SIMULTANEOUS MORPHOLOGICAL AND RHEOLOGICAL MEASUREMENTS ON POLYPROPYLENE: EFFECT OF CRYSTALLINITY ON VISCOELASTIC PARAMETERS

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Abstract

A rotational rheometer equipped with an optical module is adopted to characterize the evolution of rheological parameters and at the same time the morphology development during isothermal crystallization. This allowed the determination of the effect of crystallinity on the viscoelastic functions of an iPP. A linear multi-mode Maxwell model was then applied to obtain the modulus and relaxation time of each mode as a function of the measured crystallinity degree. It was found that at low crystallinity levels the increase of moduli with crystallinity is about the same for all the modes whereas, when crystallinity degree rises, the increase of moduli is higher for the modes characterized by higher relaxation times. Concerning the relaxation times, it was found that the increase due to crystallinity is about the same for all the modes and reaches a factor of about 10 when relative crystallinity degree is close to 10%. The effect of crystallinity on complex viscosity was also assessed by determining a shift factor due to crystallinity. It was observed that the data collected at the lowest frequencies need higher shift factors with respect to the other ones. This was ascribed to the fact that more than one shift factor is needed to describe the effect on moduli, and low frequencies stir modes with higher relaxation times, which undergo a moduli increase larger than modes with shorter relaxation times.

Introduction

Crystallization dramatically influences polymer rheology. Indeed, for semi crystalline polymers, "solidification" often takes place because of the increase of crystallinity rather than for temperature decrease. This also means that the so-called fluidity of a polymer can be completely different, at the

same temperature and under the same stress conditions, if the crystalline content of the polymer is different. This phenomenon is known from the very beginning of polymer science and is of extreme significance for polymer processing. Several researchers tried to characterize the phenomenon. Review of literature papers can be found in references (Kennedy and Zheng 2013, Lamberti *et al.* 2007, Pantani *et al.* 2005, Roozemond *et al.* 2012, Steenbakkers and Peters 2008). The most evident effect reported is that on increasing the relative crystallinity degree, namely the value occupied by crystals, viscosity increases (Han and Wang 1997, Titomanlio *et al.* 1997). This effect is normally described by introducing a shift factor due to crystallinity, similar to the shift factors due to temperature and pressure (Kennedy and Zheng 2013, Pantani, Coccorullo, Speranza and Titomanlio 2005, Sorrentino and Pantani 2009). More detailed investigations revealed that the viscoelastic parameters G' and G" increase by effect of crystallinity to a different extent (Acierno and Grizzuti 2003, Boutahar *et al.* 1998, Roozemond and Peters 2013). Recent studies of the phenomenon (Pantani *et al.* 2014, Roozemond, Janssens, Van Puyvelde and Peters 2012), starting from the description of the viscoelastic behavior of the polymer melt by a multimode Maxwell model, lead to the conclusions that the effect of crystallinity on the viscoelastic behavior of a polymer can be described by two separate effects: a shift factor for the modulus (or better for each modulus of each mode) and a shift factor for the relaxation time (again, for each mode). This observation is of extreme significance, since it allows separating the effects of crystallinity on viscosity (and thus to describe all the aspects related to the flow and thus to the solidification of the polymer) from those related to viscoelasticity (and thus to relaxation, stretch and orientation). Despite the importance of the phenomena, their characterization suffers from the difficulties in measuring simultaneously rheological properties and crystallinity evolutions during the same tests. Apart from some attempts to obtain simultaneous measurements of crystallinity and viscosity by special setups (Janssens *et al.* 2010, Roozemond, Janssens, Van Puyvelde and Peters 2012, Watanabe *et al.* 2003), more often viscosity and crystallinity are measured during separate tests having the same thermal history. This greatly simplifies the experimental approach but also introduces a degree of uncertainty concerning

the real value of crystallinity at which the phenomena occur. Since the phenomenon is dramatic, this misalignment between the measurements of crystallinity and rheology in parallel tests is a major limitation to the quantification of the effect of evolving morphology on rheological parameters. In this work, a rotational rheometer equipped with an optical module was adopted. This allowed characterizing the time evolution of viscoelastic parameters and at the same time to take pictures of the evolving morphology. A 3D rendering of the images also allowed to calculate the volume occupied by the spherulites (namely the relative crystallinity) and thus to associate a given viscoelastic response to a given crystallinity degree.

Materials and Methods

An isotactic polypropylene supplied by Montell (Ferrara, Italy), now Lyondell-Basell Industries, was adopted in this work. The commercial name is Moplen T30G, and it is a general-purpose homopolymer for extrusion/molding applications, with a melt flow index equal to 3.6g/10min (ASTM D1238/L). The molecular weight distribution was determined by a size exclusion chromatography, with weight-average molar mass M_w of 376 kg mol^{-1}, polydispersity index M_w/M_n of 6.7, and a tacticity of 87.6% (pentad content *mmmm*). The effect of the flow applied during crystallization on the morphology evolution and the crystallization kinetics of the same resin has been already explored (Coccorullo *et al.* 2003, Pantani *et al.* 2010).

The measurements were carried out with a Thermo Scientific Haake Mars rheometer, equipped with an optical module, which allows the direct observation of the morphology while rheological measurements are carried out. One of the advantages of the optical module is that it allows assessing the homogeneity of the sample before starting the test. The protocol followed for the tests is schematically presented in figure 1. The pellets were placed between the plates at the temperature of 220°C. After melting, the material was kept at 220°C for 20min, in order to erase the effect of all the previous thermal history. The measurements were carried out in oscillatory mode, in parallel plates geometry, with a controlled stress of 100Pa and frequencies ranging from 0.1 to 100rad/s. In

these conditions, for all tests, the strain amplitude was well below 1%, thus assuring a linear response. Three tests with two different gaps and two plate diameters were carried out in this work, as listed in table 1.

Table 1. Geometrical parameters of the tests carried out in this work.

Test	Gap	Plate diameter	Observation point (Distance from the center)
A	1100μm	35mm	14mm
B	1100μm	20mm	10mm
C	2000μm	35mm	14mm

The relatively large gaps were chosen in order to minimize the effects of interactions between the plates' surface and the evolving crystallization. The temperature was lowered to 140°C by applying a cooling rate of about 5°C/min. Once reached the test temperature of 140°C, 60s were waited to allow thermal stabilization and then the rheological tests started. The time needed for a complete frequency scan was about 500s (about 200s for the lowest frequency and about 1s for the highest one). An idle time of about 120s was allowed between two consecutive measurements.

The optical module allows choosing the radial position of the observation window up to a maximum of 14mm. After verifying during preliminary tests that the morphology evolution was homogeneous inside the whole observable volume, for all tests the maximum allowable distance from the center of the plate was chosen. This distance allowed monitoring the region that contributes to a larger extent to the stress measured during the tests. The camera could take pictures at different positions z along the gap, namely at different intermediate positions from the lower (z=0) to the upper (z=gap) plate. Since the focal depth was about 300μm, pictures were taken by setting the focus each 150μm starting from the lower plate up to the upper plate and cyclically repeated. The whole set of pictures (8 or 14, depending on the gap) could be collected in less than 300s.

The frequency sweep tests were repeated for an isothermal time of about 3h, for two main reasons: at higher times, the measured viscosity was so high that the amplitude became too small to assure a

reliable measurement; when the spherulites become too big, the sample becomes cloudy and thus the optical observation is not clear enough to distinguish the spherulites. It is worth mentioning that at 140°C in quiescent conditions the time needed for the sample to completely crystallize is about 8h.
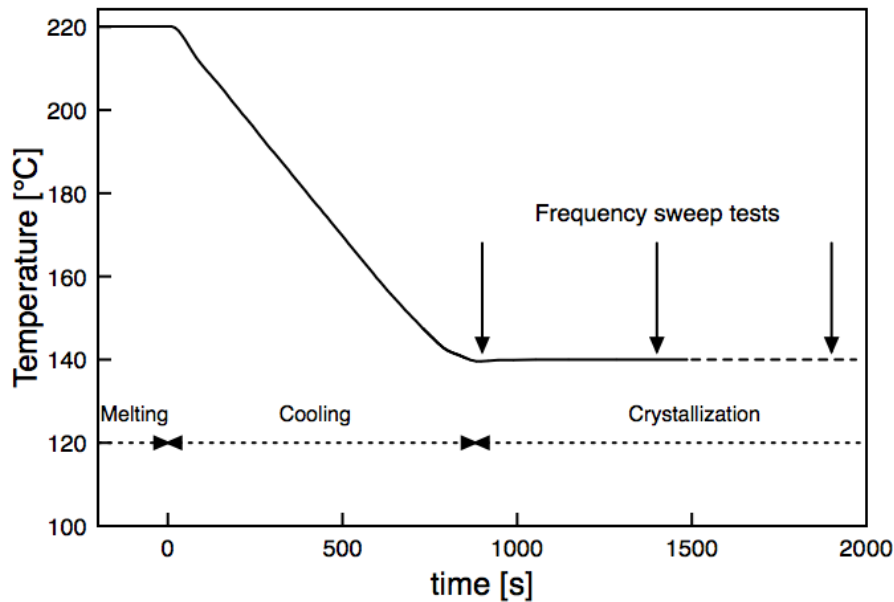

fig. 1 Temperature profile measured during a test

Results

Evolution of morphology

As mentioned above, the apparatus adopted for the test provides pictures of the evolving morphology inside the melt at different positions along the gap. In fig. 2 an example of the measurements carried out is reported. It can be seen that one spherulite (about central in the pictures) is on focus (i.e. presents quite sharp boundaries), whereas the others are slightly out of focus. This observation permits the location of a spherulite at a given position inside the polymer melt. By moving the focus along the thickness direction, all the spherulites can be located in the space and their dimensions monitored. The position of spherulites does not change excessively during the test, since oscillatory mode is selected in the rheometer. Consequently, spherulites may be monitored in time and their growth measured. As an example, in fig. 3, some of the dimensions

of the spherulites are reported versus time tests A and C (gap 1.1mm and 2mm, Fig. 3a and 3b respectively). Measurements referring to the evolution of spherulite diameters located at several distances from the lower plate are reported in each figure. It can be noticed that for the same test the growth rates (namely the slope of the plots) are about the same along the gap. A small difference in growth rate is found when the three tests are compared: the growth rates measured for the test A was $0.014\pm0.002\mu$m/s, for test B it was $0.010\pm0.002\mu$m/s and for test C it was $0.011\pm0.002\mu$m/s. All of them are close to the values reported in the literature for the same material in quiescent conditions at 140°C (0.01μm/s) (Pantani, Coccorullo, Volpe and Titomanlio 2010). The difference in growth rate can be ascribed to a small difference in temperature between the tests analyzed. Indeed, it is well known that the crystallization kinetics is extremely sensitive to temperature, thus a difference of fractions of one degree can cause measurable differences in growth rate. For the material adopted in this work, the growth rate at temperatures around 140°C change of about 25% for a change in temperature of about one Celsius degree. As mentioned above, this can be one of the reasons of the disagreement found in the literature concerning the effect of crystallinity on rheology.

For each test, also the number of spherulites could be counted. It was found that this number did not change during each test, as it happens in quiescent conditions (Coccorullo, Pantani and Titomanlio 2003). It was also found that the number of spherulites divided by the observed volume, namely the nucleation density, was about the same for all the tests and nearly equal to 10^{-7}nuclei/μm^3, which again is in line with the values reported in the literature for the same material in quiescent conditions at 140°C (Coccorullo, Pantani and Titomanlio 2003).

It was observed that, during the tests, the dimension of the spherulites reach considerable values. This means that the gap between the plates can be a critical variable: if too small a gap is set (of the order of 100μm) or a plate-cone configuration is adopted, the mechanical stress on the spherulite can suddenly determine a torque increase which can be interpreted as a premature hardening due to viscosity increase.
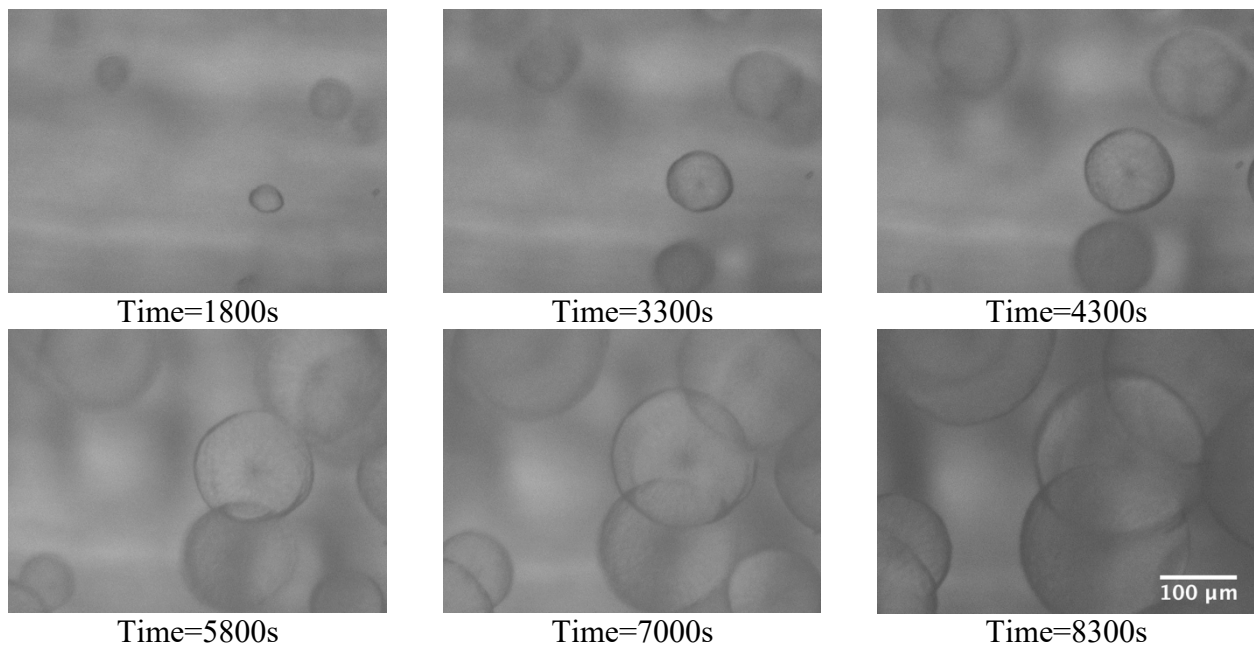
Fig. 2. Evolution of morphology at a distance from the lower plate of z=900μm for test A. The gap was 1.1mm.
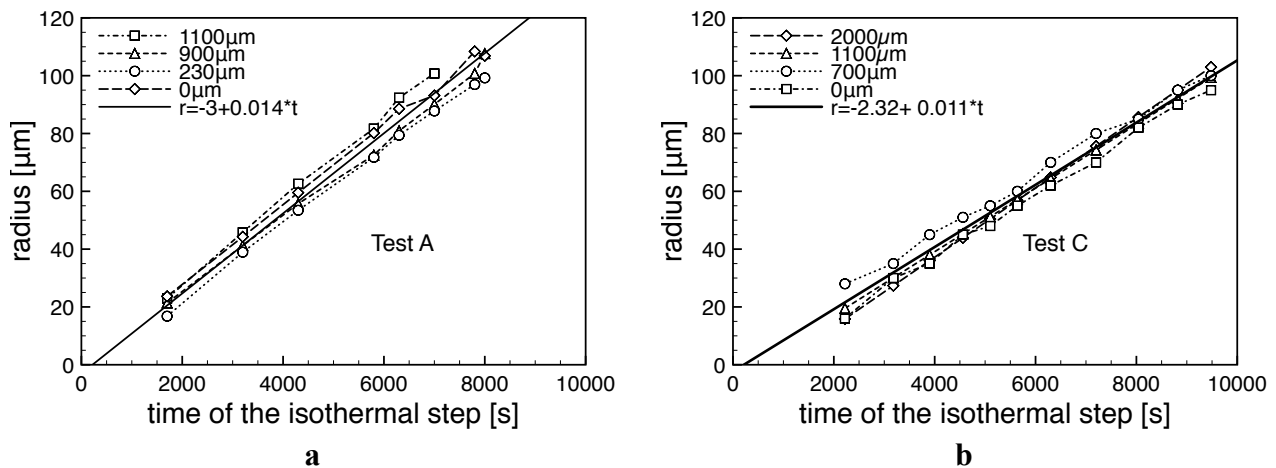

Fig. 3. Measurements of spherulitic growth rate. The measurements refer to different distances z from the lower plate, as reported in the legend. **a) Test A: gap 1100μm; b) Test C: gap 2000μm**

As mentioned above, during the test it was possible to span along the whole gap and identify both the distance z from the lower plate and (at each time) the size of each spherulite. We used the series of images taken at different focus positions along the thickness direction to rebuild in 3D the morphology at the observation position. The 3D view of the morphology evolution is reported in figures from 4 to 6, with reference to the test carried out with a gap of 1.1mm. In these figures, at

different times (increasing from fig. 4 to fig 6) pictures at selected positions along the gap are shown in the first, left column (just two distances from the lower plate are shown); the second, central column, shows the 3D representation of the same section; in the third, right column the 3D representation of the overall evolving morphology is reported; the frames reported in the right columns identify the observed volume, which is as high as the chosen gap and has a basis equal to the image dimensions of $490x367\mu m^2$. It can be noticed that some spherulites nucleate on the upper plate. The effect of this surface nucleation is obviously more significant for a smaller gap, and this is one of the reasons why relatively large gaps were adopted. It should be mentioned that in the 3D representation reported in figures from 4 to 6, the vertical position z of the spherulites could been determined with an approximation of +/- 75µm. This means that the fact that the spherulites seem to be grouped on particular planes can surely be exaggerated in the figures.

Time=3300s, z=100µm   Rendering of the same position

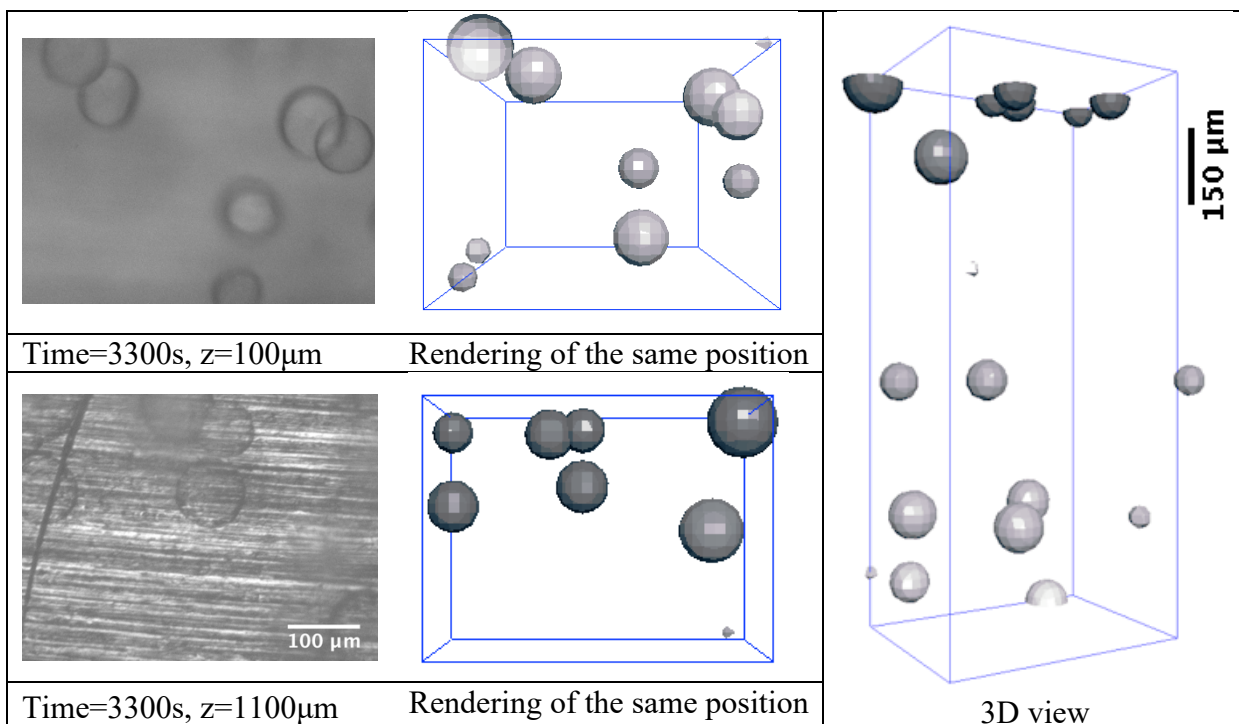Time=3300s, z=1100µm   Rendering of the same position   3D view

Fig. 4. 3D composition of the pictures taken along the gap after 3300s of isothermal step for test A. Pictures and rendering at just two distances from the lower plate are reported in the first and second columns. The gap for the test A was 1.1mm. The frame identifies the observed volume, which is $490x367x1100(=gap)$ μm^3
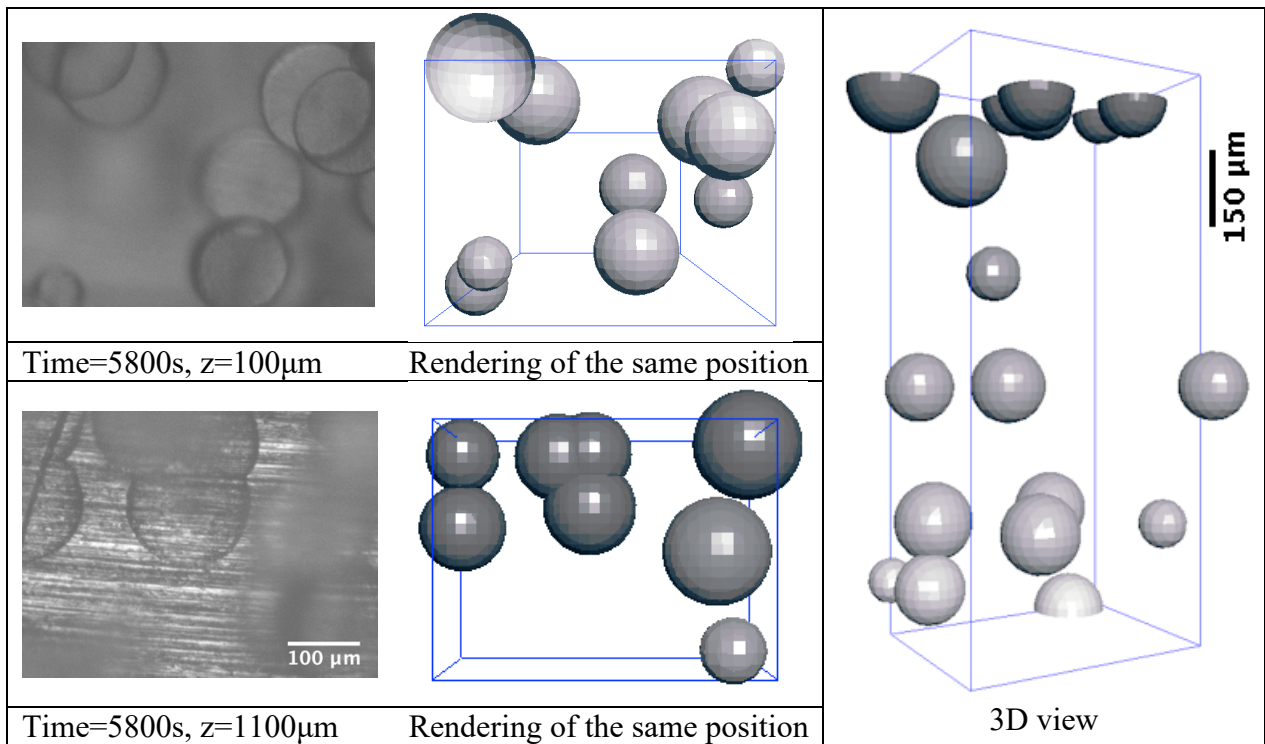
Fig. 5. 3D composition of the pictures taken along the gap after **5800s** of isothermal step for test A. Just two positions are reported. The gap for test A was 1.1mm. The frame identifies the observed volume, which is 490x367x1100(=gap) μm^3
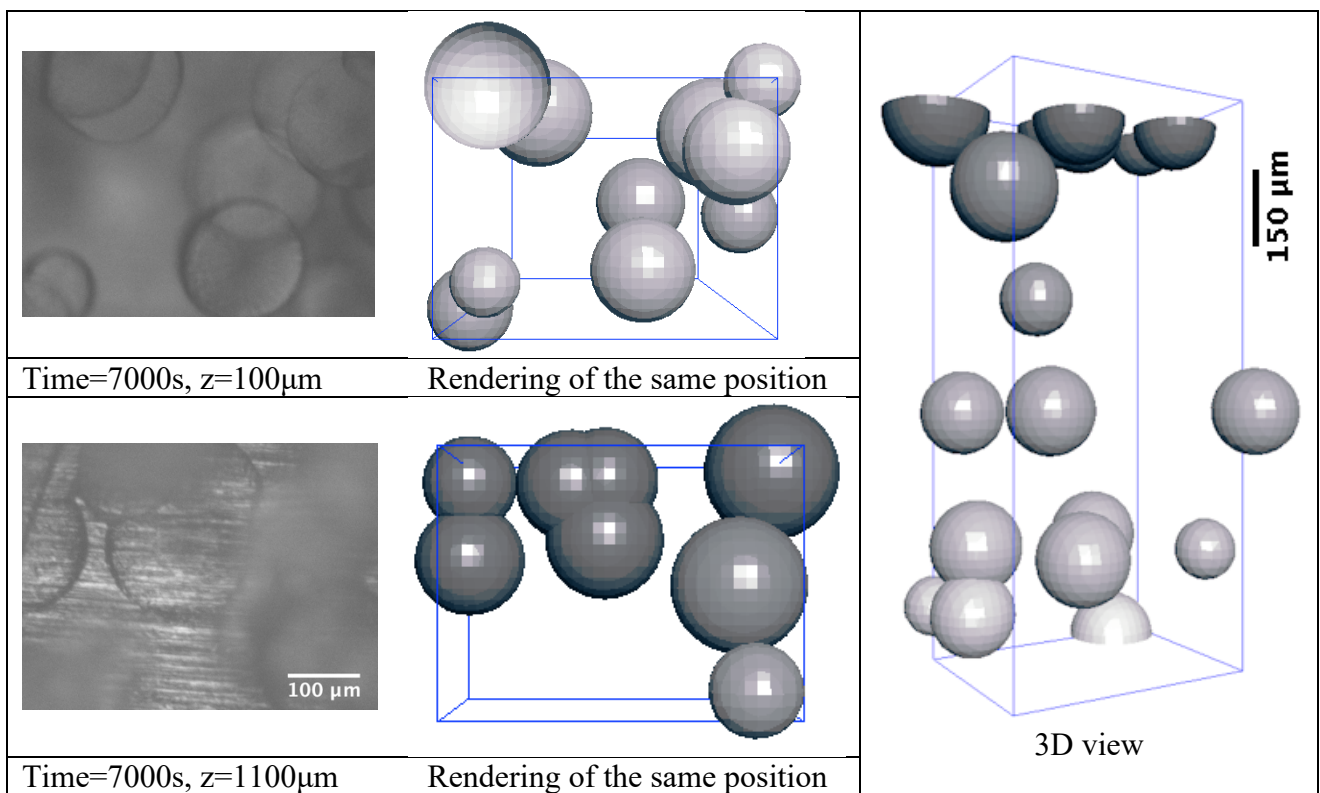

Fig. 6. 3D composition of the pictures taken along the gap after **7000s** of isothermal step for test A. Just two positions are reported. The gap for test A was 1.1mm. The frame identifies the observed volume, which is 490x367x1100(=gap) μm^3

The 3D representation of the morphology presents several advantages: the morphology of the sample is immediately captured; the volume occupied by the spherulites (namely the relative crystallinity degree, χ) can be calculated by taking into account both the impingement among spherulites and the nucleation on the plates (which reduces to one half the volume of the spherulite); also spherulites nucleated outside the observed volume, but entering that volume when growing, can be taken into account. By dividing the volume occupied by the spherulites by the volume observed (the frame identified in figures from 4 to 6, rightmost column), the relative crystallinity degree is obtained. This is reported in figure 7 for all the tests carried out in this work. It can be noticed that the crystallization kinetics is slightly faster for the test A. Following fig. 3, this is obviously linked to the larger growth rate presented by the spherulites.

As mentioned above, the 3D rendering of the morphology allows highlighting the nucleation on the plates. In order to assess the significance of the phenomenon, the crystallinity degree for all the tests was recalculated by neglecting the contribution of the spherulites on the surfaces (both bottom and top plates). The results are also reported in fig. 7 as lines without symbols. It can be noticed that the effect of surface nucleation is the highest for test A; obviously, for the same plates, increasing the gap reduces the significance of surface nucleation (test C); the 20mm plate (test B) seems to induce a lower surface nucleation, probably because of a different surface finishing. The surface nucleation introduces a further element of inconsistency when two techniques are coupled to obtain the effect of crystallinity on rheology: the significance of surface nucleation is certainly different in the two apparatuses. In the following, the reported crystallinity degrees will be those calculated keeping into account the surface nucleation, namely the complete volume occupied by crystals is considered.
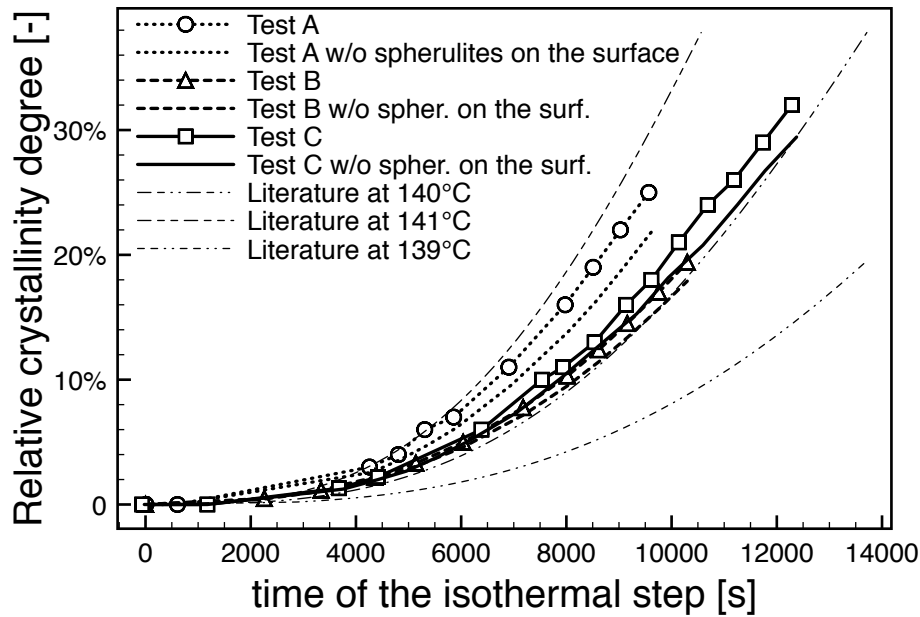
Fig. 7. Crystallinity evolution with time. The thicker lines without symbols refer to calculations made without considering the spherulites on the bottom and top plates. The thinner lines refer to predictions at different temperatures according to the data of nucleation density and growth rate reported by (Coccorullo et al. 2003)

Rheological measurements

As mentioned above, the material adopted in this work was already well characterized in the literature (Coccorullo, Pantani and Titomanlio 2003, Pantani, Coccorullo, Volpe and Titomanlio 2010, Sorrentino and Pantani 2013). In fig. 8 we report a master curve at 140°C of the viscoelastic characterization of the amorphous (χ=0) melt. Data were taken in the temperature range from 140°C to 260°C, the temperature shift factors are reported in the inset of fig. 8. It can be noticed from the shift factors that a change in temperature of a few Celsius degrees induces a negligible change in rheology, whereas crystallinity can change of a factor of about 2 if the temperature changes of just one degree (Pantani, Speranza and Titomanlio 2014).
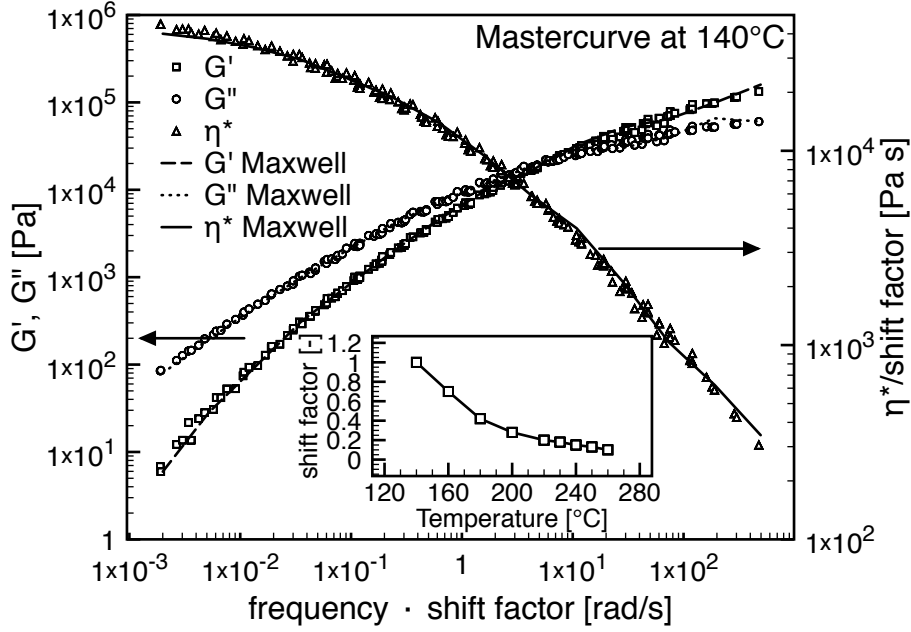
Fig. 8. Symbols: experimental functions of viscoelastic parameters for T30G at 140°C and χ=0. Lines: results of eq. 1 with the parameters reported in table 2. The inset reports the temperature shift factors.

The data reported in fig. 8 were adopted to evaluate the values of the parameters G_i and λ_i of a linear multi-mode Maxwell equation, which for the storage (G') and loss (G") moduli and the complex viscosity (η*) gives:

$$G'(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2}$$

$$G''(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega\lambda_i)}{1 + (\omega\lambda_i)^2} \qquad\qquad 1$$

$$\eta^* = \frac{\sqrt{G'^2 + G''^2}}{\omega}$$

The values of G_i and λ_i in eq. 1 at 140°C were obtained by applying a nonlinear regression method based on the Marquardt–Levenberg algorithm aimed at minimizing the average square deviation between the results of Maxwell equations (eqs.1) and the experimental results of G', G" and η*. The results of the regression performed with 6 modes are also reported in fig. 8 and the values identified for the parameters are reported in table 2

Table 2. Parameters of the Maxwell model (Equation 1) for χ=0 at 140°C.

Mode	λ_i° [s]	G_i° [Pa]
1	$3.48\cdot10^{-3}$	$1.09\cdot10^5$
2	$8.21\cdot10^{-2}$	$3.62\cdot10^4$
3	$8.43\cdot10^{-1}$	$7.76\cdot10^3$
4	$4.09\cdot10^0$	$1.71\cdot10^3$
5	$2.46\cdot10^1$	$4.00\cdot10^2$
6	$1.75\cdot10^2$	$3.37\cdot10^1$

As already reported in the literature (Acierno and Grizzuti 2003, Roozemond, Janssens, Van Puyvelde and Peters 2012), during time the moduli G'(ω) and G''(ω), and thus the complex viscosity, increase with time because of the evolving crystallinity. This is shown in fig. 9, with reference to the test A carried out in this work (very similar results were found for the other tests).
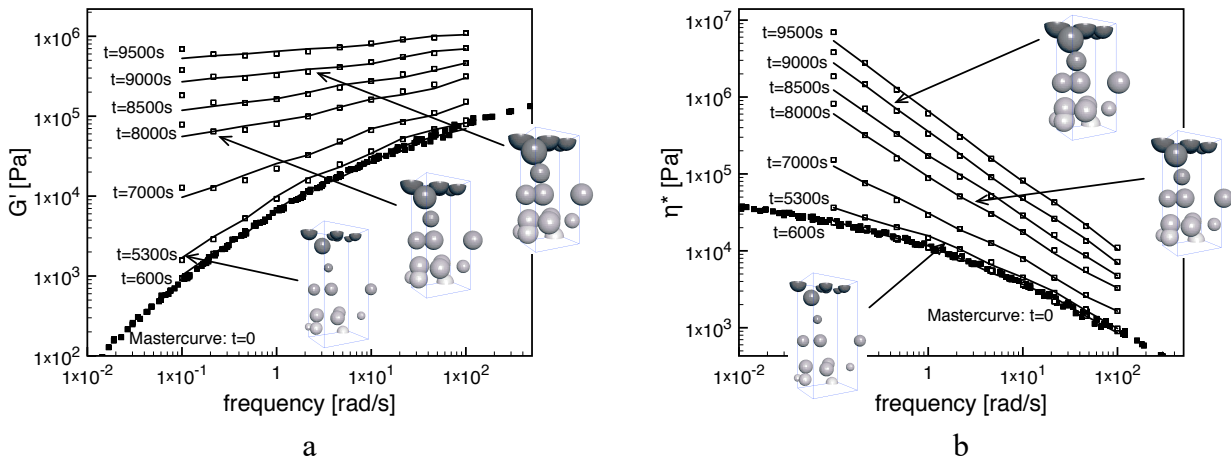

Fig. 9. Effect of time on G'(ω) and η*(ω) for Test A. Symbols: experimental data collected with a gap of 1.1mm. Lines: description by eq. 1 and 2. The pictures refer to the 3D rendering of the morphology evolution

Following literature indication (Pantani, Speranza and Titomanlio 2014), the parameters found for each mode and for each crystallinity degree were related to the corresponding parameters found on the amorphous sample (Table 2) as follows

$$G_i=\alpha_i(\chi)\ G_i^\circ \qquad\qquad 2$$
$$\lambda_i=\beta(\chi)\ \lambda_i^\circ$$

in which the parameters G_i° and λ_i° refer to the amorphous melt and are those reported in table 2. Obviously, the shift factors α_i and β are equal to 1 when the crystallinity degree χ is equal to zero.

On the basis of previous results (Pantani, Speranza and Titomanlio 2014), it was assumed that all relaxation times λ_i undergo the same percentage increase with crystallinity; namely, for each crystallinity, only one shift factor β was imposed in the regression procedure. Vice versa the values of α_i were let free to take different values, for each χ or t.

The regression analysis determined, for each time (and thus for each crystallinity), the best values of the shift factors α_i and β able to describe the curves of G'(t) and η*(t). The values found provided a good description of the experimental data for all the crystallinity degrees, as reported in fig. 9.

The values of α_i corresponding to the different crystallinity degrees are reported in fig. 10a. As expected, a higher crystallinity degree determines higher values for the moduli. At low crystallinity levels (up to about 5%) the increase of moduli due to crystallinity is about the same for all the modes, so that (in this range) it could be assumed that $G_i \cong \alpha(\chi)\ G_i°$. When the crystallinity degree rises, the increase of moduli is higher for the modes having higher relaxation times. The values of the shift factor for relaxation time, β, are reported in fig. 10b: a higher crystallinity degree induces higher relaxation times. The plot for the largest relaxation time presents a sigmoidal shape and it starts to increase significantly when crystallinity degree is close to 10%.

Also results of shift factors for relaxation times found in a previous work (Pantani, Speranza and Titomanlio 2014) are reported in fig. 10B. These results refer to a similar analysis carried out on the same material but at a different temperature (158°C instead of 140°C). These results refer to a similar analysis conducted on the same material but at a different temperature (158°C instead of 140°C). In that case, the crystallinity evolution was not measured, but estimated from a quiescent kinetic model. It is interesting to notice that the maximum value reached for the shift factor was of the same order of magnitude as the one measured in this work, even if the crystallinity degree at which the increase of shift factor takes place is much higher (of a factor of about 5) for the results obtained in this work. In that case, however, crystallization and rheology data were taken by different apparatuses and it should be considered that a few degrees of misalignment between the

rheometer temperature and the crystallization kinetic model could well justify the difference. This was already stressed when the results were presented (Pantani, Speranza and Titomanlio 2014).
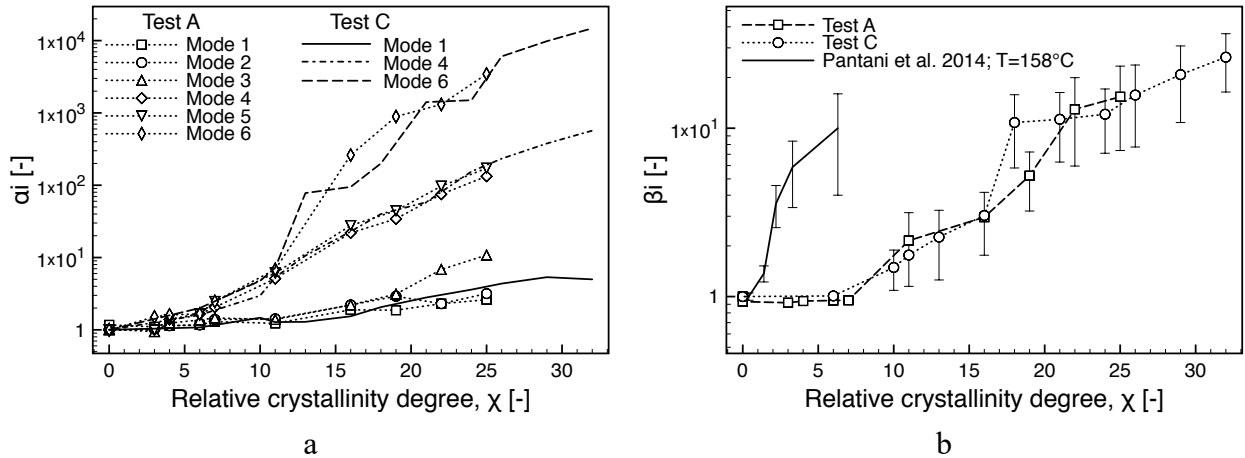

a   b

Fig. 10. Effect of crystallinity degree on the shift factors according to eq. 2. a) shift factors for moduli; for graphical purposed, just three modes for the largest gap are reported as far as moduli are concerned. b) shift factors for relaxation times; results form previous work (Pantani, Speranza and Titomanlio 2014) are also reported for comparison.

Description of the effect of crystallinity on viscosity

In order to quantify the effect of crystallinity on viscosity, it is common practice to introduce a normalized rheological function (Lamberti, Peters and Titomanlio 2007, Roozemond, Janssens, Van Puyvelde and Peters 2012) as

$$\Gamma(\omega, \chi) = \frac{\eta^*(\omega, \chi)}{\eta^*(\omega, \chi = 0)} \qquad\qquad 3$$

The values of this rheological function are reported in fig. 11 for several frequencies and for all the tests considered in this work. It can be noticed that the data collected for the all the tests are very close. Despite the general fact that the crystallinity induces an increase on viscosity, this effect depends on the frequency imposed and in particular it is lower at higher frequencies and larger at lower frequencies. This is obviously a combination of the effect of crystallinity on moduli and relaxation times: in the whole crystallinity range an increase of the relaxation time (fig. 10B) of a factor ten can be reached; however, for the modes having low relaxation time (those stirred at high frequencies) the effect of crystallinity on the modulus is small (a factor less than 10 going from the

amorphous to the largest amount of crystallinity), vice versa for the modes having high relaxation times (those stirred at low frequencies) the effect of crystallinity on the modulus is dramatic (about 3 orders of magnitude going from the amorphous to the largest amount of crystallinity).
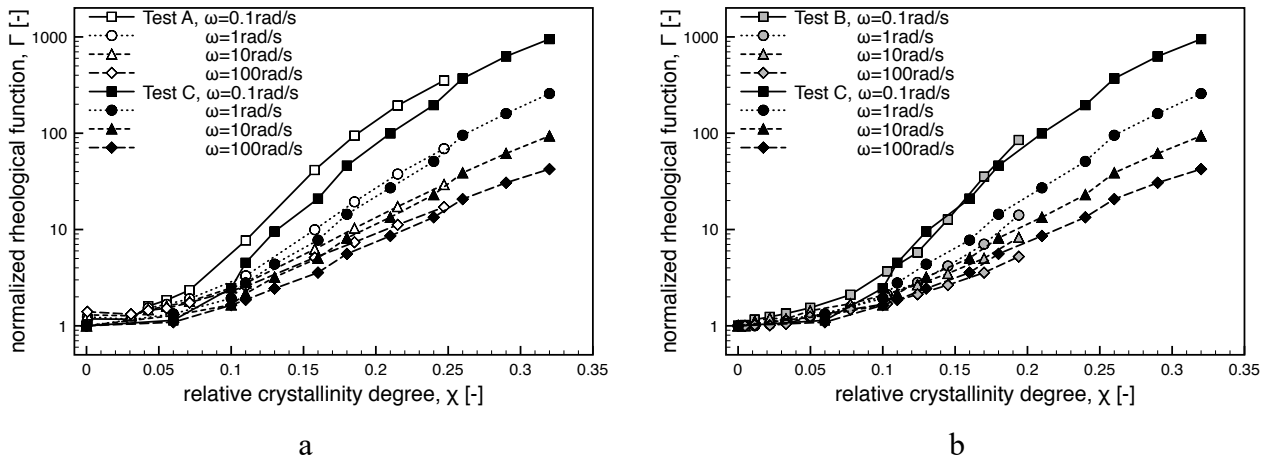

Fig. 11. Effect of crystallinity degree on viscosity for all the tests carried out in this work. T=140°C

The effect of crystallinity on viscosity is also often reported as a shift factor, δ, due to crystallinity, which is equal to 1 when crystallinity is zero and increases on increasing crystallinity (Titomanlio, Speranza and Brucato 1997). For each crystallinity degree, χ, the shift factor δ(χ) can be found by a consolidated procedure consisting in plotting the measured data of complex viscosity at different frequencies divided by δ(χ) versus the product ωδ(χ) in order to obtain a master curve including the data collected on the fully amorphous melt. The result of this procedure is shown in figure 12, in which the master curve is reported.
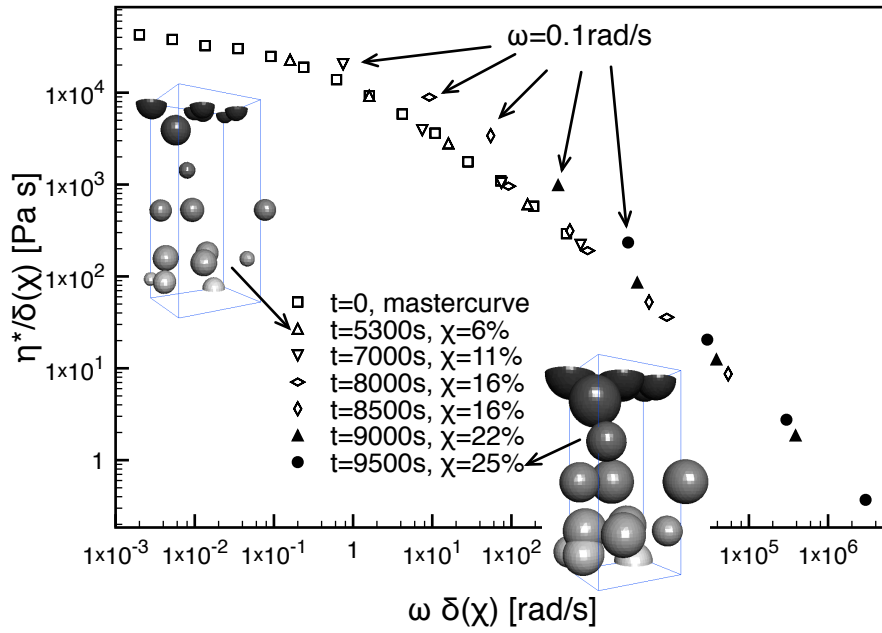
Fig. 12. Master curve at T=140°C obtained by choosing the parameter δ at each crystallinity degree. Data are decimated for clarity

It can be noticed that a master curve can be indeed obtained; however, the data collected at the lowest frequency (namely ω=0.1), depart from the master curve for crystallinities larger than 6%. A similar observation was also reported by (Roozemond *et al.* 2012). This was expected, since on the basis of the observations reported above, a single shift factor cannot describe the effect of crystallinity on viscosity. If, in fact, one single shift factor can describe the effect of crystallinity on the relaxation time (fig. 10B), when crystallinity increases, more than one shift factor is needed to describe the effect on moduli (fig. 10A), especially at low frequencies. However, in fig 10, the α_i remain very close each to the other for small values of crystallinities; this feature corresponds to the fact that the curve corresponding to χ =6% completely matches the curve χ =0 in fig.12.

The dependence of δ on crystallinity is reported in fig. 13 for both the gaps adopted in this work. Both tests lead to the same result: the shift factor increases with crystallinity and reaches a value of about 10 when relative crystallinity degree reaches a value of about 10%.

The function that describes the data (reported in fig. 13) follows the general rule adopted by Lamberti et al. (Lamberti, Peters and Titomanlio 2007),

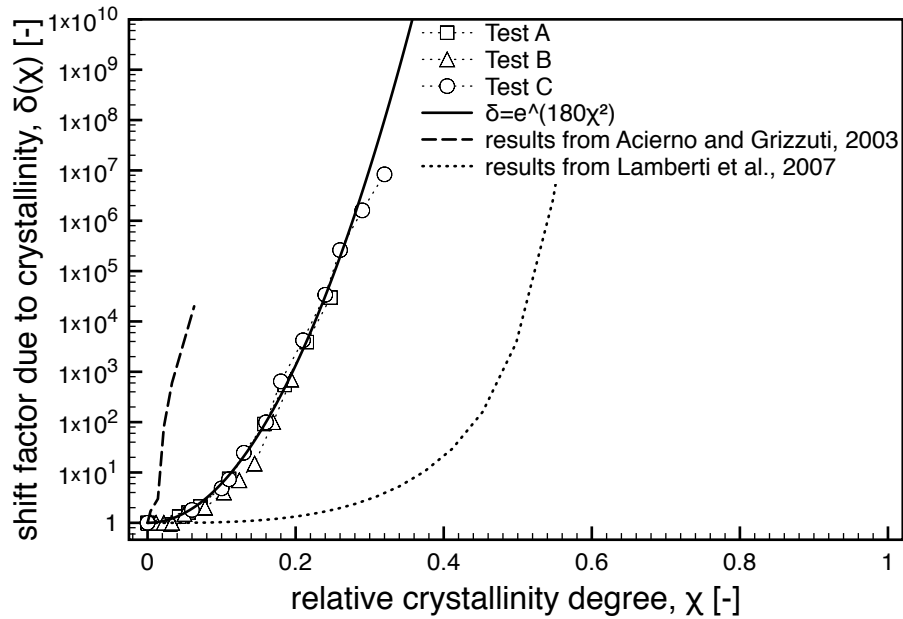$$\delta(\chi) = e^{a\chi^b} \qquad\qquad 4$$

with in our case a=180 and b=2.

Fig. 13. Dependence of the shift factor δ on crystallinity at T=140°C.

In figure 13 also the results of the shift factors calculated from other literature works carried out on the same material are reported (Lamberti, Peters and Titomanlio 2007). The data from Acierno and Grizzuti allow the determination of the shift factor from the superposition of complex viscosity curves in a wide range of frequencies, but in that case the crystallinity was estimated by Pantani et al. in a following paper (Pantani, Speranza and Titomanlio 2014). Furthermore, the rheology was measured at a temperature (158°C) different from that at which crystallinity evolved (138°C). The results from Lamberti et al. come from measurements taken in a range of temperatures from 122°C to 134°C but at just one frequency (1rad/s); the determination of the shift factor might be thus less accurate.

The differences among the three results reported in fig. 13 are significant and can be due to several factors:

- a possible effect of temperature on the phenomenon: as mentioned above, the results reported in fig. 13 refer to rheological data taken at different temperatures. This would mean

that it is not possible to separate the effects of temperature and crystallinity by means of two separate shift factors;

- an effect of nucleation density: indeed the same crystallinity can be reached with different nucleation densities (and thus with different spherulite diameters), and this could have a different influence on viscosity. Since nucleation density is also function of temperature, this effect is strictly connected to the action of temperature discussed above

- the inaccuracies in determining the real evolution of crystallinity degree inside the rheometer due the often mentioned misalignment between coupled techniques: as mentioned above this can surely justify a factor 2 in the determination of crystallinity evolution; furthermore, even at the same temperature, the surface nucleation can induce a different crystallinity degree inside the rheometer with respect to a DSC apparatus; eventually, the volume occupied by the spherulites could in principle be different from the crystallinity measured by DSC

Conclusions

In this work, rheological measurements were carried out on an iPP and simultaneously the evolving morphology was assessed by adopting a Thermo Scientific Haake Mars rheometer, equipped with an optical module. The spherulitic nucleation density and growth rate were found consistent with a quiescent crystallization.

The images taken at several positions along the gap were used to build a 3D representation of the morphology, which allowed estimating the crystallinity evolution with time.

The rheological measurements were carried out in oscillatory mode, so that the parameters G', G'' and η^* were measured during time. A linear multi-mode Maxwell model was then applied to obtain the modulus and the relaxation time of each mode as a function of the measured crystallinity degree. It was found that at low crystallinity levels (up to about 5%) the increase of moduli due to crystallinity is about the same for all the modes. However, when crystallinity degree rises, the

increase of moduli is higher for the modes having higher relaxation times, whose values increase of about three orders of magnitude for crystallinities of about 20%. Concerning the relaxation time, it was found that the increase due to crystallinity is the same for all the modes and reaches a factor of about 10 when crystallinity degree is close to 10%.

The effect of crystallinity on complex viscosity was also assessed by determining a shift factor, function of crystallinity, which is equal to 1 when crystallinity is zero and increases on increasing crystallinity. This shift factor identifies a viscosity master curve by shifting of the logarithmic viscosity curve down to smaller values and simultaneously shifting it, the same amount, toward larger frequency values. However, the data collected at the lowest frequencies need higher shift factors with respect to the other ones. This was ascribed to the fact that more than one shift factor is needed to describe the effect on moduli, especially at low frequencies.

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