composites Part B: Engineering*, 37(6), 425–436.
 18. Zhu, Z. K., Yang, Y., Yin, J., Qi, Z. N. (1999). Preparation and properties of organosoluble polyimide/silica hybrid materials by sol–gel process. *Journal of Applied Polymer Science*, 73(14), 2977–2984.
 19. Houshyar, S., Shanks, R. A. (2007). Mechanical and thermal properties of toughened polypropylene composites. *Journal of applied polymer science*, 105(2), 390–397.
 20. Chawla, K., *Composite Materials*, Springer, New York, 1998.
 21. Stickney, P. B., & Falb, R. D. (1964). Carbon black-rubber interactions and bound rubber. *Rubber Chemistry and Technology*, 37(5), 1299–1340.
 22. Shenoy, A.V., *Rheology of Filled Polymer Systems*, Springer, New York, 1999.
 23. Oberdisse, J. (2006). Aggregation of colloidal nanoparticles in polymer matrices. *Soft matter*, 2(1), 29–36.
 24. Jiang, N., Endoh, M. K., Koga, T., Masui, T., Kishimoto, H., Nagao, M., Taniguchi, T. (2015). Nanostructures and dynamics of macromolecules bound to attractive filler surfaces. *ACS Macro Letters*, 4(8), 838–842.
 25. G. Akay, F. Cimen, and T. Tincer, in *Polymer Processing and Properties*, p. 61, G. Astarita and L. Nicolais, eds., Plenum, New York (1984).
 26. Kendall, K., Sherliker, F. R. (1980). Colloidal reinforcement: the influence of bound polymer. *British Polymer Journal*, 12(3), 85–88.
 27. Heinrich, G., & Vilgis, T. A. (1995). Physical adsorption of polymers on disordered filler surfaces. *Rubber Chemistry and Technology*, 68(1), 26–36.
 28. Porter, R. S., & Casale, A. (1985). Recent studies of polymer reactions caused by stress. *Polymer Engineering & Science*, 25(3), 129–156.

Conflicts of interest

Authors declare no conflict of interests.

Notes

The authors declare no competing financial interest.

Materials & Biomaterials Science

This is an open access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

How to cite this article

S. Djellali, L. Djahnit, H. Ferkous. Influence of Particle Size and Bound polymer on the Mechanical and Rheological Properties of Polypropylene/Inorganic Powder Composites. *Materials and Biomaterials Science* 03 (2020) 040–045.