Crystallization and Rheological Behaviour of a Polyethylene Terephthalate/Glass Fibres Composite

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ABSTRACT

Crystallization rates and rheological properties taken under anisothermal conditions are compared and discussed for a polyethylene terephthalate (PET) matrix and a PET/glass fibres composite as a preliminary step towards setting conditions and checking out the influence of the morphology of the polymer on the properties. The composite material is made in the particular form of a woven tape of PET covered glass fibres with 35 weight % of glass. Hot stage microscopy does not reveal any transcrystalline phase on the glass fibers. Moreover, identical modeling equations are obtained for the crystallization rates, U, of both material types:

$$U = 1 - \exp\left(-K(T)\left(\frac{T\alpha - T}{\alpha}\right)^{n}\right)$$

where α is the cooling rate and $T\alpha$ the starting point depending on α.

For the norm η^* of the complex viscosity, the modeling relation $\eta^* = \frac{a}{T} + b + \exp(c\,(T_\alpha - T) + d)$ also show comparable behaviour except for the higher values of the composite due to the reinforcing fibres. Starting points T_α for η^* and U are close together for the matrix but further apart for the composite. T_α from G', the elastic modulus, is higher than earlier because the G' reveals more sensitivity to the early nucleation step. Since PET seems to provide good wettability on the fibres and since the final properties of the composite also seem good, the adhesion problem for composite materials remains open.

INTRODUCTION

Due to their higher mechanical properties, reinforced thermoplastic fibres are used more and more in technical applications. The setting of any semi-crystalline polymer is primarily connected to its crystallization which governs the evolution of rheological properties from the melted state to the semi-crystalline rubbery state. In many cases, the evolution of these phenomena differs for composite materials because specific kinetics inducing peculiar morphologies may /1-4/ occur near the fibres and also modify the massic effect in the matrix /5/. It is generally assumed that these transcrystalline phases give better properties to the composite material but the problem of fibres/matrix cohesion remains controversal /6/.

Thus, in light of earlier work, this paper is concerned with a comparative study of the crystallization and the rheological kinetics of a polyethylene-terephthalate (PET) and a PET/glass fibres composite /7-9/. The corelative starting temperature of each process will be particularly emphasized.

1. EXPERIMENTALS

A. Materials

The polymer used is a classical (linear) PET supplied by Rhône-Poulenc Fibres in the form of continuous melt spinned monofilament fibres directly wound on bobbins with no further elongation. Table 1 summarizes the unique characteristics. Because of its high sensitivity to moisture at high temperatures, the polymer is dried under vacuum in an air oven at 150°C for at least 6 hours /8,9/.

Glass fibres supplied by Vetrotex Saint Gobain are multifilament threads made from E glass. The titre is 1600 dtex for 200 monofilaments of 10 μ diameter which are batched for PET adhesion (35 weight %). Matrix samples used for the rheological studies are pellets of 1 mm thick made from sheets preliminarily pressed at 240°C.

Concerning the composite samples, glass fibres are firstly coated by PET fibres to obtain a 35 weight % composite thread of 4600 dtex. These threads are afterward woven into a composite tape from which disks with the same glass fibre orientation of accurate diameter can be cut and superimposed for rheological measurements. Threads are directly used for DSC. The 35% rate of glass in the composite is verified afterward by ignition of the samples, particularly for small ones.

Regarding the thermal history of the polymer, the sample is melted for 6 minutes at 285°C which seems suited to the composite as well as the matrix, according to a previous study /8/ where the limiting temperature of the polymer was found to be T_M = 274°C.

TABLE 1

Mn*	Mw*	Ip*	Mw**	DEG mol %	Cat	Synthesis
19500	39000	2	36000	2	Sb_2O_3 + MnO	transesterification

* GPC measurements
** I.V measurement is 50/50 weight % phenol/tetrachlorethane solutions according to $IV = 4.68.10^{-4}\ Mw^{0.68}$
DEG: Diethylene glycol content

B. Technical

Crystallization kinetics are studied by DSC (Perkin-Elmer DSC 4) and hot stage microscopy. For DSC, anisothermal measurements are performed at scanning rates from 1°C/min to 20°C/min. Interpretation of the data is done by a method derived from the Avrami-Evans relation and previously described /7,8/. Some isothermal scans are made for comparison. Rheological properties are measured on a RDA 700 rheometer for the following parameters: $|\eta^*|$, noted as η^* in the following, the norm of the complex dynamic viscosity $\eta'-j\eta''$; G' and G" from the complex elastic modulus G' + jG"; and $\tan\delta = G''/G'$.

Due to the six orders variation of the rheological parameters from the melted state to the caoutchoutic state and the 4th power dependence of the torque against the diameter, it appears necessary to use two sets of measuring plates to obtain the best sensitivity in the experiments. Diameter plates of 25 mm and 8 mm are used for values of η^*, respectively, under and over 10^4 Pa.s.

For the composite, after verification of the constancy of η^* against the number of elementary disks used for a pellet, samples built with three disks of a theoretical thickness of 1.5 mm are used.

RESULTS AND DISCUSSION

A. Thermal Stability

Beside the hydrolysis of the polymer at high temperature in the presence of moisture, the influence of the surrounding atmosphere must be also checked for constancy of properties. Firstly, crystallization kinetics are performed by DSC under nitrogen atmosphere at a 10°C/min cooling rate from 285°C and after a dwell time of six minutes. It appears that for the matrix and the composite no more than two measurements can be made with the same sample to observe the same temperature value at the maximum of the exothermal peak. Afterwards, this temperature decreases due to a higher molecular weight.

For rheometer measurements, if air is used as the atmosphere, η^* and G' decrease for both samples. This may be due to oxidative degradation.

However, if nitrogen is used, η^* and G' increase as the temperature rises up to 290°C at which point the increase is about 80% for 45 minutes. It is quite negligible under 260°C. For temperatures higher than 300°C (not used here), rheological parameters decrease again. This evolution under a nitrogen atmosphere can be interpreted by competition between post polycondensations of the polymer and crosslinking of chains for one part and thermal degradations for the other part.

For our purpose, this phenomenon seems to be sufficiently weak if we consider the amount of time at which the polymer is permitted to be over 260°C, except perhaps at the lowest cooling rates 1°C/min.

B. Crystallization Kinetics

Isothermal crystallization of the polymer in a temperature range of 220°C to 245°C is analysed by hot stage microscopy. As shown in Fig. 1, no nucleation effect appears at 235°C on the fiber and only small spherolites of about 5 μ can be observed in the matrix. For higher temperature values, the diameter reaches 10 μ and, with

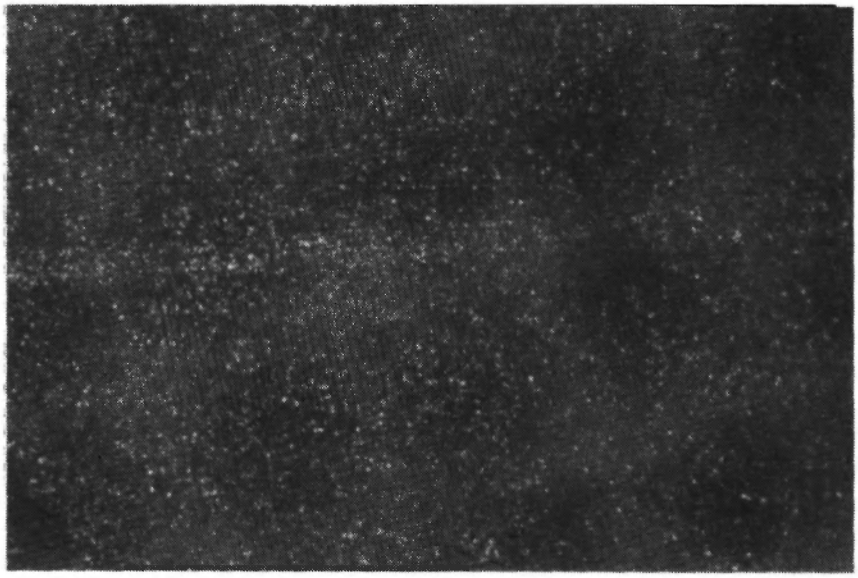

Fig. 1: Optical micrograph of PET/glass fibre crystallized at 235°C.

the help of a λ blade, it can be seen that these spherolites are positive of "type 45" but appear simultaneously in the matrix and near the fiber with no apparent growth. Table 2 gives the observed times of appearance.

As for DSC kinetics, some isothermal measurements made at 220, 225, 230 and 235°C are interpreted using the Avrami-Evans relation:

$$1 - U = \exp - K(T)(t - t_0)^n \qquad (1)$$

where U is the volumic transformation rate, K (T) the temperature dependent parameter and n the Avrami exponent. The parameter, t_0, is the effective starting point of the exothermal peak.

For anisothermal measurements, the following relation derived from Eq. 1 and previously verified for PBT /7/ and PET /8/ is used:

$$1 - U = \exp\left(- K(T)\left(\frac{T_\alpha - T}{\alpha}\right)^n\right) \qquad (2)$$

where α>o is the cooling rate and Tα the starting temperature of the exothermal peak, depending on the cooling rate. This important parameter can be determined from experimental data on the derivative dH/dt of the enthalpy as follows.

The double log relation from Eq. 2:

$$\ln - \ln(1-U) = \ln K + n \ln\left(\frac{T_\alpha - T}{\alpha}\right) \qquad (3)$$

can be derived against $\ln \frac{T_\alpha - T}{\alpha}$

TABLE 2

Temperature °C	220	230	235	240	245
Time on the fibre	20 sec	1 min 10 s	2 min 45 s	7 min 10 s	20 min
Time in the matrix (min sec)	23 s	1 min 5 s	3 min	7 min 20 s	20 min

$$\frac{d(\ln(-\ln(1-U)))}{d\ln\frac{T_\alpha-T}{\alpha}} = n - \frac{\partial K}{K\partial T}(T_\alpha-T) = p \qquad (4)$$

It has been shown experimentally that this derivative shows a constant value, p, in the vicinity of T_α. Then the following relation can be used for the determination of Tα as abscissa onsets:

$$\frac{(1-U)\ln(1-U)}{dU/dt} = -\frac{T_\alpha-T}{p\alpha} \qquad (5)$$

From the value of p obtained simultaneously, a second linear relation:

$$U^{1/p} = A\,(T_\alpha-T) \qquad (6)$$

permits another verification. It can be worth noting that analogous relations are obtained for isothermal scans which can be used for the determination of the starting time, t_o. Table 3 gives experimental results for T_α. Fig. 2 shows the linear plots of T_α versus $\sqrt{\alpha}$, both of which are close together.

At least n and ln (K(T)) can be determined by the slopes and the intercepts of isothermal straight lines of the plot of Eq. 3 in a manner similar to that used for isothermal double log plots. The complete anisothermal plot for the composite material is presented in Fig. 3 which gives results in a more extended temperature range than for the isothermal method. For both sample types, n and ln (K) are plotted in Figs. 4 and 5, respectively. Values K(T) can be represented by the following relation:

$$\ln K = A + \frac{B}{T-T_o} + \frac{CT_M}{T^2\,(T_M-T)} \qquad (7)$$

where T is in Kelvin; A, B and C are constants; T_o is the limiting lower temperature for which no further transport occurs near the crystals; and T_M is the maximum melting temperature. Table 4 gives the comparative results for the matrix and the composite. It is clear from these values that the matrix and the composite crystallize with the same kinetics within experimental errors. No nucleation effect exhausting the kinetics or giving higher T_α values occurs with this composite type.

C. Rheological Kinetics

During the shear, woven glass fibres move in the composite samples and, therefore, it is necessary to set conditions for which a reversible strain is obtained. This composite behaviour is studied at 270°C for shearing frequencies of 0.1, 1, 10 and 100 rad/s, respectively. Fig. 6 shows the plot of η*, G' and G" versus strain at 10 rad/s; it is similar to other frequencies. As η*, G' and G" decrease, the fiber structure is deformed; but, in any case, if the measuring time does not exceed 15 min to avoid degradation, the phenomenon is exactly reversible and the starting values are recovered. This permits us to believe that the experimental conditions are well suited and that the glass fibers are correctly wetted by the polymer.

Concerning the rheological kinetics, Figs. 7 and 8

TABLE 3

α	1	2	3	4	5	8	10	15
$T\alpha_{matrix}$	238.4	235.2	234.3	233.6	231.2	227.6	224.6	219.7
$T\alpha_{comp.}$	237	233.5	232.9	232.2	230	226.4	224	223.2
$T'\alpha_{matrix}$	238.2	235.6	233.9	232.5	231.1			
$T'\alpha_{comp.}$	242.8	241.2	239.5	238.3	237.5			
$T''\alpha_{matrix}$	240.9	239.2	237.5	236.5	235.4			
$T''\alpha_{comp.}$	245	244.1	243.1	242.6	242.3			

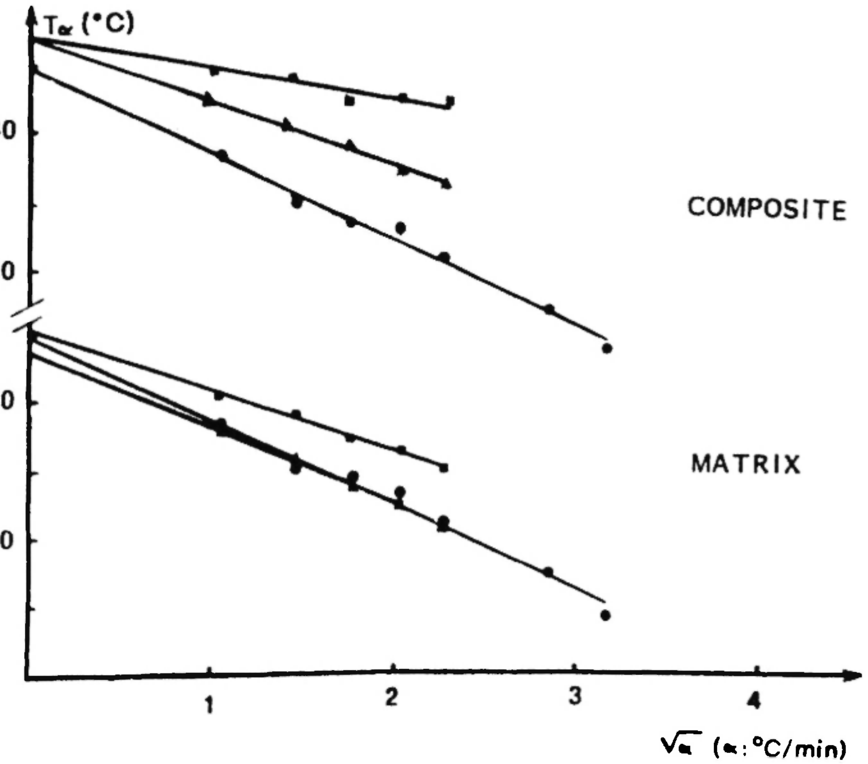

Fig. 2: Starting temperatures T_α versus $\sqrt{\alpha}$: (●) from DSC; (▲) for η^* and (■) for G'.

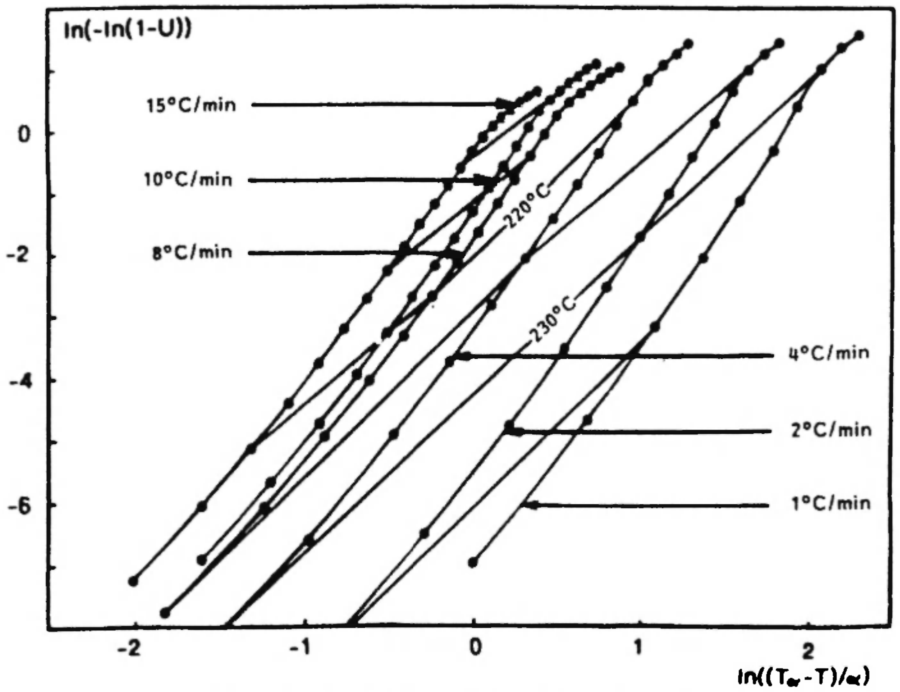

Fig. 3: Double log plot for the composite.

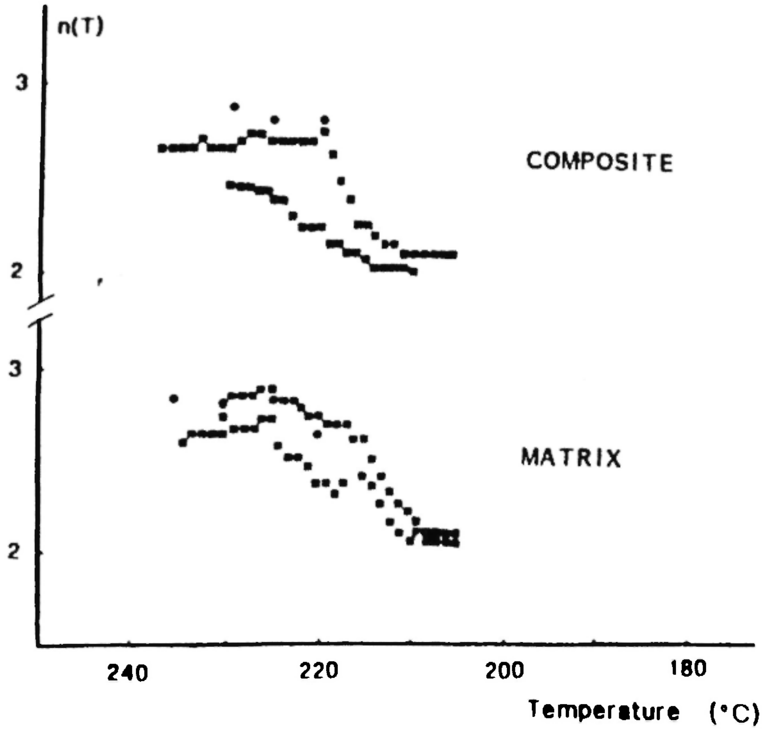

Fig. 4: Plots of n versus temperature for the matrix and the composite: (■) anisothermal measurements; (●) isothermal measurements.

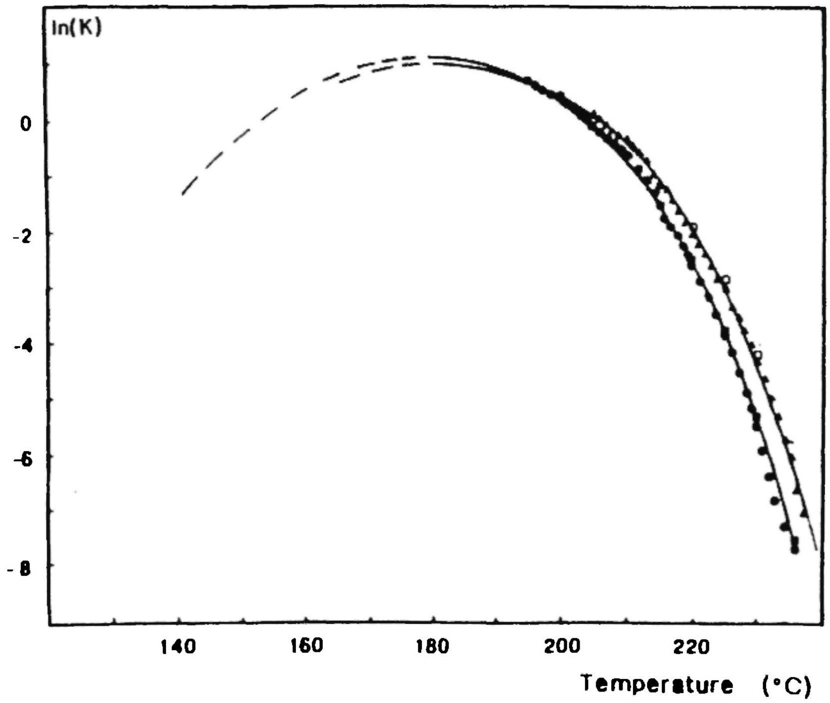

Fig. 5: K(T) versus temperature: (●) anisothermal and (■) isothermal values for the matrix; (▲) anisothermal and (❑) isothermal for the composite.

TABLE 4

Coefficients	A	B	C	T_o (K)	T_m (K)
Matrix	25.95	- 1195	525000	329	549
Composite	25.25	- 1196	525000	330	553

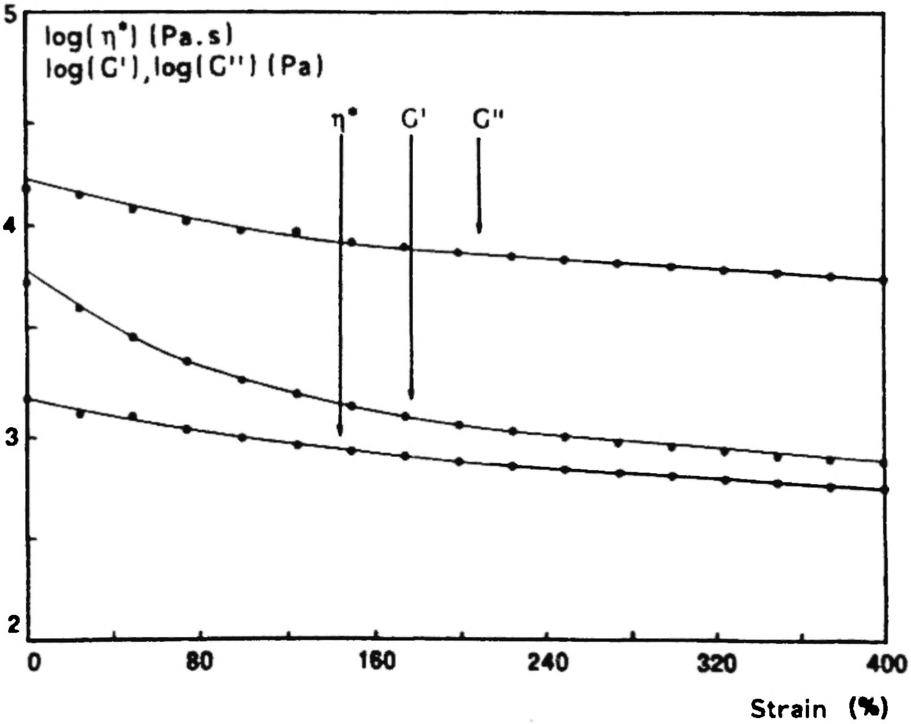

Fig. 6: Rheological parameters versus strain at 270°C and 10 rad/s for the composite.

show the plots of η^*, G', G'' and $\tan\delta$ versus decreasing temperatures at 3°C/min, respectively, for the matrix and for the composite. Fig. 9 permits comparison on the influence of α on η^* for the composite. The starting temperature values of the crystallization zone are determined by subtracting from η^* or G' the values of the extrapolated melted domain determined by Arrhenius:

$$\ln \eta^* = a + \frac{b}{T} \qquad (8)$$

for η^*, with T in Kelvin. Then the resulting data are fitted with a relation similar to Eq. 6 in order to obtain T'_α and T''_α, see Table 3. It appears immediately that the rheological starting temperatures of the composite have higher values than for the matrix. This more enhanced crystallization process may be due to higher stress conditions for the polymer in the presence of woven glass fibers. A composite experimental design against the shearing rate and the shearing frequency has been previously performed on the matrix. It was shown that a significant effect on T'_α and T''_α could be obtained for high shearing values, up to 6°C more than under quiescent conditions /9/. In the present case, as T_α and T'_α are comparable for the matrix, T'_α stays about 4°C higher for the composite. The discrepancy is the same for T''_α: the values are about 3°C higher than T'_α for the matrix but 7 to 8°C higher for the compo-

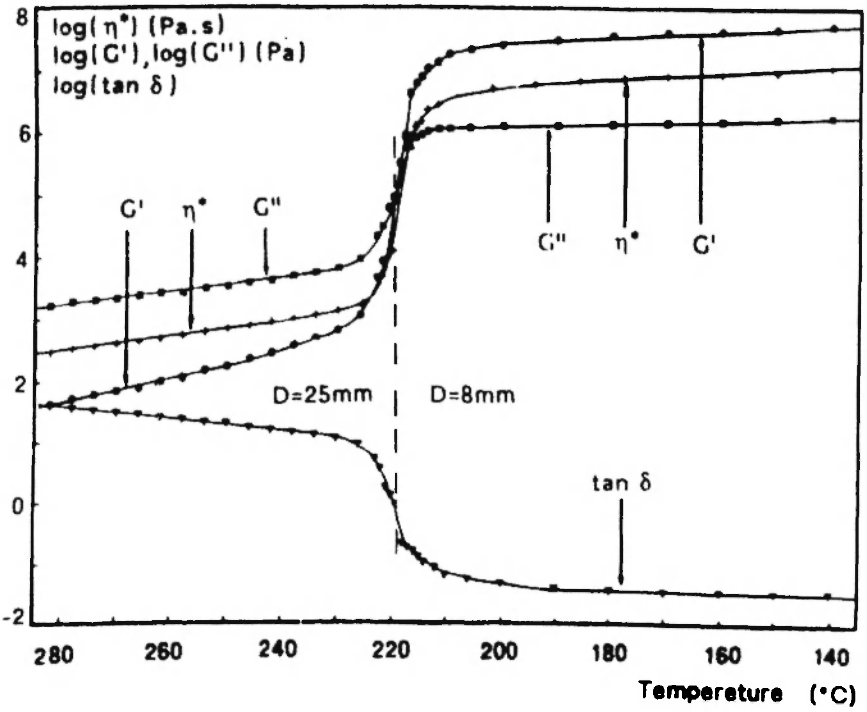

Fig. 7: Rheological parameters versus temperature for the matrix.

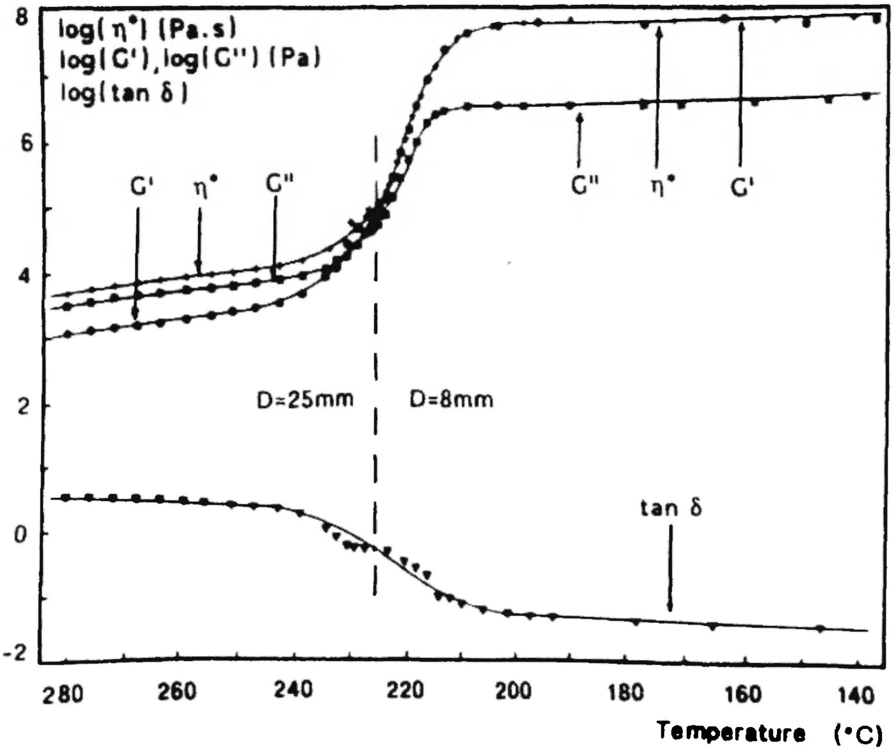

Fig. 8: Rheological parameters versus temperature for the composite.

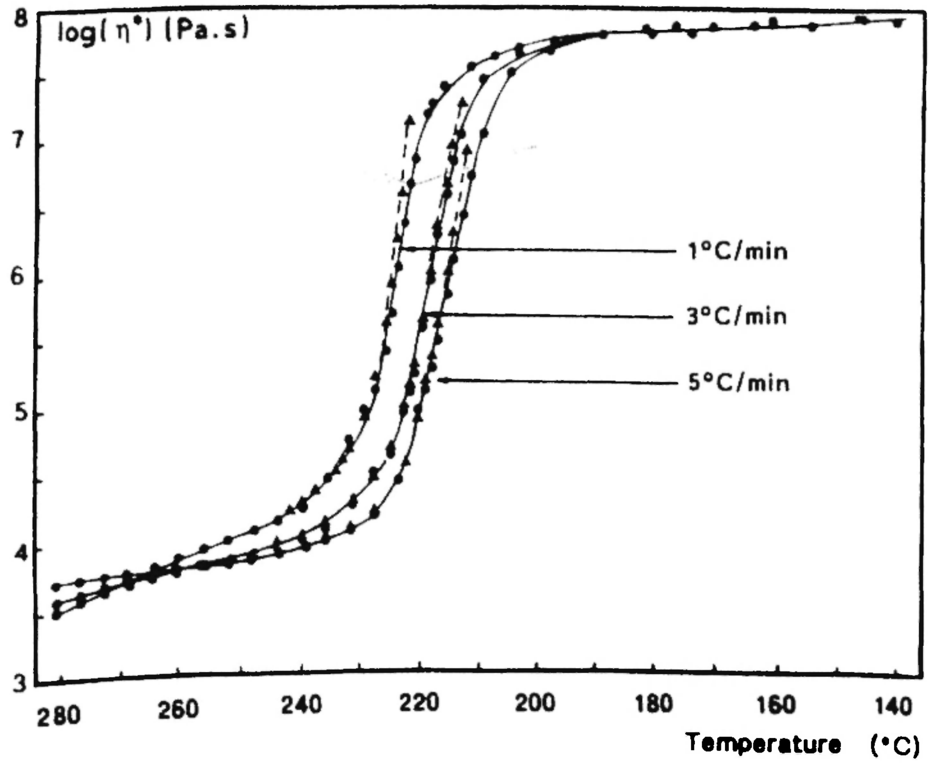

Fig. 9: Plot of η* for the composite at different cooling rates: (●) experimental; (▲) calculated.

site. Nevertheless the empirical linear relation of each T_α versus $\sqrt{\alpha}$ (see Fig. 2) is verified, and, moreover, the intercept values are close together: T = 244.7 ± 2.6°C. As previously assumed, this temperature is probably the boundary value under which nucleation occurs under quiescent conditions in a reasonably low time compared to the cooling rate used. This seems to signify a change in crystallization mechanisms at a higher temperature range; and it would be of interest to study, although it is not efficient for normal setting conditions. Even in the presence of glass fibres producing a higher resistance in the sample, the elastic modulus changes first, before the other parameters, and thus characterizes the first observable manifestation of the higher entanglements number in the polymer network.

An empirical model can also be established for rheological kinetics. For practical considerations, the most interesting part is the beginning of the phenomenon. Thus, the following equation, continuous in the range $T > T'_\alpha$, can be used:

$$\ln \eta^* = \frac{a}{T} + b + \exp\left(c\,(T'_\alpha - T) + d\right) \qquad (9)$$

where a, b, c and d are constant, and a and b are related to the Arrhenius relation (Eq. 8) with T in Kelvin, the exponential being negligible for $T > T'_\alpha$. A similar relation can be written for modeling G'. Table 5 gives some calculated values and Fig. 8 permits a comparison of experimental and calculated points for some scanning rates. Good accuracy is obtained for the matrix as well as for the composite.

3. CONCLUSION

The rheological behaviour and the crystallization kinetics plainly confirm the absence of the nucleation effect on glass fibers for a PET composite. The effect is then just a higher level for the viscosity and for the

TABLE 5

	α (°/min)	1	3	5
MATRIX	a	9584	7515	7030
	b	- 11.86	- 7.9	- 7.28
	c	0.535	0.392	0.391
	d	- 0.814	- 2.341	- 1.63
COMPOSITE	a	11564	8045	5760
	b	- 12.61	- 6.26	- 1.92
	c	0.262	0.147	0.260
	d	- 1.23	0.32	- 1.19

elastic modulus due to the particular system of woven glass fibers. The early crystallization is set by G', more sensitive to the entanglements in the matrix at a few degrees higher than the starting values of η^* or the starting values of the transformation rate. Concerning the composite, the high mechanical stresses produced by the glass fibres enhances the crystallization of the polymer with higher starting values. These T_α are important parameters for the quantitative descriptions of the phenomenon. They seem to characterize the effective growth of the spherolites after the induction period. Their values change with the experimental conditions of the crystallization process but, even under quiescent conditions, actual fundamental theories do not permit prediction from T_M, the intrinsic value for the polymer over which nothing can occur. Moreover, in the case of mechanical stress, the effective value to choose, T''_α from G' or T'_α from η^*, can not yet be really established.

Since the solid composite reveals good mechanical properties due to fiber-matrix cohesion, the problem of adhesion of the polymer enhanced by transcrystalline structures remains open.

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