

THERMAL, PHYSICAL AND MECHANICAL PROPERTIES OF COMPOSITE POLYOXYMETHYLENE / CALCIUM CARBONATE (POM/CaCSQO₃)

Submitted on 29/01/2020 – Accepted on 24/05/2020

Abstract

Polymers may replace advantageously the traditional materials of structure. We can distinguish among others their lightness, their moderate cost, their various processes which allow to implement and to shape them simultaneously. In the thermoplastic polymers case numerous are their peculiarities which make them interesting. The majority of studies of the thermoplastics and their composites become only attached to their mechanical properties; their behavior is more complex and establishes an obstacle major which requires more thorough studies. Our objective is the incorporation of a mineral filler the CaCO₃ in the polyoxymethylene (POM) in the context of the development of a new composite material and to define its thermals, physical and mechanicals properties.

So, our work consists in studying the thermals, physical and mechanicals properties of the composite Polyoxymethylene / CaCO₃.

Keywords: thermal, physical and mechanicals, properties, Polyoxymethylene, CaCO₃.

L. LATRECHE *
N. HADDAOUI

Laboratory of Physical
Chemistry of High Polymers
(LPC HP), University Ferhat
Abbas Setif 1, Algeria.

* karilatrech@gmail.com

INTRODUCTION

The polyoxymethylene is a polymer also called POM according to the standard ISO. It exists either under copolymer (CPOM), or homopolymer (HPOM) shape, both forms differ little. The POM is an opaque semicrystalline polymer and its natural color is white but it is often colored. The homopolymer shape presents slightly better mechanicals characteristics. It is marketed in various granules; the average thickness of a granule is about 3 mm [1, 2]. The polyoxymethylene is one of the most important and widely used thermoplastics, filled with rigid inorganic fillers such as calcium carbonate to create high stiffness and modulus and/or to reduce the cost. Moreover, the development of POM and its composites or blends will improve thermal, physical and mechanical properties and allow a high percentage of use in different sectors [3-5].

CaCO₃ is one of the important fillers used in the industries of plastics, rubber and paint. One of the most problematic issues for the use of CaCO₃ is its hydrophilic property. Calcium carbonates are white, not toxic, insoluble powders in the pure water, but dissolve in the water charged of CO₂ gas. Calcium carbonates represent the most used filler on the plastic sectors [6]. A surface treatment of the calcium carbonate is essentially made to reduce the superficial tension and improve the dispersal of filler in the matrix. The modification of the surface by surfactants has been extensively studied. For example, the surfactants containing reactive functional groups such as silane coupling agents, titanate coupling agents or stearic acid [7-10] can all improve the hydrophobic properties of CaCO₃.

2. EXPERIMENTAL PROCEDURE:

2.1. Materials:

-**Polymer:** The polymer used in this study was polyoxymethylene, it was supplied by Dupont de Nemours under the name Delrin HPOM it is a commercial granular homopolyoxymethylene, It has a density of 1.42 g/cm³ and a melting flow index (MFI) of 1.70g/10 min, its melt temperature is about 165°C.

- **Fillers:** We used three different fillers: Calcium carbonate (CaCO₃) used were provided by the Tunisian Society of Industrial Calcium Carbonate (STICC). Having been used in two different sizes, the corresponding trade names are HERMACARB 2FT and HERMACARB 5FN. The calcium carbonate (CaCO₃) provided by STICC sold under the designation Hermacarb 2FT is a treated filler micronized with high purity and whiteness, while the calcium carbonate (CaCO₃) sold under the name Hermacarb 5FN is untreated filler and characterized by its whiteness and purity, we treat the 5FN with stearic acid [5] and we called it (5FT) (Table 1).

Table 1: The chemical composition of CaCO₃, chemical analysis by X-ray diffraction revealed the following capacities for both types:

Name	Symbols	Weight composition (%)
Calcium carbonate	CaCO ₃	99,92
Magnesium oxide	MgO	0,04
Titanium Dioxide	TiO ₂	0,02
Potassium oxide	K ₂ O	0,01
Iron oxide	Fe ₂ O ₃	0,01

Both varieties of calcium carbonate used mainly differ by their size. The physical properties of each type are as follows:

Table 2: The physical properties of the fillers:

Parameter	values for 2FT	values for 5FN
Moisture %	0,10	≤0,20
Density: g/cm ³	2,60	2,70
Average diameter of particle microns	2	5

2.2. Preparation of composite POM/CaCO₃:

CaCO₃ was dried in an oven at 100 °C for 24 hours to ensure removal of moisture before using and premixed with POM, then specimens were prepared by melt mixing in a brabender plasticorder at a rotor speed of 60 rpm, at the temperature of 190 °C. After that the composite was granulated into pellet by using granulator, then pellets were put into the mould and pressed at 25 bars during 8 minutes at moulding temperature of 190 °C. Weight compositions used of POM / CaCO₃ were : (97.5/2.5, 95/5, 90/10, 85/15, 80/20, 75/25, 70/30).

3. CHARACTERIZATIONS:

3.1. Thermal Characterization:

3.1.1. Heat distortion temperature (HDT):

The HDT was obtained in accordance with ASTM D648, which describes HDT as the temperature where a specimen (3 x 13 x 127 mm³) deflects by 0.25 mm under 1.8 MPa while heated in an oil bath at a rate of 2 °C/min. At least 5 specimens were tested and the average value was used for the data plot.

3.1.2. Vicat softening temperature:

Vicat softening temperature tests (VST) were used to determine the softening temperature of the material. A

Zwick Vicat softening temperature tester at 50 N force and 5 °C/min heating rate was used to determine temperature at which the indenter penetrates 1 mm into the material. At least 5 specimens were tested and the average value was used for the data plot.

3.2. Physical Characterization: Density measurement:

Density is measured with a pycnometer by weighing a substance, usually in the liquid state, that is placed in the device and fills the pycnometer to a mark on its neck or to the upper edge of a capillary tube, corresponding to the nominal volume of the pycnometer. The major advantages of the pycnometric method for the determination of density are high accuracy of measurement (to 10⁻⁵ g/cm³).

3.3. Mechanical Characterization:

3.3.1. Hardness «Shore D»:

The test procedure followed ISO / 869, on a typical durometre D which is intended for the hard polymers. The test consists in applying to samples of (50/50/3 mm³) in dimensions a penetrator of 5 kg and then we read directly the sinking after 10 seconds. The measures are made in the room temperature; the results are given by the average of five values so obtained.

3.3.2. Tensile test:

The tensile properties were determined using dumbbell specimens of (115×12.7×3 mm³) in dimensions. The test was carried out using a universal testing machine with a crosshead speed of 10 mm/min. The test procedure followed ASTM D 638-72. From the experimental stress-strain curves, tensile properties (modulus of elasticity and elongation at break) of the composite were calculated at room temperature. Five specimens were tested and the average values were used for the data plot.

3.3.3. Notched Izod impact strength:

Izod impact strength properties were determined at room temperature with a CEAST 6546/000 machine provided with a 15 J pendulum according to the ASTM D 256-73, and using specimens of (63×12.7×3 mm³) in dimensions. Specimens were molded with a notch radius of 0.5 mm. The radius was chosen such that the tip of the notch was located in the residual compressive zone. At least five specimens were tested and the average value was used for the data plot.

4. RESULTS AND DISCUSSION:

4.1. Thermal properties:

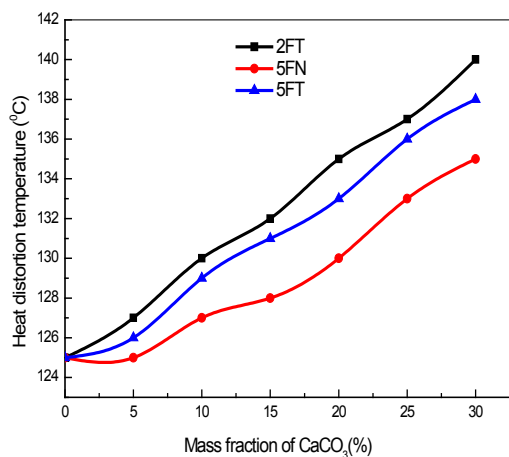


Figure 1: Heat distortion temperature of POM / CaCO₃ as a function of mass fraction of CaCO₃

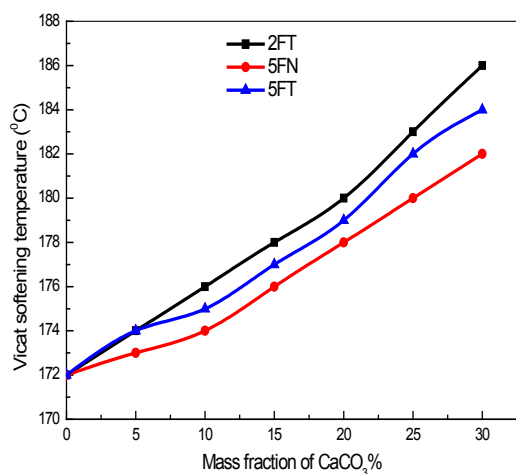


Figure 2: Vicat softening temperature of POM / CaCO₃ as a function of mass fraction of CaCO₃

The presence of filler changes the properties of the polyoxymethylene in the composite, it affects the molecular mobility and causes a certain order, the heat distortion temperature of POM/CaCO₃ (HDT) can be offset, reduces the ability of macromolecular chains to move against each other causing an increase in the vicat softening temperature. Thermal tests can give very different results, depending on the exchange rate of CaCO₃. Figures 1 and 2 show the variations of heat distortion temperature and the vicat softening temperature of the composite POM/CaCO₃ when we vary the rate of CaCO₃, thus varying the molecular mobility of polyoxymethylene in the composite. We noted that the heat distortion temperature, the vicat softening temperature gradually grow with the increase in the rate of CaCO₃ that may be due to the increase of the order so the crystallinity within the material, these figures also show that the temperature of heat distortion temperature (HDT) and the

vicat softening temperature of the composite POM/CaCO₃ are influenced by the size and the treatment of fillers.

4.2. Density measurement:

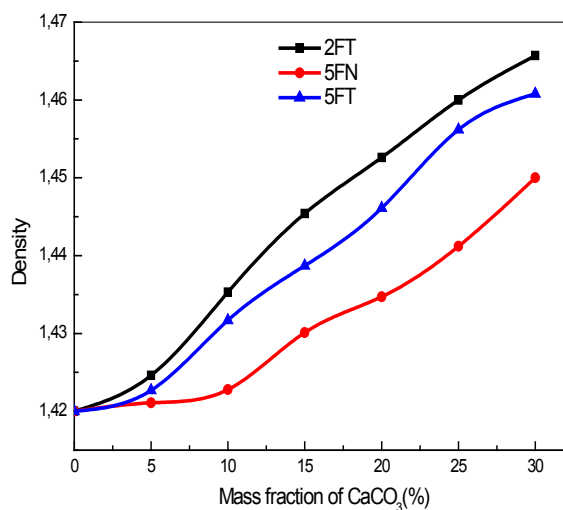


Figure 3: Density of POM / CaCO₃ as a function of mass fraction of CaCO₃

The Figure 3 shows the variations in the density of the composite POM/CaCO₃ when we vary the rate CaCO₃. Siegmann et al [11] without calculating the change in free volume, have speculated that the increase of heat distortion temperature (HDT) load being related to the decrease of the free volume. As the heat distortion temperature (HDT) and the density varied in the same way, the evolution of the (HDT) can be also partly due to the evolution of free volume with different heat treatments.

4.3. Mechanical properties:

4.3.1. Hardness «Shore D»:

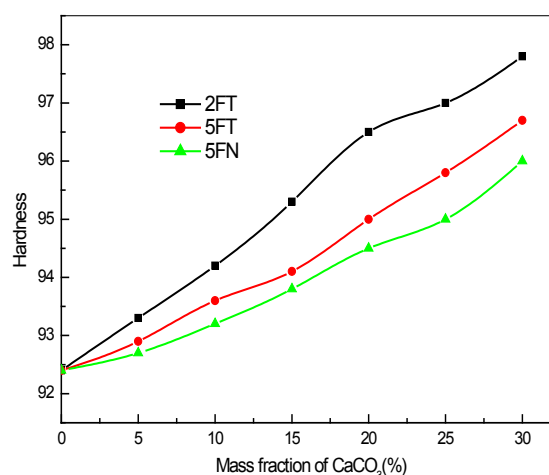


Figure 4: Hardness «Shore D» of POM / CaCO₃ as a function of mass fraction of CaCO₃

Changes in the Shore D hardness of the composite POM/CaCO₃ with the rate of CaCO₃ are presented in the Figure

4. As observed, the hardness increases with increasing rate of CaCO₃. For low rate of CaCO₃, the macromolecules are least reorganized, it induces an increase of the free volume which lowers the hardness and therefore low density (ρ). According Van Krevelen [12] the density (ρ) is connected to the elasticity modulus (E): $E \propto \rho^7$. This means that the samples have a lower density also have a lower modulus of elasticity, as can be seen on the figure 5. Structural changes were also demonstrated by measuring their mechanical properties, from figures 5 and 6, we can see that the values of the modulus of elasticity of composites increase with the increase in the rate of CaCO₃. The effect of particle size and filler treatment is also well marked. Shore D hardness and modulus of elasticity vary in the same direction and depend on particle size and filler treatment. Composites POM/ CaCO₃ (2FT and 5FT) with treated fillers present better thermals, physical and mechanicals characteristics than composites with untreated fillers (5FN). Shore D hardness, density, modulus of elasticity of various composites POM/ CaCO₃ increase with increasing of CaCO₃ rate.

4.3.2. Tensile test:

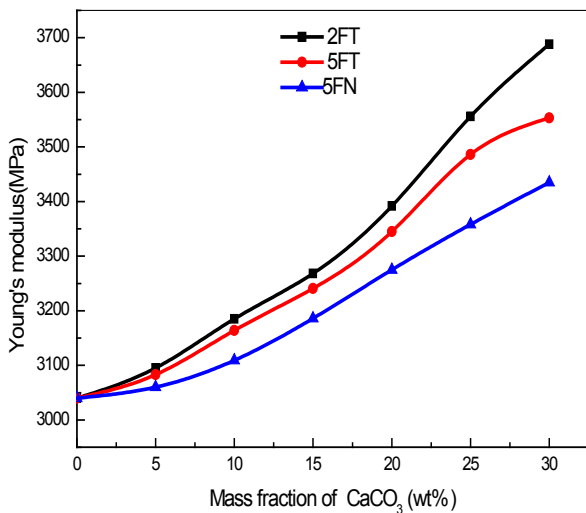


Figure 5: Modulus of elasticity of POM / CaCO₃ as a function of mass fraction of CaCO₃

Figure 5 shows that the young's modulus increases with the amount of CaCO₃ introduced into the polyoxymethylene matrix. This curve means that the known particle size of CaCO₃ and incompatibility between polyoxymethylene and CaCO₃ problems do not come into play until a mass fraction of 5 % of CaCO₃, modules change relatively little, it seems that the small amount of CaCO₃ doesn't affect the mechanicals characteristics of the polyoxymethylene matrix, so the POM which is clear and especially in majority imposes its properties [13, 14]. From the mass fraction around 6% of CaCO₃, the filler gradually gaining its strength characteristics and the young's modulus increase gradually. Figure 6 puts in evidence the variations of elongation at break of our composite with the rate of

CaCO₃ introduced and above shows the influence of the particle size (2FT and 5FT) and the treatment of fillers(5FN and 5FT).

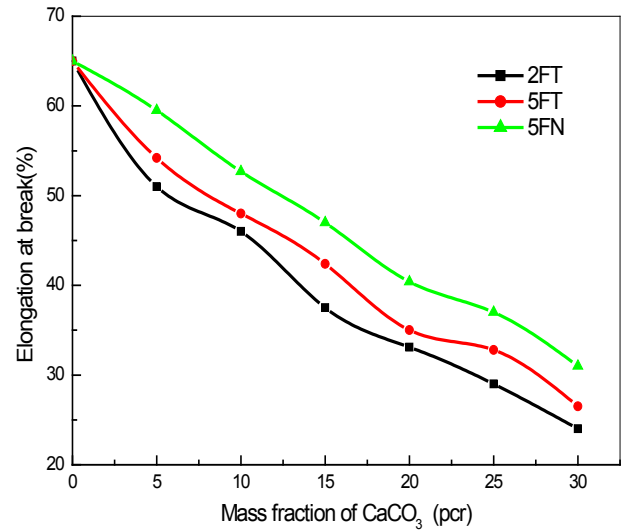


Figure 6: Elongation at break of POM / CaCO₃ as a function of mass fraction of CaCO₃

4.3.3. Notched Izod impact strength:

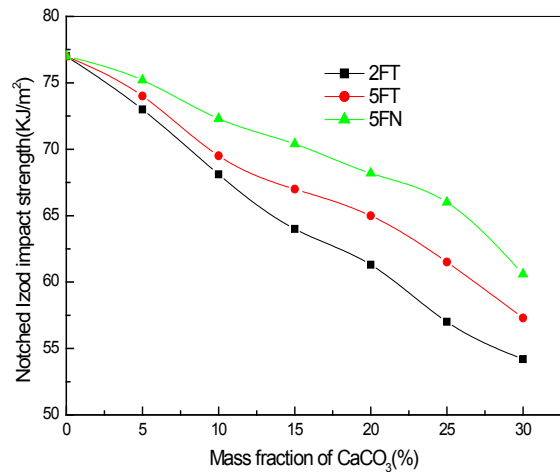


Figure 7: Notched Izod impact strength of POM / CaCO₃ as a function of mass fraction of CaCO₃

Figure 7 shows the evolution of the notched Izod impact strength of the composite POM/ CaCO₃ with the rate of CaCO₃, this notched Izod impact strength decrease with the increase of CaCO₃. The influence of filler treatment (5FN and 5FT) and the particles size(2FT and 5FT) appear on all properties studied. The notched Izod impact strength of composite POM/ CaCO₃ for low rates of CaCO₃ increases which can be explained by an increased amount of amorphous therefore an increase in molecular mobility of this phase stage and therefore a reduction in

stiffness[14,15] . With high rates, it is observed that notched Izod impact strength of the composites decrease which can be attributed to the reduction of the molecular mobility of the amorphous phase reduced.

5. CONCLUSIONS:

The heat distortion temperature (HDT) and the vicat softening temperature gradually grow with the increase in the rate of CaCO₃ that may be due to the increase of the order so the crystallinity within the material.

A significant increase in the heat distortion temperature (HDT), the vicat softening temperature, density, Shore D hardness and young's modulus of the composite POM/CaCO₃ with increasing level of incorporation of the filler CaCO₃.

A relative decrease in elongation at break, notched Izod impact strength, this decrease which can be explained by an increased amount of amorphous therefore an increase in molecular mobility of this phase stage and therefore a decrease in rigidity.

The influence of treatment of the filler and the size of the particles appear on all properties studied.

6. REFERENCES:

- [1] F. Pardos. Polyacetals (POM). In : Plastiques. Paris : Techniques de l'ingénieur, AM 3385, 2002
- [2] W. Xu, P. P. He. Journal of Applied Polymer Science, 2001, 80,304
- [3] Z. Tinxu, X. Agen. European Polymer Journal, 1999, 35, 1901
- [4] Xiaodong .Wang, Xiuguo .Cui, European Polymer Journal 41(2005) 871–880
- [5] L. Latreche, N. Haddaoui, M. E. Cagiao, Revue Roumaine de Chimie 62,3(2017)267-276.
- [6] C. A. Naudin, C. Clozza, Charges. In : Plastiques et Composites. Paris : Techniques de l'ingénieur, A 3220, 2004
- [7] Z. Demjén, B. Pukánszky, Journal of Colloid and Interface Science. 190(1997) 427–436.
- [8] T. Nakatsuka, H. Kawasaki, K. Itadani, Journal of Applied Polymer Science. 27 (1982) 259–269.
- [9] T. Nakatsuka, H. Kawasaki, K. Itadani, Journal of Colloid and Interface Science. 82 (1981) 298–306.
- [10] L. Latreche ,N. Haddaoui, M. E. Cagiao ,Russian Journal of Applied Chemistry 89,10(2016)1713-1721.
- [11] A. Siegmann, A. Bouchman and S. Kenig, Polymer Engineering and Science, 22, (1982) 40-47 [12] DW .Van Krevelen. Properties of Polymers: Amsterdam, Elsevier (1972).
- [13] M. Arroyo, M. Ramos, M. Sanchez-Berna et J.P. Vigo Matheu, Journal of Polymer Engineering. 9(1990)85-104
- [14] V. Sabin-Chiarilli, J. Pabiot , European Polymer Journal 36(2000) 1387–1399
- [15] C. Albano, Journal of Composite Structures. 48 (2000) 49-58.