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Study of the Relative Variations of the Thermal Properties and Crystallinity of Blends (PP/EPR)/Calcium Carbonate

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Abstract

The objective of this paper is to investigate the relative variations of the constants of the thermal properties and the degree of crystallinity of the mixtures (PP/EPR)/Calcium carbonates elaborated with the Micro Bivis. We have strengthened the basic copolymer PP/EPR of a low level (5%) by three calcium carbonates models socal312, socal322v, Winnofil spm. We then subjected the different mixtures obtained, two cycles of a thermal loading under differential scanning calorimetry DSC. We finally focused on the thermal properties of isotactic polypropylene (T_{fP}, T_{cP}, ΔH_{fP}, ΔH_{cP}) and we calculated the degree of crystallinity of the mixtures. Reducing the energy cost of implementing mixtures is one of the objectives of this work. We quantified the relative variations of the above properties with those of the base copolymer. It shows that at a low loading rate of calcium carbonate, there is a decrease in the enthalpies of crystallization during the second exothermic cycle, with values that can reach 5.53 J/g_{PP} for the basic copolymer PP/EPR. During the second endothermic cycle, there is an overall increase in isotactic polypropylene melting temperature values for all the blends as well as for the basic copolymer PP/EPR. There is evidence that calcium carbonates are useful for lowering the melting energy of isotactic polypropylene, even at a low loading rate for the majority. The number of endothermic cycles accentuates this phenomenon which is linked to the presence in our composites, of a so-called confined amorphous phase.

Keywords

DSC, PP/EPR, $CaCO_3$, Crystallinity, Micro Bivis

1. Introduction

Future consumption trend of PP and its compounds showed an increase in the market demand [1]. The PP/EPR copolymer has its own properties [2]. In this state, it is not resilient enough to be used in applications such as the manufacture of automotive bumpers [3]. To compensate for this failure, it is therefore added calcium carbonates to treat superficially. Originally, the addition of mineral fillers to polymers [4] [5] [6] main objective was to reduce costs. Nano-inorganic fillers used in the semi-crystalline polymers are usually talc and calcium carbonate, but one uses also the mica and wollastonite [7]. In addition, the nano fillers are used to perform a functional role, such as increasing the rigidity or improving the dimensional stability of polymers [8] [9]. The substantial changes mixtures can generate unpredictable differences in the cost of implementation choice and properties of mixtures. It is shown that rates around 4% - 6% by volume of nanoscale particles of $CaCO_3$, promote the formation of β-type crystals, thus increasing the impact resistance of PP [4] [5] [10] [11].

The development of semi-crystalline polymers whose functional properties are optimized requires a good knowledge of the relationship between their mechanical behavior and their microstructure [12]. This microstructure is a function of the molecular parameters (molecular mass, crosslinking rate) and the shaping conditions and in particular the crystallization conditions. Semi-crystalline polymers have different structures on different scales. On a macroscopic scale, a semi-crystalline polymer can be considered as a homogeneous material where coexists one or more amorphous phases and crystalline lamellae. Detailed knowledge of the structure and mechanical properties of each of these phases are necessary to predict the macroscopic mechanical behavior of the material. In this study, knowledge of the model thermal properties allows good control of the behavior of mixtures based on the PP/EPR copolymer reinforced with calcium carbonate nanofillers. These mixtures are generally used for the production of automotive bumpers. The behavior of mixtures over two cycles of thermal loading is studied. Under these conditions, the polymer will have undergone thermodegradation. It is therefore important to know how these mixtures behave in a context where they are often subjected to several thermal loading cycles during processing and recycling operations.

A polymer chain is formed by the distribution of basic units called monomers. It can be linear or branched. On a microscopic scale, organizing chains in different ways can form either an amorphous polymer or a semi-crystalline polymer. The structure of semi-crystalline polymers is characterized by the coexistence of several phases: one or more amorphous phases and a crystalline phase [13]. The structure of a semi-crystalline polymer is formed from the crystalline zone where the molecular chains are ordered and the amorphous zone where the chains are disordered [12]. The crystallized zones are denser than the amorphous zones. The lamellae are generally 10 to 20 nm thick [13] [14], that is to say a thickness much less than the length of the macromolecular chains, which are

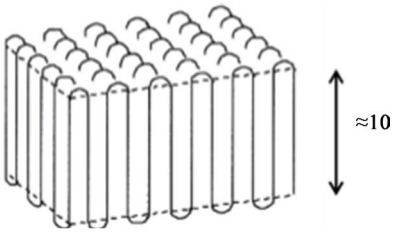

Figure 1. Chain folding model in a polymer single crystal [13] [15].

approximately 10 to 20 μm in length [15] [16] (**Figure 1**).

The same macromolecular chain can belong to both amorphous and crystalline zones [12]. They are the binding molecules which provide the bond between the crystalline zones. The thickness of the crystalline lamellae as well as of the interlamellar amorphous phase can be influenced by recrystallization conditions: the recrystallization temperature and the cooling rate.

This work is devoted to the study of the relative variations of the constants of the thermal properties and the degree of crystallinity of the mixtures (PP/EPR)/Calcium carbonates (95)/5 made at Micro Bivis. It is divided as follow: the first section is the present introduction, the second is methodology, the third is the discussion and the final section is the conclusion.

2. Methodology

2.1. Materials

The component characteristics of mixtures are: the copolymer PP/EPR used as template of mixtures is mainly a combination of the two components (predominantly propylene, ethylene) in different proportions. Commercially, this material is available in form of granules. A variety of additives processes, adapted to the conditions of implementation and use of the product, are introduced in the formulation of the material. Thus, the copolymer PP/EPR contains 22% extractable fraction EPR. In the present work, we used three types of calcium carbonates or fillers by adding the copolymer (PP/EPR).

Three types of calcium carbonates or fillers have been used and added to the copolymer (PP/EPR). They are the socal312, socal322v, Winnofil spm, marketed by the Solvay company. The incorporation of low mass rate not exceeding 15% for calcium carbonates modified fillers in the blend is more than enough to generate physical or chemical interactions required at the interface between the two phases of the mixture and which will be at the origin of good impact properties of the material [17].

Socal312 and socal322v are ultrafine, white and odorless coated precipitated calcium carbonate. They are used as a rheology control agent in PVC-underbody-car coatings, in printing inks as pigment-cost saving product leading to rheological control possibilities, and as an antisettling filler in solvent-based paints and lacquers. They provide high yield value and viscosity, pseudoplastic rheological behaviour and good adherance, and possesse a very high fineness, roundeal regular

crystals and the organic surface treatment. The last one is winnofil spm. It is an ultrafine coated precipitated calcium carbonate manufactured by a synthetic crystallization process. It is used as an extender in printing inks to provide improved tint and transparency. It offers a very good dispersibility and enhances the thixotropic properties; improve the slump resistance and rheological control. Winnofil reduces the pigment settling in undercoat and heavily filled solvent based paint. They are shown in **Table 1** [18] [19] [20].

2.2. Methods

For the Micro twin-screw-type "DSM Micro 15 Compounder", the parameters of mixtures on the micro twin screw are: mold temperature: 190˚C, speed: 100 tr/min, mixing mass introduced: 14 grams for 95/5 blends, the ring is collected after 15 minutes (≈6 grams) and the remainder after 30 minutes. For all DSC testing, the samples were subjected twice to the following thermal cycle: −100˚C to 200˚C with a temperature ramp of 10˚C/min with an isothermal hold at 200˚C for 2 minutes; 200˚C to −100˚C with a temperature ramp of −10˚C/min with an isothermal hold for 2 minutes at −100˚C. The sample temperature is continuously compared to the temperature of a reference. The sample and reference are placed in the same oven whose temperature varies linearly with time, ΔT (temperature difference between the sample and the reference) is then measured as a function of oven temperature. The reference is an empty capsule; Manipulation is done on scanning of an inert gas (argon) to avoid any reaction of material to be analyzed with oxygen. These measurements are performed using a DSC 30 de Mettler-Toledo SA system. The equipment is calibrated with indium, zinc and lead: the calibration check is done with indium (T_m = 156.6˚C ± 0.5˚C; ΔH = 28.45 J/g ± 0.5 J/g). Polymer pieces are set aside (<20 mg of product), and are introduced into a 40 µl aluminum capsule with a lid with a hole, and then weighed with a Mettler-Toledo balance with an accuracy of ±1 µg.

The torque variation of are shown in **Figure 2**.

In the case of a reinforcing or a mixture of polymers, the degree of crystallinity of the composite can be determined by the formula (Equation (1)) [15]:

Table 1. Socal312, Socal322v and Winnofil SPM main properties [18] [19] [20].

Property	Unit	Socal312	Socal322v	Winnofil SPM
$CaCO_3$ content	%	98.9	98.8	98.7
Mean particle diameter	micron	0.07	0.055	<0.1
Specific surface (BET)	m^2/g	19	25	20
Loss on drying (at 105˚C)	%	0.25	0.4	0.4
Coating content	%	2.9	3.3	2.7
Brightness	%	95.8	93.8	-
Yield value	Pa	160	180	-
Viscosity	Pa.s	2.4	2.4	-

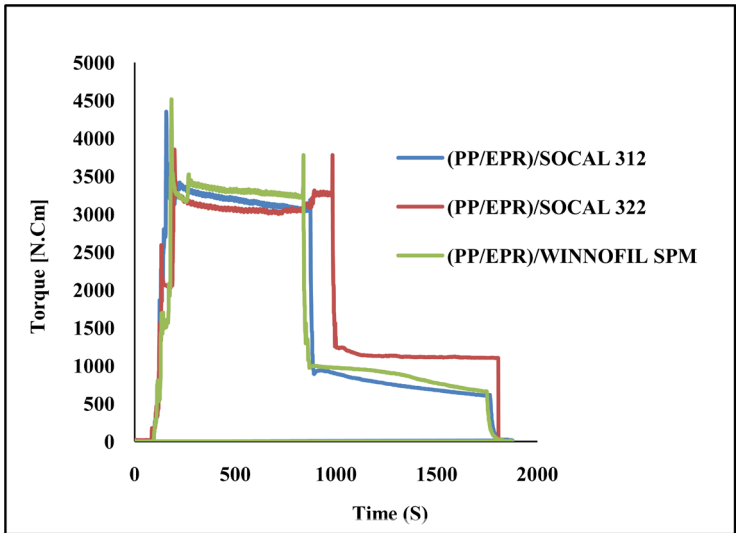

Figure 2. Torque variation of mixtures delivered by the Micro Twin screw [3].

$$\chi_{Com} = \frac{\Delta H_F}{\Delta H_F^0} * 100 \tag{1}$$

$\Delta H_F^0 = 209\,\mathrm{J/g}$ [21] [22], is the enthalpy of fusion of a sample of isotactic polypropylene, 100% crystalline in phase. The crystallinity level value of the polypropylene phase is normalized by Shoinaike *et al.* [23] below (Equation (2)):

$$\chi_{PP} = \frac{\chi_{Com}}{W_{PP}} \tag{2}$$

where W_{pp} is the mass fraction of *iPP* in composites.

3. Results and Discussion

3.1. Results

Figure 3 shows the DSC curves in the direction of the endothermic transformations of Components and (PP/EPR)/Calcium Carbonates (95)/5 Mixtures' developed micro twin screw; for the first thermal cycle; Figure 4 shows the DSC curves in the direction of the exothermic transformations of Components and (PP/EPR)/Calcium Carbonates (95)/5 Mixtures' developed micro twin screw; for the first thermal cycle. Figure 5 shows the DSC curves in the direction of the endothermic transformations of Components and (PP/EPR)/ Calcium Carbonates (95)/5 Mixtures' developed micro twin screw; for the second thermal cycle; Figure 6 shows the DSC curves in the direction of the exothermic transformations of Components and (PP/EPR)/Calcium Carbonates (95)/5 Mixtures' developed micro twin screw; for the second thermal cycle. Table 2 shows the local variations of the fusion enthalpies; Table 3, the local variations of the crystallinity rate of composites and *iPP*. Table 4 shows the variations in the values of the crystallization temperatures; Table 5 gives the variations of the values of the melting temperatures; Table 6 is devoted to changes in the values of crystallization enthalpies.

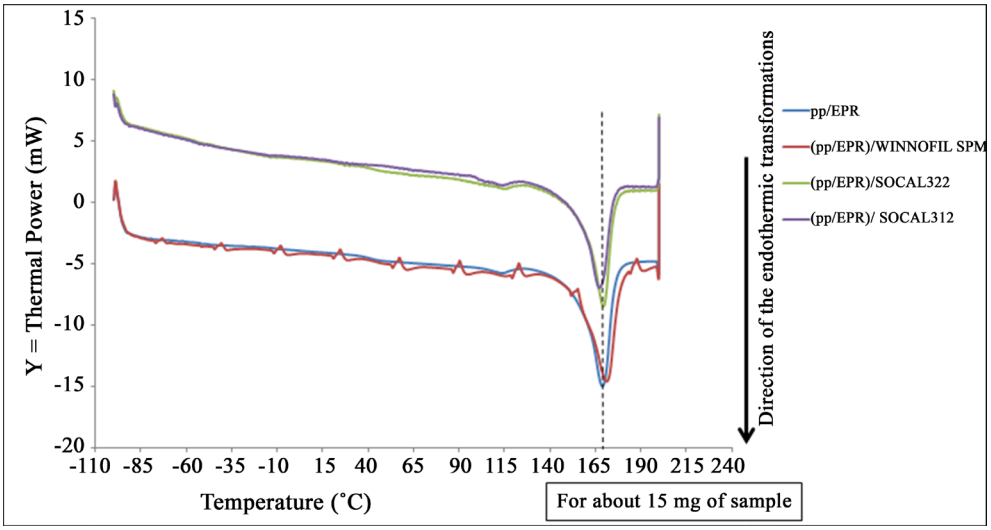

Figure 3. DSC curves in the direction of the endothermic transformations of Components and (PP/EPR)/Calcium Carbonates (95)/5 Mixtures' developed micro twin screw; for the first thermal cycle [17] [24].

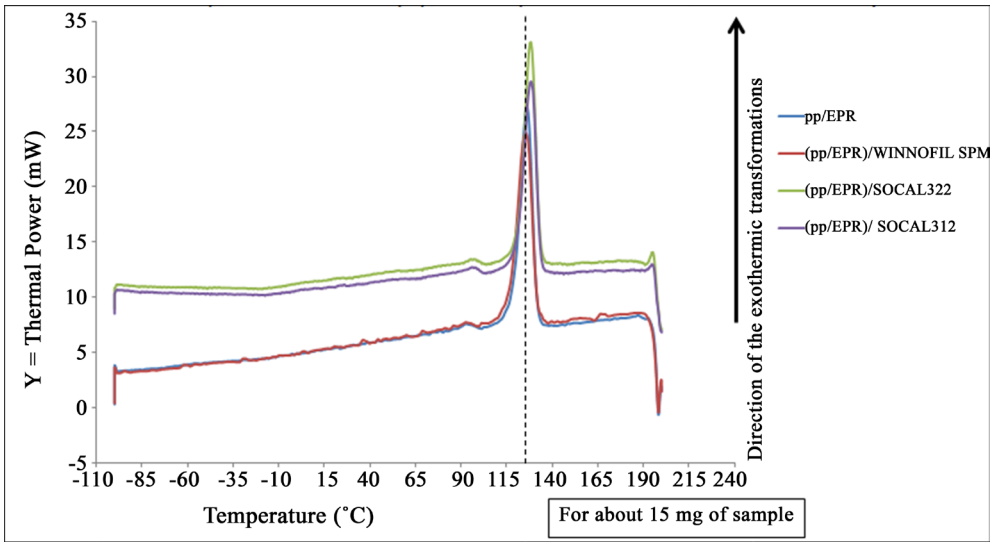

Figure 4. DSC curves in the direction of the exothermic transformations of Components and (PP/EPR)/Calcium Carbonates (95)/5 Mixtures' developed micro twin screw; for the first thermal cycle [17] [24].

Table 2. Local variations of melting enthalpies.

MIXTURES	First fusion		Second fusion		Effect of the Thermal Cycle
	ΔHfp (J/g_{PP})	$\delta\Delta Hf_{PP}$ (J/g_{PP})	ΔHfp (J/g_{PP})	$\delta\Delta Hf_{PP}$ (J/g_{PP})	$\delta\Delta Hf_{PP}$ (J/g_{PP})
(PP/EPR)	−95.34	-	−103.78	-	−8.44
(PP/EPR)/SOCAL312	−96.09	−0.75	−100.40	+3.39	−4.31
(PP/EPR)/SOCAL322V	−91.17	+4.17	−98.27	+5.51	−7.10
(PP/EPR)/WINNOFIL SPM	−86.81	+8.53	−92.19	+11.59	−5.38

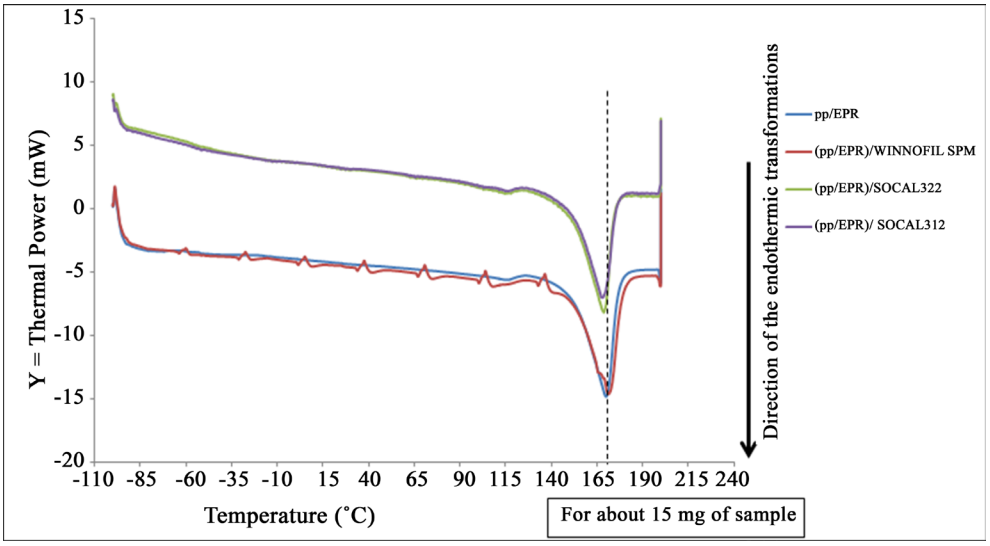

Figure 5. DSC curves in the direction of the endothermic transformations of Components and (PP/EPR)/Calcium Carbonates (95)/5 Mixtures' developed micro twin screw; for the second thermal cycle [17] [24].

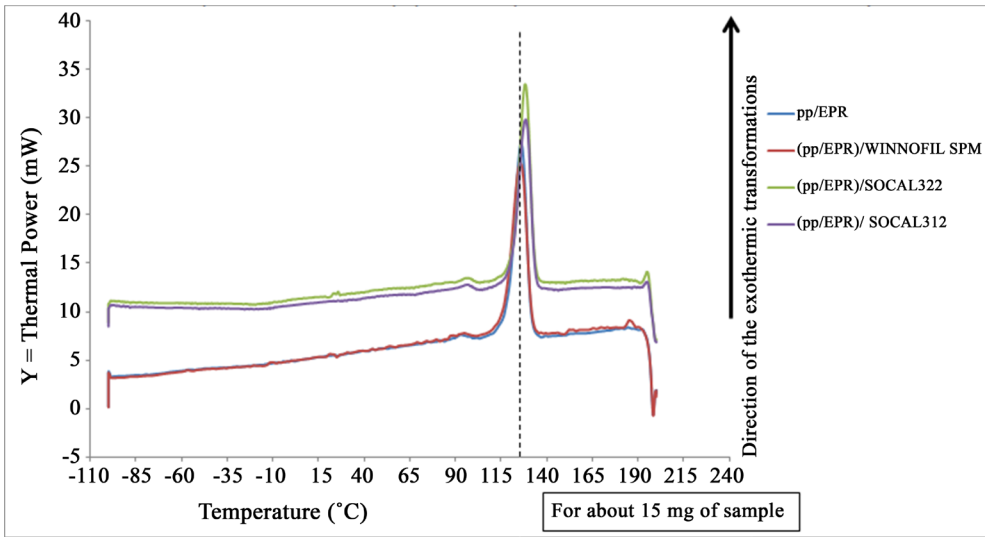

Figure 6. DSC curves in the direction of the exothermic transformations of Components and (PP/EPR)/Calcium Carbonates (95)/5 Mixtures' developed micro twin screw; for the second thermal cycle [17] [24].

Table 3. Local variations of crystallinity rate of composites and *iPP.*

MIXTURES	First fusion				Second fusion				Effect of the Thermal Cycle
	X_c (%)	δX_c1 (%)	X_{PP} (%)	$\delta X_{PP}1$ (%)	X_c (%)	δX_c2 (%)	X_{PP} (%)	$\delta X_{PP}2$ (%)	$\delta' X_{PP}$(%)
(PP/EPR)	45.62	-	58.48	-	49.66	-	63.66	-	+5.18
(PP/EPR)/SOCAL312	45.98	+0.36	58.94	+0.46	48.04	−1.62	61.58	−2.08	+2.64
(PP/EPR)/SOCAL322V	43.62	−2.00	55.92	−2.56	47.02	−2.64	60.28	−3.38	+4.36
(PP/EPR)/WINNOFIL SPM	41.53	−4.08	53.25	−5.23	44.11	−5.55	56.55	−7.11	+3.30

Table 4. Variations of values of crystallization temperatures.

MIXTURES	First crystallization		Second crystallization		Effect of the Thermal Cycle
	Tc (˚C)	δTc1 (˚C)	Tc (˚C)	δTc2 (˚C)	δTc (˚C)
(PP/EPR)	126.50	-	125.16	-	−1.34
(PP/EPR)/SOCAL312	127.50	+1.00	127.66	+2.50	0.16
(PP/EPR)/SOCAL322V	128.50	+2.00	127.66	+2.50	−0.84
(PP/EPR)/WINNOFIL SPM	125.50	−1.00	125.33	+0.17	−0.17

Table 5. Variations of values of melting temperatures.

MIXTURES	First fusion		Second fusion		Effect of the Thermal Cycle
	Tf (˚C)	δT_{f1}(˚C)	T_f(˚C)	δT_{f2} (˚C)	δT_f (˚C)
(PP/EPR)	168.50	-	170.5	-	+2
(PP/EPR)/SOCAL312	166.33	−2.17	168.00	−2.50	+1.67
(PP/EPR)/SOCAL322V	168.83	+0.33	169.66	−0.84	+0.83
(PP/EPR)/WINNOFIL SPM	170.83	+2.33	171.33	+0.83	+0.5

Table 6. Variations of the values of crystallization enthalpies.

MIXTURES	First crystallization		Second crystallization		Effect of the Thermal Cycle
	ΔHcp (J/g_{PP})	$\delta\Delta Hc_P$ (J/g_{PP})	ΔHcp (J/g_{PP})	$\delta\Delta Hc_P$ (J/g_{PP})	$\delta\Delta Hc_P$ (J/g_{PP})
(PP/EPR)	111.69	-	106.17	-	−5.53
(PP/EPR)/SOCAL312	108.92	−2.77	107.90	+1.74	−1.02
(PP/EPR)/SOCAL322V	103.87	−7.82	103.52	−2.65	−0.35
(PP/EPR)/WINNOFIL SPM	95.92	−15.78	95.83	−10.34	−0.09

3.2. Analysis

Figure 2 shows that the mixtures (PP/EPR)/calcium carbonates socal312, socal322v or Winnofil spm were prepared under the same conditions, indeed profile curves and couple values are almost similar. There is at around 15 minutes running a drop in couple, this is due to the fact that the ring is collected, shear therefore becoming important, however this action should have no effect on the thermal degradation rate. A previous study has shown that [3], the thermal degradation of the blends (95/5) made on the micro twin-screws is more pronounced at high temperatures with ratios up to 28% in the case of the use of socal312, this is almost reversed with increasing the filler content of 10%, except for Winnofil spm where is always observed the first phenomenon, but less pronounced.

Calcium carbonates favor a reduction of the enthalpies of fusion, for all the mixtures and the basic copolymer PP/EPR. This observation is valid regardless

of the endothermic cycle (**Table 2**). Only Socal312 in the first endothermic cycle causes an increase in the fusion energy of isotactic polypropylene. It can therefore be inferred that calcium carbonates are useful for lowering the melting energy of isotactic polypropylene, even at a low loading rate for the majority. The number of endothermic cycles accentuates this phenomenon. Thus, a reduction of 11.59 J/g_{PP} can be achieved in the case of the use of Winnofil spm as reinforcement of the composite material. In this case, the thermal history of the mixtures plays a negative role from the energy point of view. Indeed, the absolute values of the melting enthalpies of the mixtures are greater during the second endothermic cycle compared to the first. This fact can be attributed to the local crosslinking of the amorphous zones of the semicrystalline copolymer used. The crosslinking of the amorphous phase has the consequence of requiring additional energy to melt the crystalline-P-sequences of the mixture. This result has a direct consequence for recycling, in that it limits to a finite number of times, the recycling of said composite by maintaining a good quality/price ratio of the products resulting from these different recycling [25]. Indeed, during the growth of the spherolites, the mobility of the macromolecular chains is reduced because of the mechanical stresses imposed by crystals on the adjacent amorphous zones [26] [27] [28] [29]. The amorphous phase is therefore said to be confined and considered to be rigid. The presence of this third phase will also affect the behavior of the mobile amorphous phase. Consequently, the phenomenon of enthalpy relaxation decreases with the increase of the rigid amorphous phase [28] [30]. The change of the microstructure and the fraction of the rigid amorphous phase will modify the mechanical properties of the semicrystalline polymers. The behavior of nanophases is important for mechanical, thermal, optical and other macroscopic properties. The first experimental study to demonstrate the existence of the rigid amorphous phase has been reported by Menczel and Wunderlich for several semi-crystalline polymers [31] [32] [33] [34]. It has been found that only the mobile amorphous phase intervenes at the glass transition during the DSC tests. The rigid amorphous phase has a low heat capacity due to the limited mobility of the chains. The temperature at which the rigid amorphous phase loses its restricted mobility behavior is an issue still debated. This transition could take place either between the glass transition temperature of the unconstrained amorphous phase and the melting point [27] [35], or occur at the same time as the melting [36].

At low calcium carbonate loading rates, irrespective of the thermal cycle of the exothermic reactions and for all the reinforcements used with the exception of Socal312 during the first cycle, there is a decrease of the crystallinity of the composite and isotactic polypropylene (**Table 3**). Note, however, that these variations are not identical for composites and for isotactic polypropylene, this is due to the inverse relationship between these two quantities. Thus, the variation in the crystallinity degree of the isotactic polypropylene is always greater than that of the composite from which it is derived. We also obtain that, whatever the

thermal cycle, Winnofil spm is calcium carbonate which causes a greater variation in the degree of crystallinity of the basic copolymer PP/EPR, with variations of up to 7.11% during the second heat cycle. Socal312 is the calcium carbonate which causes the least decrease of the crystallinity level of the basic copolymer PP/EPR, with minimum variation values of 0.46% during the first exothermic cycle. In addition, it is shown that at low levels of reinforcement, the second thermal cycle, exothermic reactions increase the degree of crystallinity of the basic copolymer, composites and isotactic polypropylene from these composites, with increases of up to 5.18% in the case of PP/EPR. It was estimated that the degree of crystallinity of the PP in mixture PP/elastomer/calcium carbonate is between 50% and 52% [10], in our case the EPR elastomers significantly increase the values given by the literature. It can be inferred that there is nucleation on the surface of our nanofillers, in effect it has been shown that calcium carbonate generated a small nucleating effect [37] [38] following a small increase in crystallization temperature T_c mixtures, this effect would be actually conditioned by the surface energies of calcium carbonates [39].

During the exothermic reactions, during the first cycle, we observe from the values of **Table 4**, a slight increase of isotactic polypropylene temperatures of crystallization of the mixtures except in the case of the use of Winnofil spm. The second cycle accentuates this increase, whatever the nature of the reinforcement used, with maximum increases of +2.5˚C when using Socal312 and Socal322v. The variations in the crystallization temperatures show that the second thermal cycle has a very strong behavior of the mixtures studied. However, comparing the first exothermic cycle with the second shows that, the second heat cycle slightly lowers the crystallization temperature values of the isotactic polypropylene except when using Socal312. These slight differences observed when going from one thermal cycle to another remain sufficiently weak, which justifies the perfect superposition of the curves (**Figure 4**). Given the error of the Mettler-Toledo SA system measurements on DSC 30 of ±0.5˚C, these slight differences can be characterized as negligible. The second heat cycle has a greater influence on the basic copolymer PP/EPR, where a temperature variation of 1.34˚C is observed, resulting in an imperfect overlap of the curves during both cycles (**Figure 6**). For the endothermic reactions, during the first thermal cycle, there is a slight increase in the isotactic polypropylene melting temperatures of the mixtures (**Table 5**). This increase is greater in the case of the use of Winnofil spm with a variation of 2.33˚C and is negligible for Socal322v. Only Socal312 is responsible for lowering melting temperature values when used at a low loading rate. In addition, during the second melting cycle, there is a decrease of melting temperatures, except for Winnofil spm where there is always an increase but less than in the first heat cycle. The melting temperatures of the mixtures during the second endothermic cycle increase overall for all the mixtures and also for the basic copolymer PP/EPR. This slight increase in values is at the origin of the bad superposition of the curves for both cycles (**Figure 3** and **Figure 5**). It can therefore be deduced that at low loading rates of calcium carbonates, the phe-

nomena are present but are not accentuated. Winnofil spm whatever the thermal cycle, increases the melting temperatures. This is true in contrast when using Socal312. It is only in the second thermal cycle that Socal322v behaves like Socal312. During the first thermal cycle, and for all the mixtures, the calcium carbonates decrease the crystallization enthalpy values of the isotactic polypropylene of the mixtures (**Table 6**). During the second exothermic cycle, there is a decrease in the energy of crystallization, less important than in the first cycle, this will be due to the homogeneity of the mixture. For all the mixtures, there is a decrease in crystallization enthalpies during the second exothermic cycle, with values of up to 5.53 J/g_{PP} for the basic copolymer PP/EPR.

4. Conclusion

The investigation of the relative variations of the thermal properties and crystallinity of poorly reinforced blends (PP/EPR)/calcium carbonate socal312, socal322v, Winnofil SPM developed micro-screw and subjected to two thermal cycles of loading was the object of the study. It appears that calcium carbonates are useful in lowering the melting energy of isotactic polypropylene, even at a low loading rate for the majority. The number of endothermic cycles accentuates this phenomenon. During the first heat cycle, there is a slight increase of the melting temperatures of the-P-sequences of *iPP*. There exists in our composites, a so-called confined amorphous phase which is considered to be rigid. Its presence affects the behavior of the mobile amorphous phase. Consequently, the phenomenon of enthalpy relaxation decreases with the increase of this confined amorphous phase. The results presented in this study are a database revealing behavioral trends of the copolymers studied. However, these results remain valid only in the context of the use of low reinforcement rates and the use of the microb Bivis as a mixer. This work is therefore a continuation, namely the change of the mixer, the increase in the charge rate. These various considerations will lead to the analyses of the effect of the mixer used and the effect of increasing the rate of reinforcement in influencing the results of this study. Other studies could be devoted to the analysis of the crystalline phases present in the mixtures, and the sizing of the crystalline lamellae. It will be possible to integrate morphological observations into these different studies, allowing real-time evaluation of certain properties of these mixtures. This entire field of work will aim to deepen knowledge of these composites which are used, among others, in the automotive field for the production of bumpers.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Abbreviations

Com: Composite index;

PP: Index relating to isotactic polypropylene used;

CP: Index relating to the crystallization of the isotactic polypropylene used;

FP: Index relating to the melting of isotactic polypropylene used;

T: is the temperature;

ΔH: is the enthalpy variation of the mixture;

χ_{Com}: is the degree of crystallinity of the composite or mixture;

χ_{PP}: Value of the crystallinity level of the polypropylene phase of the composite;

T_{CP}: Corresponds to the peak crystallization temperature of the *iPP* phase of the studied mixture;

T_{FP}: Corresponds to the peak melting temperature of the *iPP* phase of the studied mixture;

ΔH_{CP}: Represents the value of the enthalpy change at the peak of crystallization, of the isotactic polypropylene contained in the mixture considered;

ΔH_{FP}: Represents the value of the enthalpy change at the melting peak of the isotactic polypropylene contained in the mixture studied;

"$\delta\_\mathrm{var}iable$" characterizes the difference in the value of the variable of the studied mixture compared to that of the base copolymer. Its value is representative of the effect of the calcium carbonate studied on the properties of the base copolymer during the same thermal cycle;

"$\delta'\_\mathrm{var}iable$" is the difference of the values of the variables of the study, between the second heat cycle and the first one. Its value is indicative of the influence of the thermal history of a polymer or copolymer, when subjected to several cycles of thermal stresses.