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ANALYSIS OF THE ISOTHERMAL CRYSTALLIZATION OF POLYPROPYLENE/WOOD FLOUR COMPOSITES

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Isothermal crystallization and melting of isotactic polypropylene in binary polypropylene–wood flour composites has been studied by DSC, and the influence of an ethylene-methacrylic acid copolymer interfacial agent analyzed. Wood flour induces a slight nucleating effect, reducing the basal interfacial free energy of nucleation and increasing the overall crystallization rate. The interfacial agent generates a compatibilization phenomenon and an increase in the basal interfacial free energies with respect to the binary composites. In both binary and ternary systems the melting behaviour is a function of undercooling and is unaltered by the presence of either wood flour or the interfacial agent.

Keywords: *crystallization, interfacial free energies, polypropylene, wood flour*

Introduction

Over recent years there has been considerable growth in the applications and use of polymer composites reinforced with vegetable fibres as alternatives to metals or wood. The substitution of inorganic reinforcements with vegetable fillers or fibres such as sisal, jute, flax, hemp, banana and coconut [1–5] provides a number of interesting advantages, such as lower environmental contamination due to biodegradability and combustion, lower density and improved deformability which leads to reduced abrasion and damage to the processing equipment, and a high aspect ratio which is recommendable for efficient stress transfer. Further, from an economic and environmental standpoint, vegetable reinforcements are cheaper alternatives which are found in renewable and recyclable sources [6].

However, the use of cellulose based materials as reinforcements for thermoplastics has only received moderate acceptance, principally due to processing difficulties mainly derived from low thermal stability and the absorption of humidity [1, 6–8]. The most important disadvantage is poor resistance and low stress transfer efficiencies, particularly in the case of polyolefin compounds. This is due to the incompatibility between hydrophilic, polar fillers and hydrophobic, apolar polymers which leads to poor or no adhesion during blending. Different methods have been employed to appease this problem, mainly based on chemical modification of the filler or the use of compatibilizing agents with the aim to increase the adhesion between substrates through the reduction in interfacial tension, thus producing finer dispersions and stable, more regular morphologies.

Compounds of isotactic polypropylene (iPP) reinforced with sawdust or wood flour are low cost materials which contribute to the solution of environmental problems. Polypropylene is recyclable, of low cost and has favourable mechanical properties, and wood flour is cheap, highly available and renewable. Recently a number of studies on this family of composites have been reported, in particular the analysis of the influence of water absorption in the mechanical properties [9], thermal stability [10, 11], and the morphology and mechanical properties in the presence of compatibilizing agents [12–20]. However, few studies have considered the crystallization and melting behaviour of iPP in wood flour composites [21–30]. These fundamental studies are essential to the understanding of the solid-state properties obtainable in these materials.

Recently, we have reported the study of the dynamic crystallization behaviour of binary systems of polypropylene and wood flour, WF by differential scanning calorimetry, as a function of the composition and the presence or not of an interfacial agent as a compatibilizer [31]. In this respect, the present work considers the kinetic parameters of the isothermal crystallization of polypropylene in this type of composites, and the evolution of the energies associated with crystalline nucleation and their relationship with the possible existence of compatibilization processes between the polypropylene matrix and the wood reinforcement.

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Experimental

Materials

A commercial grade of polypropylene, ISPLEN® PP 070 G2M (Repsol-YPF, Móstoles, Spain) with a melt flow rate (MFR) of 10.0 g/10 min (230°C/1.6 kg) and a density of 0.902 g cm^{-3} was employed. The wood flour, WF, was provided by Galparkét (As Pontes, A Coruña, Spain) and is principally oak waste recovered from flooring manufacture which was sieved with a 100 μm mesh to obtain an acceptable particle size distribution. The interfacial agent used was a commercial ethylene-methacrylic acid copolymer partially neutralized with zinc metal ions, SURLYN 9970 (DuPont de Nemours, Geneva, Switzerland), with an MFR=14.0 g/10 min (230°C/1.6 kg) and density of 0.940 g cm^{-3}.

Binary formulations of polypropylene/wood flour (PP/WF) with 90/10 and 80/20 mass%, and ternary formulations polypropylene/wood flour/ionomer (PP/WF/I) with 5 and 10 mass% of ionomer with respect to the composition of wood flour existing in the composite, were studied, Table 1. Prior to the preparation of the composites, the wood flour was kept at 100°C for 24 h in a vacuum oven, and the zinc ionomer was dried at 60°C for 12 h. After the drying stage, the binary and ternary composites were prepared via extrusion using a Brabender DSE 20 co-rotating twin-screw extruder with a constant profile of temperatures of 180°C from the feed zone to the die and a screw speed of 45 r.p.m., and granulated into beads. Details of the thermal stability and dynamic crystallization and subsequent melting behaviour have been described previously [31].

Table 1 Composition of the PP/WF samples studied

Sample	PP/mass%	WF/mass%	Ionomer/mass%
iPP	100	0	0
C1	90	10	0
C2	90	9.5	0.5
C3	90	9.0	1.0
C4	80	20	0
C5	80	19	1.0
C6	80	18	2.0

Physical properties

Isothermal crystallization was studied using a Perkin-Elmer DSC7/7700/UNIX differential scanning calorimeter (Perkin-Elmer España SL, Madrid, Spain), calibrated with indium (T_m=156.6°C, ΔH_m= 28.45 kJ kg^{-1}) and zinc (T_m=419.47°C, ΔH_m= 108.37 kJ kg^{-1}). Approximately 12 mg samples in the form of beads were weighed in aluminium capsules, and studied under a nitrogen gas flow of 25 mL min^{-1}.

The thermal history applied prior to crystallization consisted in heating to 210°C and holding for 5 min in the molten state, after which the samples were cooled to each crystallization temperature, T_c at a rate of 64°C min^{-1}. The exotherm was subsequently registered as a function of time until crystallization was considered to be complete. Isothermal crystallization was followed by a heating cycle to 210°C at a rate of 10°C min^{-1}. The corresponding crystallization exotherms were integrated to determine the times associated with each level of crystalline transformation. The apparent transition enthalpy, ΔH_{app}, was determined from the area under the transformation curve, taking the upper and lower limits in the corresponding deviations from the baseline. The conversion from apparent enthalpy to degree of crystallinity, (1–λ), was calculated using the following equation:

$$(1-\lambda)=100\left(\frac{\Delta H_{app}}{\Delta H_m}\right) \qquad (1)$$

where ΔH_m=207.1 kJ kg^{-1}, corresponding to the melting enthalpy of 100% crystalline iPP [32]. The melting temperature, T_m was considered as the maximum of the melting endotherm obtained in the heating cycle.

X-ray diffractograms were obtained using synchrotron radiation at HASYLAB, at the DESY synchrotron, Hamburg, Germany. The samples were measured as films prepared by compression and crystallized in a Mettler FP90/FP82 HT temperature cell (Mettler-Toledo, Greifensee, Switzerland).

Results and discussion

Isothermal crystallization behaviour

The isothermal crystallization behaviour of iPP in binary and ternary systems with wood flour was analyzed over the crystallization temperature range between 121 and 138°C.

Figure 1 shows the evolution of the crystallization exotherms of iPP. As the crystallization temperature increases, the exotherms shift in the time axis. Both the induction time and the width of the exotherms increase, which reflects a reduction in the crystallization rate with decreasing undercooling of the system, ΔT. The crystallization exotherms of iPP in the binary iPP/WF composites present shorter induction times and a narrower area than those corresponding to raw iPP, which shows an apparent increase in the crystallization rate under isothermal conditions, Fig. 2. On the other hand, in the case of the ternary systems, iPP/WF/I, an apparent reduction in the crystallization rate can be observed, since the

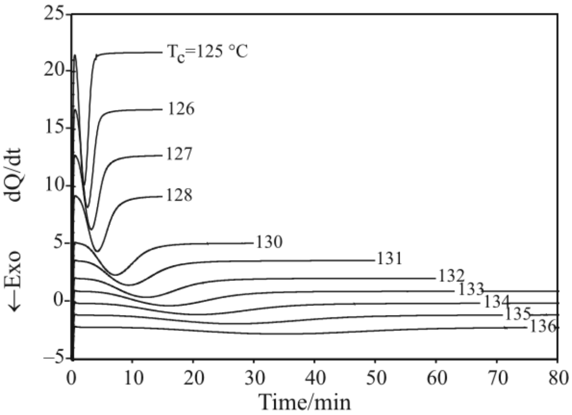

Fig. 1 Crystallization exotherms for polypropylene under isothermal conditions at the indicated crystallization temperatures

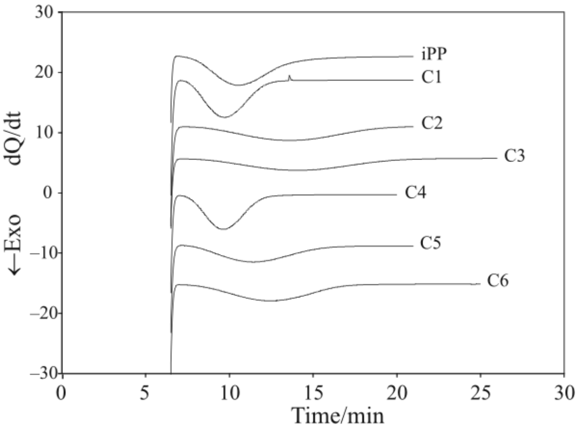

Fig. 2 Isothermal crystallization exotherms for binary iPP/WF and ternary iPP/WF/I systems, at 128°C. The baselines are displaced along the ordinate axis (arbitrary units) for clarity

exotherms clearly shift to longer transformation times. Both behaviours are generalized, and occur over the whole crystallization range analyzed.

The rate of crystallization, G was analyzed using the values of $\tau_{0.1}$ which corresponds to the time necessary to reach a degree of crystalline transformation of 10%. This parameter represents the global crystallization rate for each crystallization temperature considering that $G\sim(\tau_{0.1})^{-1}$. A pronounced change in the crystallization rate can be observed as the temperature increases, in other words, as the undercooling decreases. Also the apparent increase in the isothermal crystallization rate of iPP on the addition of wood flour in the binary composites, shown previously by comparison of the crystallization exotherms, is now reflected over the full temperature range analyzed. It can be deduced from this that the wood flour produces a nucleating effect on the crystallization of polypropylene.

The addition of the interfacial agent in the ternary composite systems produces important modifications in the crystallization of polypropylene, as can be seen in Fig. 3. In all the ternary composites a reduction in the isothermal crystallization rate of polypropylene can be observed with respect to that of both raw iPP, and of iPP in the binary composites. This suggests that, on the one hand, the interfacial agent cancels out the nucleating effect of the wood flour and, on the other, it generates a compatibilizing phenomenon between the wood flour and the polypropylene matrix. This compatibilizing effect is more apparent at the lower range of the isothermal crystallization temperatures analyzed, and seems to be independent of the concentration of interfacial agent present for each composite type. The compatibilizing effect is consistent with previous scanning electron microscopy observations on these binary and ternary composites crystallized under dynamic conditions [31] where a more homogeneous morphology is encountered in the samples with the interfacial agent, and the fibrous WF material is clearly seen to be coated by the polymer matrix.

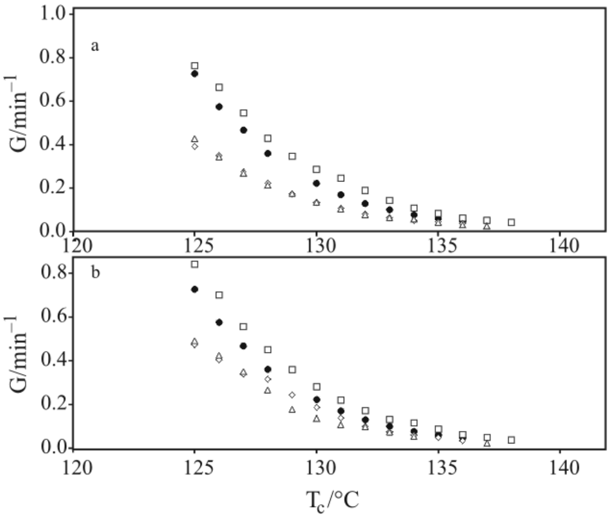

Fig. 3 Variation in the isothermal crystallization rate, G with the crystallization temperature for a – raw iPP and iPP in the 90/10 composites ● – iPP, □ – C1, △ – C2, ◇ – C3 and b – raw iPP and iPP in the 80/20 composites ● – iPP, □ – C4, △ – C5, ◇ – C6

The crystallization kinetics has been analysed using the Avrami and Göler–Sachs models [33]. The Avrami model takes into account the perturbation of adjacent crystalline nuclei in the crystallization process and the Göler-Sachs model assumes free crystalline growth. In the representation of these models for each crystallization temperature over the temperature range analyzed considering a crystalline transformation <25%, values of the Avrami exponent of $n\approx4$ were determined in all cases. Thus, the crystallization of iPP can be considered to occur through a mainly homogeneous nucleation process with subsequent 3-dimensional growth, and that this mechanism is unmodified by the presence of the vegetable filler or the interfacial agent, in both the binary and ternary systems. However, the nucleation efficiency of the WF can be clearly observed during the isothermal crystallization of the samples. The effect is not too strong and the results of the kinetic evaluation suggest that both heterogenous and homogeneous nucleation take place simultaneously during the crystallization. Other authors have described fractional values of *n* between 2 and 3 in the isothermal crystallization of polypropylene in the presence of sisal fibres [34], and 3 in the presence of lignin [35].

The determination of the mode of nucleation and growth allows the analysis of the overall crystallization rate of the crystallization process from the rate constant, *k* at each crystallization temperature by the following expression [36]:

$$k = \frac{\ln 2}{\tau_{0.5}^{n}} \qquad (2)$$

where *n* is the Avrami exponent value associated to each crystallization temperature, and $\tau_{0.5}$ is the time needed to reach 50% crystalline transformation. Values of *k* obtained for each composite and crystallization temperature are given in Table 2. These data confirm both the nucleating effect of the wood flour on iPP and the compatibilizing effect of the interfacial agent in the ternary systems, Fig. 4.

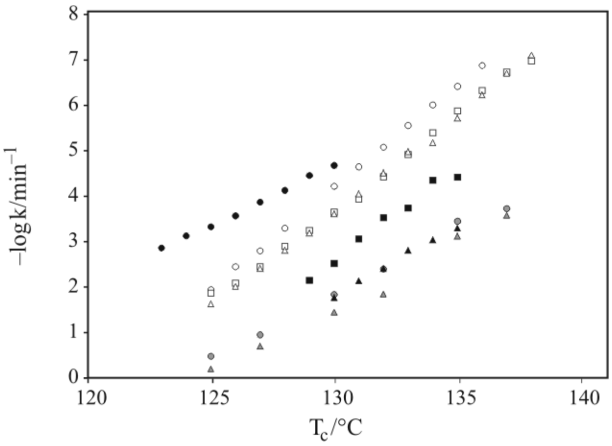

Fig. 4 Variation in the isothermal crystallization rate constant *k* as a function of the crystallization temperature in iPP/WF composites (this work), ○ – iPP, □ – C1, △ – C4, PP/sisal fibre composites [34], ● – iPP, ▲ – 80/20, and PP/lignin composites [35], ● – iPP, ■ – 95/5, ▲ – 85/15

When the values of the rate constants obtained in the isothermal crystallization of iPP in the wood flour composites obtained in this work are compared with the scarce data available in the literature from analogous composites with vegetable fibres or fillers (non-compatibilized systems without interfacial agents), a very similar behaviour is observed with respect to the nucleating effect that the vegetable component has on the polyolefin matrix. In polypropylene composites with sisal, the presence of 20 mass% of fiber produces a slight increase in *k* [34]. This nucleating effect, manifested by the relative increase in *k*, is maintained over the whole crystallization temperature range analyzed. The effect is very similar to that observed in this work where, for the same crystallization temperature of 130°C, the rate constant varies from $6.03\cdot10^{-5}$ min^{-n} for raw iPP to $2.45\cdot10^{-4}$ min^{-n} for iPP/WF 80/20 (C4). On the other hand, in composites with lignin in a PP matrix very similar to that used in this study, the presence of 15% vegetable filler pro-

Table 2 Values of the rate constant *k* calculated from Eq. (2)

T_c/°C	–log*k*/min^{-n}						
	iPP	C1	C2	C3	C4	C5	C6
125	1.94	1.87	3.12	2.99	1.63	2.76	2.69
126	2.45	2.09	3.33	3.44	2.02	3.07	3.00
127	2.80	2.45	3.76	3.84	2.41	3.45	3.38
128	3.30	2.90	4.16	4.26	2.81	3.55	3.84
129	–	3.25	4.59	4.65	3.19	4.01	4.57
130	4.22	3.65	5.05	5.05	3.61	4.46	5.00
131	4.65	3.94	5.50	5.52	4.05	5.00	5.46
132	5.08	4.43	5.97	6.02	4.51	5.52	5.51
133	5.56	4.92	6.34	6.40	4.98	6.00	6.03
134	6.01	5.40	6.79	6.61	5.18	6.47	6.62
135	6.42	5.88	6.94	7.12	5.72	6.75	–
136	6.88	6.33	7.39	7.66	6.23	7.40	–
137	–	6.73	–	–	6.71	–	8.09
138	–	6.98	–	–	7.11	–	–

duces a much higher nucleating effect, as can be deduced from the variation in the *k* values at the same temperature (130°C), from $2.1\cdot10^{-5}$ min^{-n} for raw iPP to $1.7\cdot10^{-2}$ min^{-n} for the 15% lignin composite [35]. As far as we are aware there are no reports in the literature of isothermal crystallization rate constants for these types of materials where interfacial agents acting as compatibilizing systems are present. However, the reduction observed in *k* in the case of the ternary iPP/WF/I composites seems to be coherent.

Melting behaviour after isothermal crystallization

After isothermal crystallization at different crystallization temperatures, the binary and ternary composites were heated at 10°C min^{-1} to the molten state. The melting behaviour of raw iPP shows a single endotherm with a well defined maximum and some asymmetry in the lower temperature region, where shoulders are apparent.

In Fig. 5 the curves at different crystallization temperatures for the iPP/WF and iPP/WF/I composites, respectively, are compared. In all cases both the main endothermic maximum and the associated lower temperature shoulder shift to higher temperatures with increasing crystallization temperature, T_c. This is related to the formation of families of crystals whose size increases with the reduction in the degree of undercooling. The shift of both endotherms with increasing T_c suggests the existence of partial crystal size segregation in the isothermally formed crystallites. The smaller crystals generate the lower temperature shoulders, and the enthalpy contribution of the melting of the larger more perfect crystals is included in the higher temperature endotherm. However, a contribution from the melting-recrystallization-melting of more imperfect crystals cannot be ruled out [37]. A value for the thermodynamic equilibrium melting temperature, T_m^0 of 210°C was determined using a conventional extrapolation method [38].

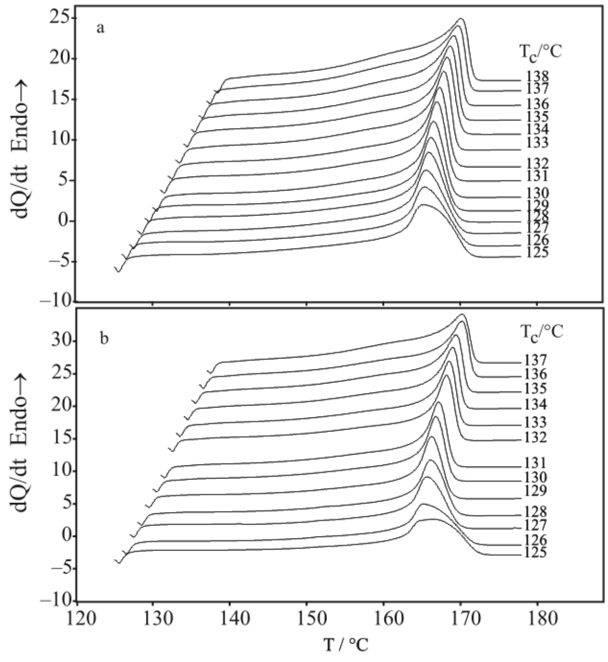

Fig. 5 DSC curves for the heating cycle at 10°C min^{-1} of a – iPP in the C4 binary composite and b – iPP in the C6 ternary composite after isothermal crystallization from the melt at the indicated crystallization temperatures. The baselines are displaced along the ordinate axis (arbitrary units) for clarity

For all the systems analysed, the apparent melting temperature is within the interval of 160–170°C, which corresponds to the melting of monoclinic iPP crystals [37]. From the analysis of the wide angle X-ray diffractograms recorded under isothermal crystallization conditions, only reflections associated with the monoclinic structure of isotactic polypropylene were detected. No evidence of the fundamental crystalline reflection at 2θ=16.2° corresponding to the (3 0 0)-plane of the trigonal structure [37] was observed.

Temperature coefficient

When polymeric materials are crystallized with low undercooling, i.e. high crystallization temperatures, the crystallization rate is higher the greater the undercooling. This implies that the crystallization process is controlled by the nucleation stage, i.e. by the free energy needed for the formation of a stable crystallite or the free energy of nucleation, ΔG^*.

In the case of homogeneous nucleation and three dimensional growth the overall rate of crystallization can be determined by the following expression [33]:

$$\log G+\left[\frac{U}{2.3R(T_c-T_\infty}\right]= \log G_0-\left[\left(\frac{8\Pi\sigma_e^2\sigma_u}{2.3R\Delta H_m T_c}\right)\left(\frac{T_m^0}{\Delta T}\right)^2\right] \qquad (3)$$

where σ_e and σ_u are the basal and lateral interfacial free energies of the crystallite, respectively, and $U/2.3R(T_c-T_\infty)$ represents the transport term through the liquid–crystal interface at the crystallization temperature T_c [39]. The temperature T_∞ is that at which the viscosity of the system is infinite, and is equivalent to the value $T_g - 30$ which is 231.1 K for polypropylene. The parameter *U* is variable, and a value of 6.270 kJ kmol^{-1} is generally adopted.

The existence of three crystallization regimes in isotactic polypropylene is well documented [40–50] and associated with discontinuities in the temperature coefficients as a consequence of different modes of crystal growth. In the case of iPP the transition from

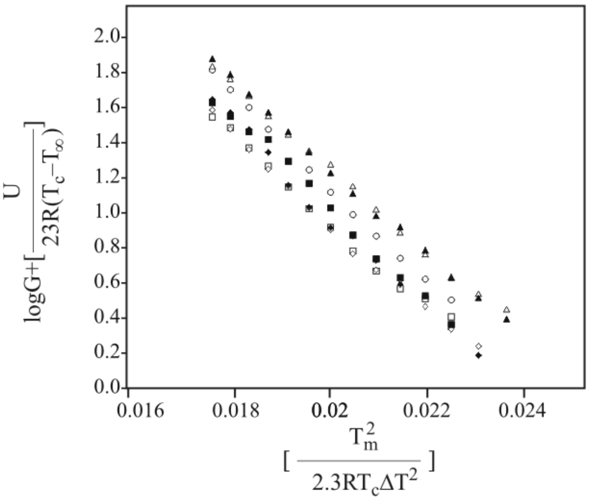

Fig. 6 Temperature coefficient for all the materials studied, as determined by Eq. (3). ○ – iPP, △ – C1, ▲ – C4, □ – C2, ◇ – C3, ■ – C5, ◆ – C6

Table 3 Calculated values for the basal interfacial free energy

Sample	σ_e/kJ kmol^{-1} (Eq. (4))	$\sigma_e \cdot 10^{10}$/kJ cm^{-2} (Eq. (5))
iPP	4.406	1.71
C1	3.879	1.50
C2	4.025	1.57
C3	3.975	1.55
C4	4.030	1.56
C5	4.326	1.68
C6	4.389	1.70

Regime III–Regime II takes place at a crystallization temperature between 135–137°C, and the transition from Regime II–Regime I takes place between 148–155°C [43–45, 51]. From this information, the crystallization of the composites studied in this work occurs in Regime III and the crystalline growth rate depends both on the nucleation rate and the lateral growth rate. In this respect, the representation of the first term in the expression given in Eq. (3) *vs.* $(T_m^0)^2/2.3RT_c\Delta T^2$ is presented in Fig. 6 for all of the samples analyzed, considering the previously cited value of 210°C for T_m^0.

By assuming the lateral interfacial free energy σ_u to be constant and independent of molecular mass, and equal to $0.1\Delta H_m$ [52], the values for the basal interfacial free energy σ_e were calculated and are given in Table 3.

Conversely, in agreement with the kinetic theory of crystallization [48, 53, 54], independent of the type of regime, the crystallization rate G can be given by:

$$\log G + \left[\frac{U}{23R(T_c - T_\infty)}\right] = \log G_0 - \left(\frac{K_{g(III)}}{23T_c\Delta T}\right) \quad (4)$$

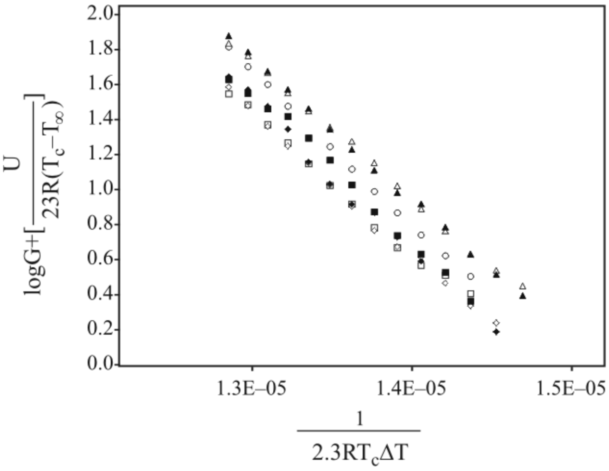

Fig. 7 Temperature coefficient for all the materials studied, as determined by Eq. (4). ○ – iPP, △ – C1, ▲ – C4, □ – C2, ◇ – C3, ■ – C5, ◆ – C6

where $K_{g(III)} = 4\sigma_u\sigma_e b_0 T_m^0 / k\Delta H_m$ for Regime III, k being the Boltzmann constant, $1.38 \cdot 10^{-26}$ kJ K^{-1} and $b_0 = 6.26$ Å, representing the thickness of a crystalline monolayer added during growth. The representation of the first term of Eq. (4) *vs.* $1/2.3RT_c\Delta T$ is presented in Fig. 7 for all of the samples analysed.

As is the case for T_m^0, the literature values for ΔH_m are both variable and dispersed and are fundamentally conditioned by the method of determination [37]. However, it is possible to eliminate the influence of this parameter in the comparative analysis of the values of the interfacial free energies by applying the approximation of Hoffman *et al.* [53], which establishes that the interfacial free energy can be given by the following expression,

$$\sigma_u = \alpha\Delta H_m (a_0 b_0)^{1/2} \quad (5)$$

where $\alpha \approx 0.1$ and $a_0 b_0 = 34.37$ Å^2 which represents the chain cross section in the iPP crystal, and the values of the basal interfacial free energy can be obtained from the following expression:

$$\sigma_e = \frac{kK_{g(III)}}{4b_0 T_m^0 \alpha (a_0 b_0)^{1/2}} \quad (6)$$

and are given in Table 3, where the value of 210°C was taken for T_m^0, as previously indicated.

To our knowledge there is no data in the literature for the basal interfacial free energy associated with the isothermal crystallization of isotactic polypropylene in composites with vegetable fillers. Previous isothermal crystallization studies of iPP in the presence of 5 mass% WF do not show variations in the value of the basal interfacial free energy [30].

The values for the basal interfacial free energy for iPP published in the literature oscillate between $4–23 \cdot 10^{-9}$ kJ cm^{-2}, the differences being attributed principally to the value of T_m^0, chain tacticity, the presence of folding irregularities due to chain defects, and molecular mass distribution [44, 45, 51, 55–58]. From the data obtained in this work, it seems evident that the reduction in the values of σ_e in the binary PP/WF compounds, with values of 1.50 and $1.57\cdot10^{-8}$ kJ cm^{-2} for the 90/10 (C1) and 80/20 (C4) composites, respectively, compared to the value of $1.71\cdot10^{-8}$ kJ cm^{-2} in the case of raw PP, Table 3, is associated with the nucleating effect of the vegetable filler, in agreement with Beck [59], and similar to that which occurs in the presence of nucleating agents [60–63], nanofillers [64] or different types of fibres where transcrystallization is observed [65]. On the contrary, the presence of the interfacial agent in the ternary compounds, especially in the case of the 80/20 composites (C5 and C6), seems to compensate or practically eliminate the nucleating effect of the vegetable filler.

The presence of a foreign substrate in the iPP melt frequently reduces the critical size of the crystalline nucleus necessary for subsequent growth, since the generation of an interphase between the polymeric crystal and the substrate may be less restricted than the creation of a crystalline nucleus from the melt. As a matter of fact, heterogeneous nucleation occurs through the reduction of the free energy of nucleation, which gives rise to a higher nucleation rate and, as such, a higher crystallization rate. If we consider that the free energy of nucleation, i.e. the free energy necessary for the formation of a nucleus of a critical size, is given by the expression,

$$\Delta G^* = \frac{4b_0\sigma_u\sigma_e T_m^0}{\Delta H_m \Delta T} \quad (7)$$

it is possible to follow its evolution with the overall crystallization rate G, Fig. 8. The free energy of nucleation, which increases with smaller undercooling, is lower for the PP/WF composites than for raw iPP at the same crystallization temperature, which confirms that the energy barrier for nucleation is lowered in the presence of the WF component, which leads to an increase in the overall crystallization rate.

The presence of the interfacial agent in the ternary compounds clearly cancels out the nucleating effect of the WF through a reduction in the crystallization rate, as was indicated earlier. This effect is accompanied by a significant change in the values of the respective basal interfacial free energies. In many binary semicrystalline–amorphous polymeric systems it is well-known that the reduction in the crystallization rate of the semicrystalline component is an indication of the existence of miscibility between the systems [66]. Further, in binary semicrystalline–semicrystalline polymer systems where one component has a nucleating effect over the other, the corresponding increase in the rate of crystallization disappears in the presence of a compatibilizing agent [67]. In the present case the intervention of factors such as the existence of interactions between the matrix and the interfacial agent will undoubtedly generate a certain level of compatibilization in the system. Further studies are currently underway in order to elucidate their nature.

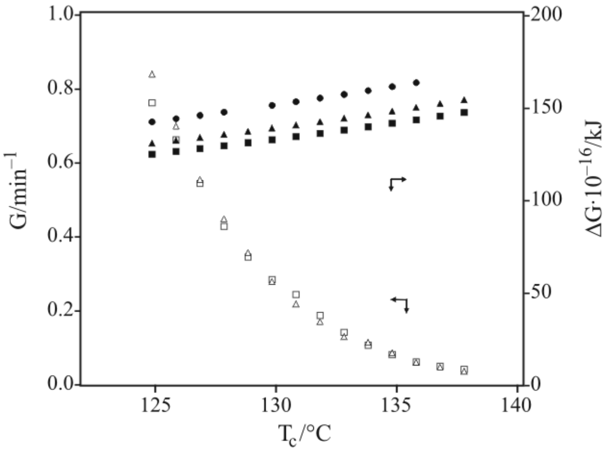

Fig. 8 Variation in the overall crystallization rate, G, ○ – iPP, □ – C1, △ – C4, and the free energy of nucleation, ΔG^*, ● – PP, ■ – C1, ▲ – C4, as a function of the crystallization temperature

Conclusions

The vegetable filler induces a slight nucleating effect on the isothermal crystallization of isotactic polypropylene which appears to be independent of concentration in the composition and crystallization temperature range analyzed. This induction phenomenon is manifested by a reduction in the values of basal interfacial free energies for polypropylene in binary composites with wood flour, and thus a reduction in the free energy of nucleation and an increase in the global crystallization rate. The addition of an interfacial agent inverts this effect. An increase is observed in the overall isothermal crystallization rate, while maintaining the monoclinic crystalline structure as in the case of the binary compounds. The interfacial agent not only cancels out the nucleating effect attributed to the presence of WF but also reduces the rate of crystallization with respect to neat iPP, which could be explained by a compatibilization phenomenon.

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