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Polymer 42 (2001) 3139–3152

polymer

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New morphologies in immiscible polymer blends generated by a dynamic quenching process

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Received 12 June 2000; received in revised form 27 July 2000; accepted 14 August 2000

Abstract

New types of morphology in immiscible polymers blends, obtained by a process named dynamic quenching process [Cassagnau P, Michel A. French Patent, No 0004420, 6 April 2000], are presented. The dynamic quenching process consists of crystallizing under shear or elongational flows, a semi-crystalline polymer (or solidifying an amorphous polymer) dispersed in melt thermoplastic matrix. Using this new process, polybutylene terephthalate (PBT) and polycarbonate (PC) have been dispersed in an ethylene vinyl acetate (EVA) copolymers matrix in a twin-screw extruder. A coral structure of the PBT domains and a fine nanoscale ($100 \times 300\ \mathrm{nm}^2$) of PC rods have been so elaborated. The development of the morphology during processing was qualitatively discussed in terms of crystallization under shear or elongational flows of fine PBT droplets dispersed in a melt EVA matrix. Coral PBT structure forms a network-type structure, which confers to the material an yield stress behavior. Considering EVA/PC blends, the mechanism of the morphology development is different. As PC is an amorphous polymer, the viscosity ratio and the elasticity of the PC phase considerably increases with decreasing temperature to the PC glass temperature. Furthermore, the dynamic quenching process can be used as a way to control and to form a rod morphology at high concentrations of PC. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Morphologies; Polymer blends; Extrusion

1. Introduction

Because the final morphology of the blend of immiscible polymers has a controlling influence on the properties of the materials, the development of morphologies during the blending process has been extensively studied in these past two decades. There have been many studies, which have reported on the influence of processing conditions on the resultant morphology. The mechanical properties of polymer blends can largely vary, even if the mean particle size and particle size distribution of the minor phase only slightly change. It is well known that the morphology of a polymer blend is determined by shear rate, interfacial tension, composition, flow field and viscoelasticity of the components. Furthermore, different types of morphologies of the dispersed phase can be obtained such as for example nodular, laminar or fibrillar. To generate a fibrillar morphology of the dispersed phase, fiber spinning is obviously advantageous because the elongational flow field in the spinning process is more effective than in the shear flow field. For example, polypropylene (PP)/polyamide 6 (PA6) or PET/PA6 blends with fibrillar morphology were obtained by using spinning process [1–3]. However, it has been reported that PA6 fibrils in PP/PA6 blends can also be obtained under ordinary extrusion processing conditions [4]. In our previous works, we have shown that stretching at the die-exit of the extruder is efficient in generating fibrillar morphology for PE/PBT [5] and PP/PA [6]. Lamellar morphology in the case of PP/EVOH (ethylene vinyl alcohol) with particular thermo-mechanical, rheological and barrier properties was reported by Faisant et al. [7]. Kamal and co-workers obtained laminar morphology in PP/EVOH [8,9] blends and HDPE/PA-6 [10] blends under controlled processing conditions using a special die design incorporating converging and diverging sections. More recently, thermoplastic nanocomposites constituted by HDPE/PP blends was reported in the literature [11]. HDPE and PP were melt mixed in an extruder and the resulting compound was fibrillated by drawing it through a pair of steel rollers at 138°C.

On the other hand, these different blend systems can be viewed as organic composites in which the dispersed phase plays the role of reinforcing fillers. Generally, organic

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PII: S0032-3861(00)00602-9

composites consist of dispersing in situ a small amount of another elongated solid polymer or a thermotropic liquid crystalline polymer phase in a thermoplastic matrix. For example rod-like composites are processed in two steps. In the first step, the two polymers are melt blended in order to obtain a good dispersion and then the dispersed phase is oriented as fiber in the matrix. In a second step, the previous extrudate is reprocessed in order to obtain the final product. The processing conditions of this second step are carefully controlled to preserve the shape of the morphology of the dispersed phase. Consequently, the process temperature is set above the melting temperature of the matrix but below the melting temperature of the dispersed phase [5,12]. This approach can only be applied to very specific polymer blends. Indeed, blending temperature of the components must be low enough to avoid thermal degradation of the low melting temperature component (matrix). Furthermore, the matrix must have a lower melting temperature than the reinforced phase in order to offer a large enough temperature window for processing.

In the present work, we describe new types of morphologies obtained at the time of the development of the polymer/polymer composites by a new process named dynamic quenching [13]. The term, dynamic quenching, means that these new morphologies are obtained by freezing the morphology of the dispersed phase in the melt visco-elastic matrix under shear and/or elongation flow. For illustrating this new concept, two types of blends are considered in the present paper. The first one is a blend constituted by a copolymer of ethylene and vinyl acetate (EVA) and polybutyleneterephthalate (PBT) as dispersed phase. EVA copolymer contains 28% by weight of vinyl acetate and the melting temperature is about 80°C. PBT is a semi-crystalline polymer characterized by a high melting temperature ($T_m = 225°C$). The second blend is a blend composed by the EVA and polycarbonate (PC) as dispersed phase. The polycarbonate is an amorphous polymer characterized by a glass temperature, T_g, about 150°C. The idea of the present work is then to study the influence of the nature (semi-crystalline or amorphous) of the dispersed phase on the morphology development of blends elaborated by a dynamic quenching process.

Another aim of the present work is to show how a particular morphology can modify the thermo-mechanical properties and the flow behavior (creep) at a temperature at which the matrix behaves as a viscoelactic liquid and the dispersed phase as a viscoelastic solid. Furthermore, such a system presents new developments in the field of filled elastomers and the control of co-continuous morphologies.

2. Experimental

2.1. Materials

As mentioned earlier, two blend systems were employed in the present study:

(i) *EVA/PBT blends*: As the matrix phase, we used copolymers of ethylene and vinyl acetate (EVA) supplied by Atochem (Evatane 2803, density = 950 kg/m^3) in pellet form. It contains 28% of vinyl acetate by weight and its melting temperature is about 80°C. As the dispersed phase, we used a PBT supplied by DuPont (Crastin S600, density = 1310 kg/m^3). It was vacuum dried at 100°C for at least 4 h in order to minimize the hydrolysis in the melt during processing. The melting temperature of the PBT is 225°C. EVA and PBT crystallize at very different temperatures, 60 and 205°C, respectively. The interfacial tension between the EVA and PBT phases was determined from the dynamic rheological experiments using Palierne's model [14]. The value of the interfacial tension can be estimated from this model as the value leading to the best agreement between experimental complex moduli data ($G^*(\omega)$) and theoretical curves. At 240°C, the interfacial tension was estimated to be about 5 mN/m.

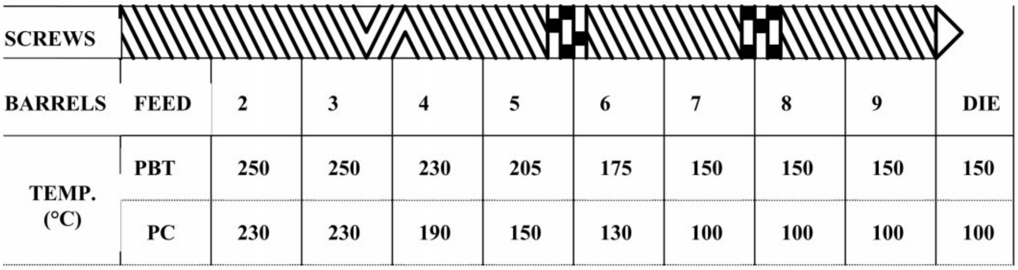
(ii) *EVA/PC blends*: We used the same EVA as described above. As the dispersed phase, we used a polycarbonate (PC) supplied by Bayer (Makrolon 2658) in pellet form. PC is an amorphous polymer with a T_g around 150°C. The interfacial tension between EVA and PC was measured from the method described above. At 200°C, the interfacial tension was estimated to be 2.5 mN/m [15].

2.2. Processing equipment

The processing equipment consisted of a co-rotating twin-screw extruder from Leistritz (model LSM30-34). The different characteristics are the following: intermeshing screws, centerline distance: $C_1 = 30$ mm, screw diameter: $D = 34$ mm, barrel length: $L = 1.2$ m, L/D ratio = 35). The extruder barrel is divided into nine equal zones. Each zone has individual electrical resistance heaters and a water-cooling system. The extruder is equipped with slit die designed for producing ribbons of polymer blends and controlling pressure and melt temperature. The processing conditions are described in the dynamic quenching process section.

2.3. Observation of phase morphology

The morphology of the blend was examined by scanning electron microscopy (SEM) using a JEOL microscope (JSM35). The samples were fractured in liquid nitrogen and vacuum metallized before analysis. The two phases can be distinguished on a micrograph without extraction of the dispersed phase excepted for the EVA/PBT blends obtained from the dynamic quenching process. However, the EVA phase can be selectively extracted in tetrahydrofuran (THF) at 60°C. After the EVA extraction, the inclusions of PBT remain in suspension in THF. Then, one droplet of the present suspension is put down on the sample support. After evaporation of the solvent, the PBT inclusions can be directly observed.



BARRELS		FEED	2	3	4	5	6	7	8	9	DIE
TEMP. (°C)	PBT		250	250	230	205	175	150	150	150	150
	PC		230	230	190	150	130	100	100	100	100

Fig. 1. Dynamic quenching process: screw configuration and temperature profile applied to EVA/PBT and EVA/PC blends.

2.4. Melt viscoelatic measurements

Viscoelastic properties were measured with a Rheometrics mechanical spectrometer (RMS800) using a plate/plate geometry. Nitrogen was used to prevent thermal oxidation. Frequency sweep and temperature sweep experiments were performed on the different blend samples. Depending on frequency and temperature, the strain was set small enough so that the rheological behavior was linear viscoelactic. Sampling was made directly on the ribbon that comes from the slit die of the extruder.

3. Dynamic quenching process

A usual process for the elaboration of a polymer blend is the melt blending process. As for example using an extruder, the feed section of the barrel is commonly kept relatively cool. The solid granules or powders are quickly conveyed down the screws to the heated sections where melting or softening (amorphous polymers) occurs. Further mixing in the fluid state leads to the final morphology of the blend. At the die exit of the extruder, the hot blend is quenched by water or air cooling. An important problem, which generally arises with polymer blends is the shape and size stability of the morphology as the morphology depends on the processing conditions. Apart from the material influence (viscosity ratio, interfacial tension), the screw configurations as well as the processing parameters, such as the screw velocity and flow rate, determine the resulting phase morphology. Therefore, modification of polymer blends by interfacially active compatibilizers has extensively been investigated to obtain polymer blends with stable desirable morphology. Another way, explained in Section 1, is to use the polymer/polymer composite concept. In a first step, the morphology of the blend is elaborated and this blend can be reprocessed in a second step at a temperature lower than the melting or softening of the temperature of the dispersed phase. However, this may limit the choice of the polymers to be used with this approach.

The idea of the dynamic quenching process is to freeze the morphology of the minor phase dispersed in a viscoelastic matrix under flow. The formation of the dispersion and the development of the blend morphology in a processing operation present a dynamic process which is determined by the equilibrium of the processes of particle breakup and coalescence of the dispersed phase, taking place in parallel under flow. If the melt temperature progressively decreases so that it becomes lower than the temperature of crystallization of hardening of the minor phase the dynamic process of breakup and coalescence will drastically modify. The morphology of the blend will thus completely modify and we can expect a new type of morphology. Furthermore, in situ reinforcing organic composites can be directly generated in one step.

Such a process requires successive continuous steps of changing temperature of the blend system. However, the initial mechanism of morphology development is intimately connected with the melting or softening process. Experimental observations suggest that while flowing through some strong shear and elongation zones inside the extruder, a quasi-final morphology can be achieved, which is for the most part already created in the melting section of the extruder [16,17]. Furthermore, it was also observed that this morphology does not significantly change while passing through the different screw sections going down the screws to the die. Scott and Macosko [18,19] experimentally proved in batch mixer that most of the reduction in the dispersed phase size occurs at short mixing times, in conjunction with the melting or softening process. Then, in order to perform a dynamic quenching process in a twin-screw extruder, the configuration of the screws and the temperature profile were designed taking into account these different experimental observations. The screw configuration and the temperature profiles are illustrated for EVA/PBT and EVA/PC blends in Fig. 1.

EVA and PBT (or PC) pellets were introduced in the inlet of the extruder (barrel 1, feed zone). Then, polymers are melted in the first left-handed element (barrel 3). Through this negative conveying element, characterized by a high back pressure, a drastic reduction of the domains size of the minor phase occurs in a few seconds during the melting (or softening process). Going down the screws (barrels 4 and 5), the melted blend is conveying at a temperature higher than the temperature of melting of (softening) the dispersed phase. The melt temperature is measured by an infrared-sensor. The check temperature of barrel 6 is about the melt temperature of the minor phase. The check temperatures of barrels 7–9 plus the die are lower ($T_{\mathrm{barrel}} - T_{\mathrm{m}} \approx 50°\mathrm{C}$) than the melting temperature of PBT or softening temperature of PC. Going down the screws inside the barrel elements 7–9, the dispersed phase undergoes a dynamic quenching process under flow of the EVA matrix. Assuming a nodular morphology of the PBT (or PC) phase at the exit of the left screw element, droplets of the dispersed phase are going to crystallize (or solidify) in melt viscoelastic matrix under complex flows. As the transition between liquid and solid occurs in dynamic process where shear and elongational flow can be superposed, unexpected types of morphologies can develop inside barrels 7–9 plus the die.

Due to the low thermal conductivity of the polymers and the viscous dissipation of high viscosity materials, the melt temperature of the blend system is obviously not the temperature of the control system. The melt temperature was then controlled at the die by a second infrared sensor. Furthermore, the processing conditions are suited taking into account the phenomena of self-heating by viscous dissipation. The screw rotational speed and the total flow rate were fixed to 160 rpm and 4 kg/h, respectively. Only two short mixing zones (positive conveying) were placed going down the screw from barrel 6 to barrel 9 as shown in Fig. 1.

4. Results and discussion

4.1. EVA/PBT blends

EVA and PBT were processed at temperatures higher than the melting temperature of PBT (usual process). Fig. 2a and b shows the morphologies of these blends for the concentrations in weight of 20 and 30%, respectively, of the PBT phase. As expected, a fine dispersion in EVA matrix of spherical PBT droplets can be observed. Due to the phenomena of coalescence, the size of the particles increases with increasing PBT concentration. The average volume diameters d_{v} of PBT particles are $d_{\mathrm{v}} = 0.8\ \mu\mathrm{m}$ and $d_{\mathrm{v}} = 1.5\ \mu\mathrm{m}$, respectively.

Frequency sweep experiments were performed at different temperatures lower than 200°C in order to keep the elastic solid PBT phase dispersed in the melt EVA matrix. From these experiments, a master curve of the complex shear modulus G^* was built at 180°C. Fig. 3 shows the effect of the 30% PBT concentration on the shear complex modulus at 180°C. The presence of PBT results in an increase of the storage and loss moduli over the whole range of frequencies compared with the complex shear modulus of the pure EVA matrix. Denoting ϕ as the volume fraction of semi-crystalline PBT droplets, the dependence of the complex moduli on frequency can be expressed as follows:

$$G^*(\omega) = G_{\mathrm{m}}^*(\omega)\left(\frac{1 + 3/2\phi}{1 - \phi}\right) \tag{1}$$

where $G_{\mathrm{m}}^*(\omega)$ is the complex shear modulus on the EVA matrix.

On the other hand, these results show that there is no interparticular interactions between the PBT particles in the observation scale corresponding to the experimental frequency window investigated in the present study. Indeed slight interactions were considered in the literature [15,20] on similar blend systems from the observation in the low frequency region of a pseudo-equilibrium plateau modulus.

4.2. EVA/PBT blends by dynamic quenching

The morphologies of these new systems were attempted to be quantified as reported in the previous part. However, the contrast between the two phases is not well defined and the morphology cannot put in evidence from this method. Fig. 4 shows a picture obtained by transmission electronic microscopy (TEM). Some PBT domains can be defined, however the contrast is not good enough in order to quantify the finest structure of PBT domains. Fortunately, the EVA matrix can be selectively dissolved in THF solvent so that a fine powder of PBT were extracted. As described in Section 2, isolated PBT particles can be observed with a good contrast by SEM analysis. However, the SEM pictures in the present case are not representative of the spatial distribution of PBT particles in the blend. Only, the specific morphology of individual particles is observed from this method. Then, Fig. 5a–c shows the morphologies of different PBT particles for a concentration of 20 and 30% of the PBT phase. An unexpected type of morphology is observed and it is the first time that this type of morphology is reported in the literature. We name this new type of morphology: coral morphology. Indeed, SEM pictures describe a complex morphology without any well-defined shape as in a coral structure. This morphology is constituted of a micro-porous body full of ramifications. However, Fig. 5c rather shows a complex fibrillar structure. Furthermore, the global size of the morphology is rather rough. This morphology defines a mean critical size of about 5 μm whereas some filaments linked to this morphology present a thickness lower than 0.5 μm.

At this stage of the study, only a qualitative explanation on the formation of such particular morphology can be discussed. The morphology of melt polymer blends is a result of an equilibrium between break up and coalescence between the particles. Furthermore, the drop deformation, its aspect ratio and its eventual breakup are controlled by two dimensionless parameters, namely the viscosity ratio of the dispersed phase and the matrix:

$$\lambda = \eta_{\mathrm{d}}/\eta_{\mathrm{m}} \tag{2}$$

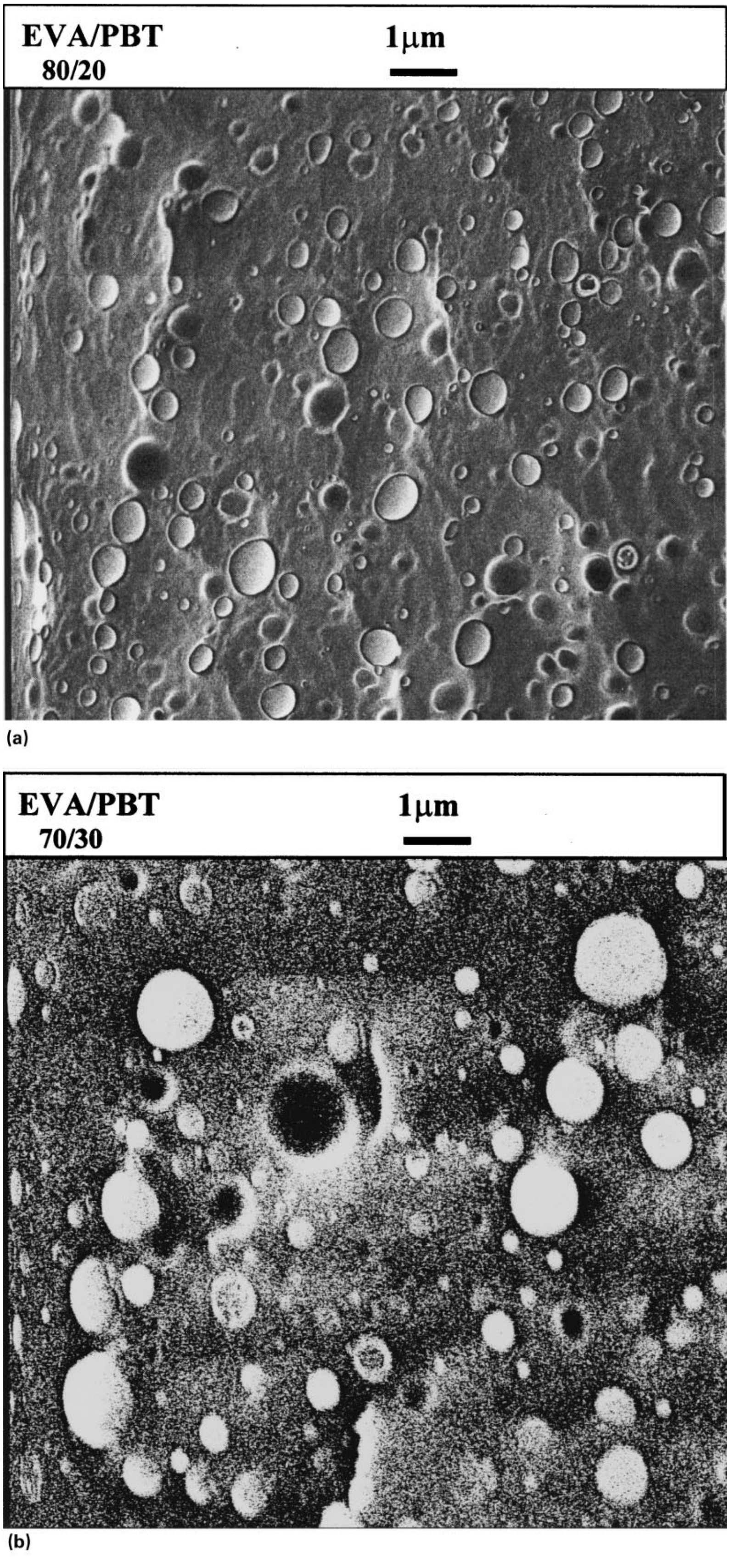


Fig. 2. Morphologies of EVA/PBT blends obtained from a usual process. SEM pictures (a) 20% PBT, (b) 30% PBT.

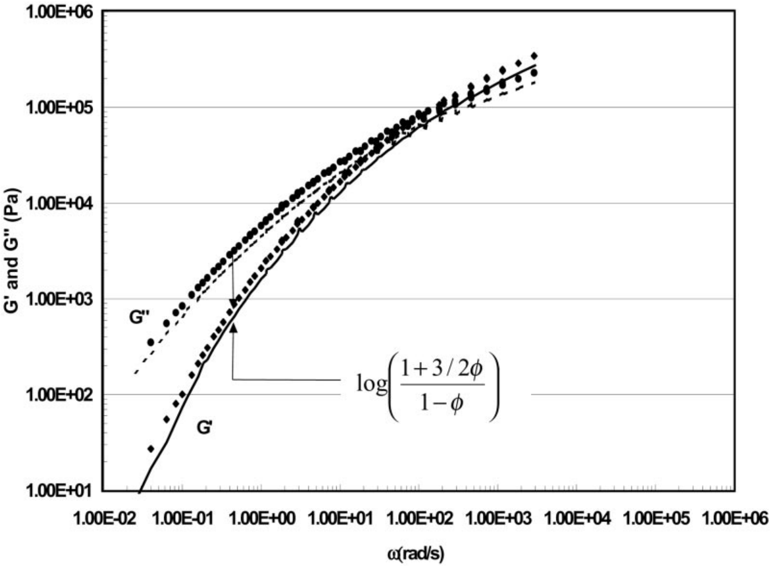


Fig. 3. Viscoelastic behavior of EVA/PBT composites elaborated from a usual process (morphology in Fig. 2b); master curve at $T = 180°\text{C}$ (solid PBT particles); 30% PBT.

and the capillary number

$$K = \sigma R/\alpha \tag{3}$$

which represents the ratio between viscous stresses (shear or elongational), σ, that tend to deform the drops and interfacial stresses, σ/R, that resist to the deformation and tend to restore the initial shape of the drop, R being the drop radius and α the interfacial tension. From experimental studies, a critical capillary number K_{cr} can be defined. Depending on the ratio K/K_{cr}, the drop will either deform or break [21–23]:

$K/K_{cr} < 1$ the drop can deform but not break (4)

$1 < K/K_{cr} < 4$ the drop deforms and can break (5)

$K/K_{cr} > 4$ the drop deforms into fiber (6)

Furthermore, the particle deformation and breakup are transient phenomena in a sense and they require a specific time, which must be defined. During flow, the main critical parameter is the ratio between the rate of the thread diameter reduction by Rayleigh instabilities and by flow (shear or extensional). This leads to a relationship between the time of breakup and the rate of deformation (shear or elongational).

In an extruder, the flow fields are complexes. However, in particular zones of the extruder, the flow field is more simple. For example in a long capillary or slit die, one can assume a shear flow. An elongation flow can be generated by a stretching system at the die exit. Going down the screws, elongation and shear flow coexist. However, in conveying and positive mixing zones shear flow is prominent whereas in converging zone elongation flow is prominent. In the present case, λ varies slightly with the temperature in the range of the temperatures comprised between 250°C (melt system) and the temperature of crystallization of PBT (205°C). As the critical capillary number

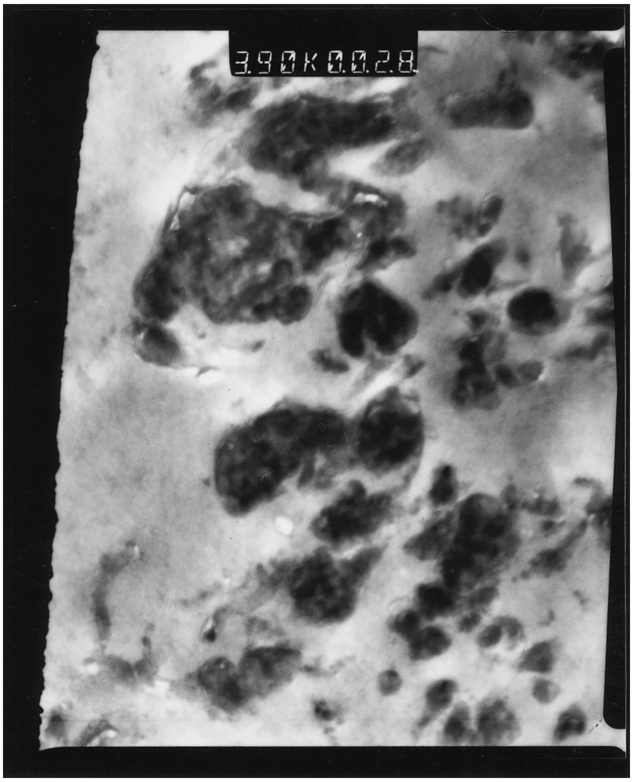


Fig. 4. Morphology of EVA/PBT blends elaborated from the dynamic quenching process. TEM picture, 30% PBT.

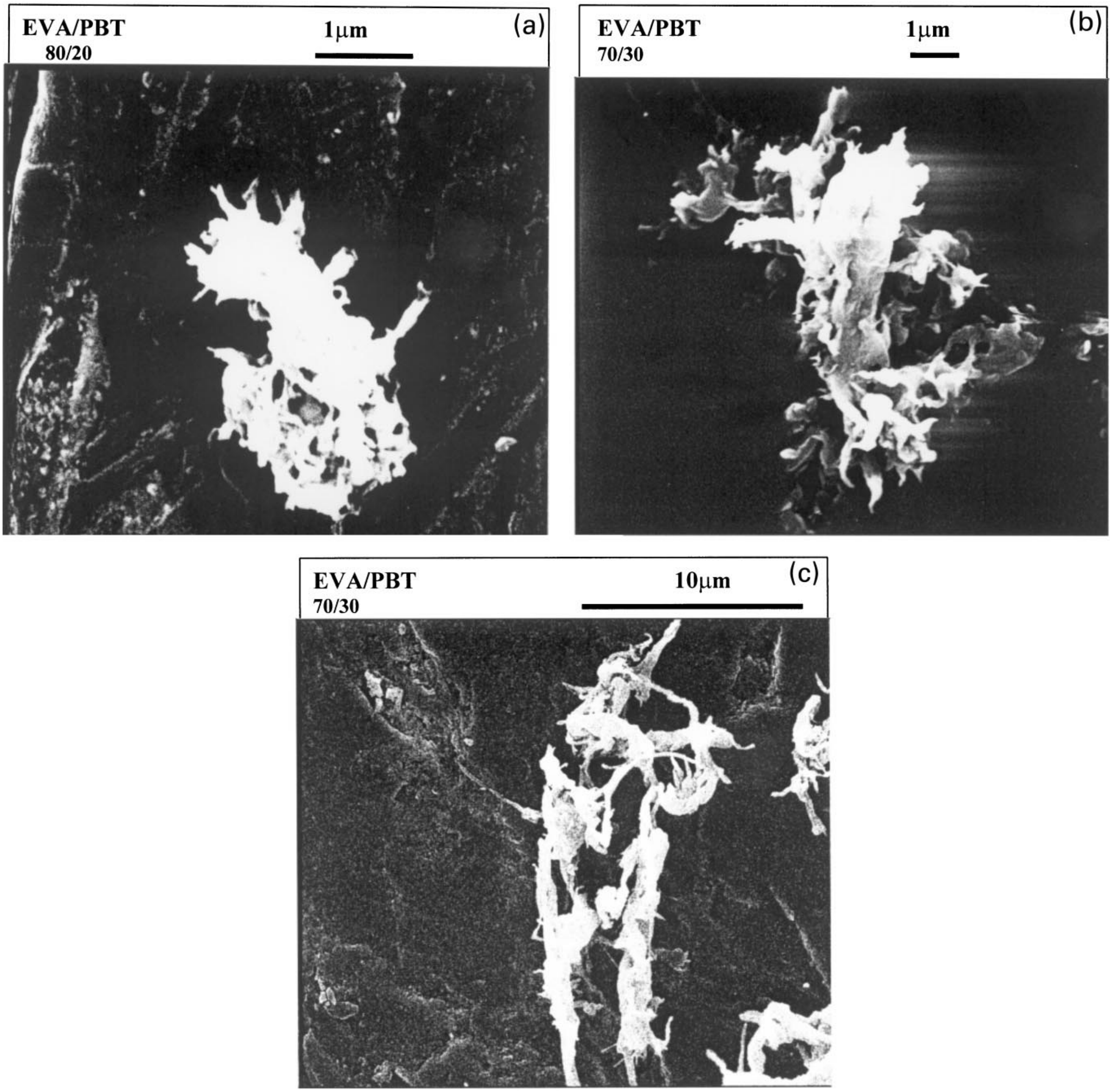


Fig. 5. Morphology of EVA/PBT blends elaborated from the dynamic quenching process. SEM picture after extraction of the EVA matrix, coral morphology. (a) 20% PBT, (b) and (c) 30% PBT.

K_{cr} depends on the type of flow and K depends on the shear or elongational rate, different types of transient deformation (Eqs. (3)–(5)) can be encountered in the different zones of the extruder.

The dynamic quenching process freezes the morphology resulting of the transient equilibrium imposed by the rheology of the two components and the type of flow fields. However, as the polymers are characterized by a low thermal conductivity coefficient, the freezing process, which corresponds to the crystallization of the dispersed phase, cannot be instantaneous. On the other hand, a previous study [24] on crystallization at high super-cooling of PBT droplets dispersed in a molten polyethylene matrix showed that the size of the PBT inclusions is the main parameter governing the crystallization behavior. It was proved that the finest PBT particles are still in the melt state at high super-cooling ($\Delta T = 80$°C). These results were explained by a size distribution of nuclei, the larger being activated at higher temperature which means that the larger PBT particles crystallize at low super-cooling of PBT and the finest PBT droplets crystallize at high super-cooling. Crystallization at high super-cooling of static PBT dispersed

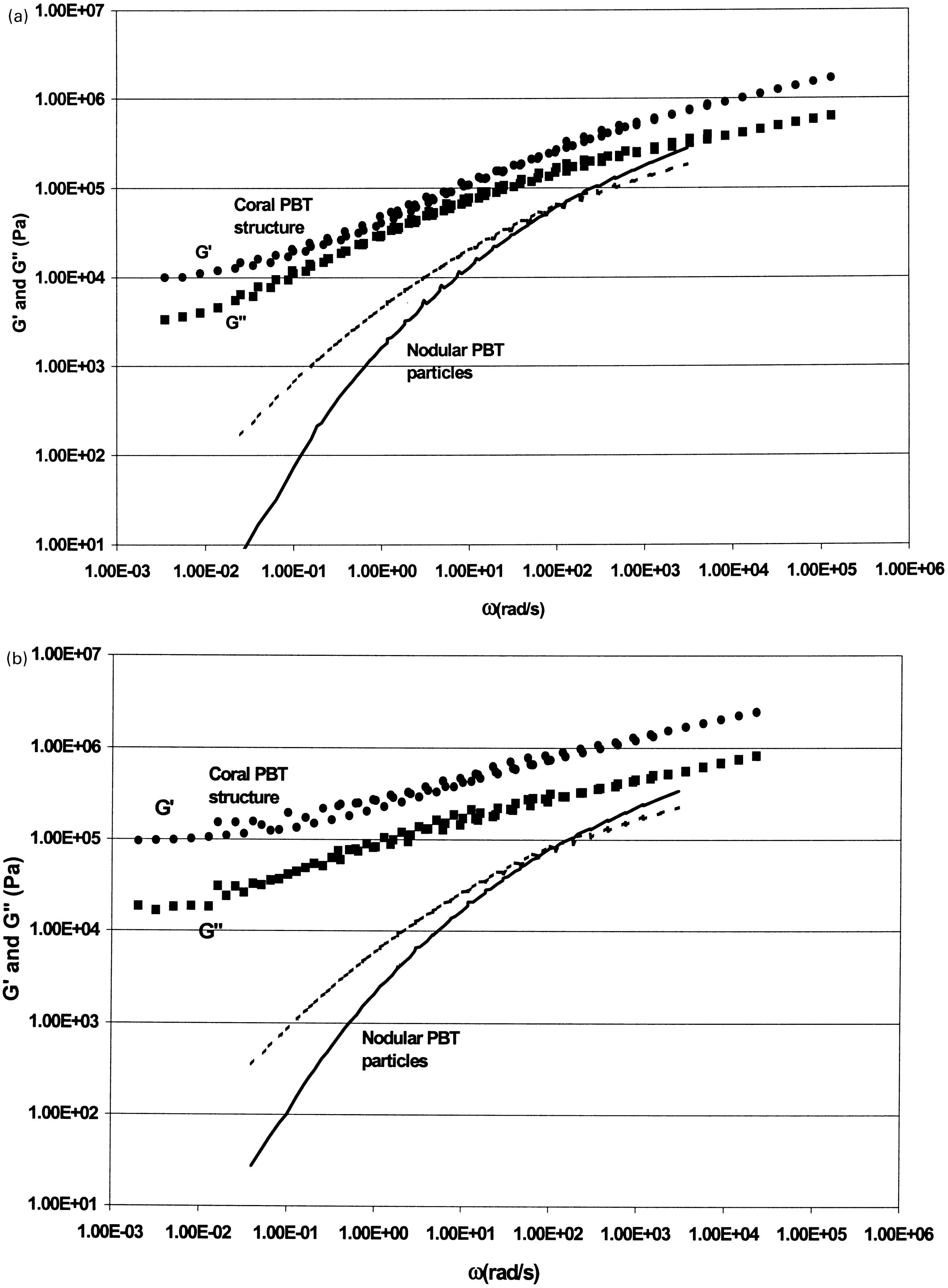


Fig. 6. Viscoelastic behavior of EVA/PBT composite with a coral morphology. Master curve at $T = 180°C$ (a) 20% PBT, (b) 30% PBT.

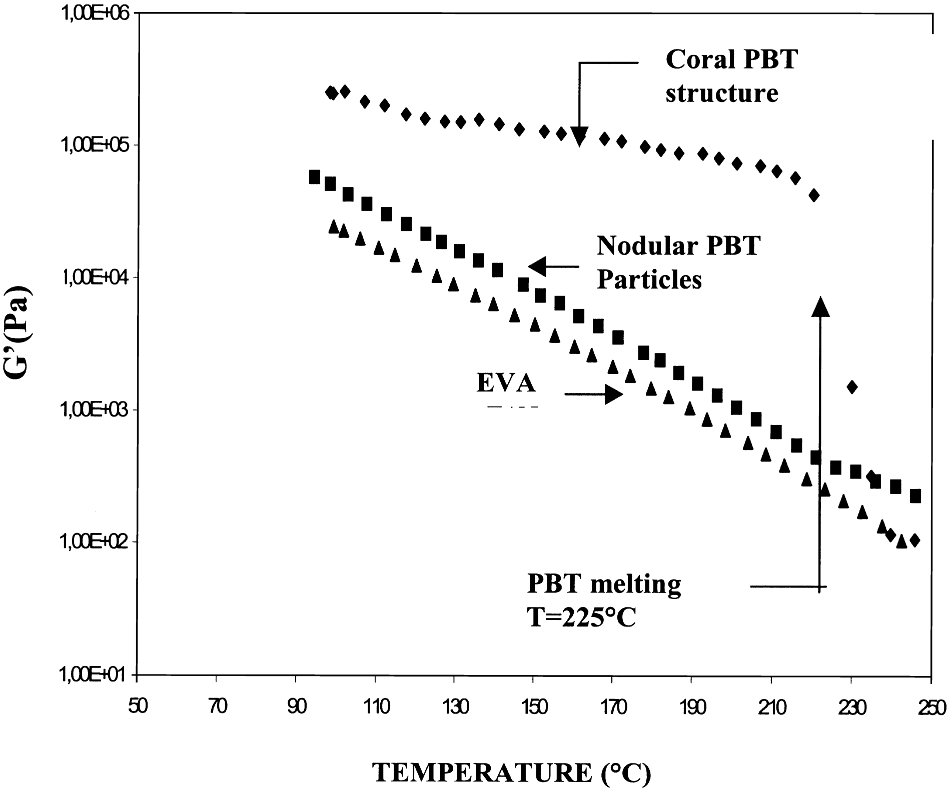


Fig. 7. Variation of the storage modulus versus temperature ($\omega = 1$ rad/s), coral PBT structure, 30% PBT.

droplets was pointed out in the range of temperatures (110–205°C). Furthermore, the semi-crystalline morphology of homopolymers that develops under intense shear and elongational flow fields is typically very different from what is observed for quiescent crystallization of the same polymer under static conditions. For example, in isotactic polypropylene [25,26] an increase of crystallinity during shearing is observed which is mainly due to a multiplication of the number of nuclei so that the crystallization is shear enhanced.

Consequently, the crystallization of the PBT dispersed phase simultaneously involves two different physical mechanisms in a transient state imposed by a temperature gradient and a superposed shear and elongation flow during

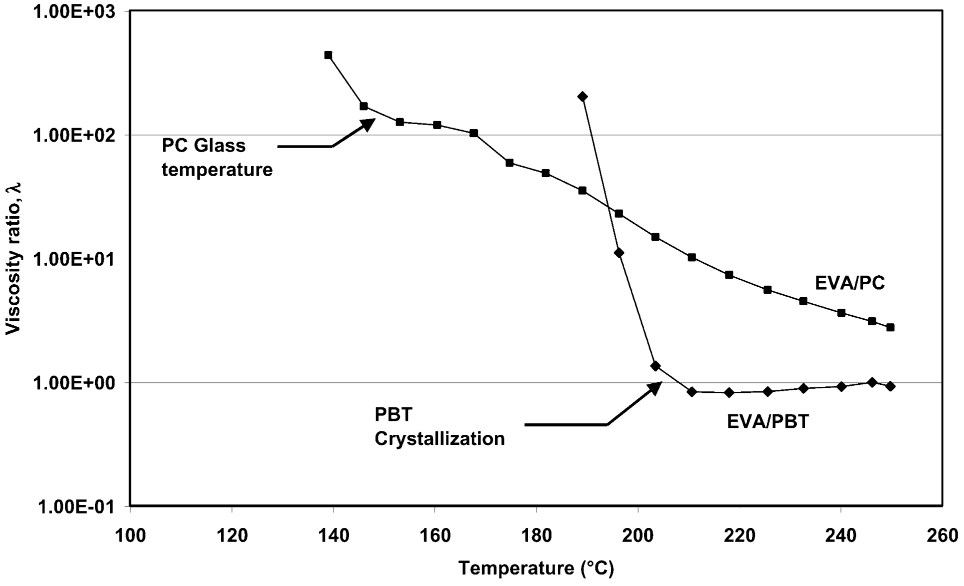


Fig. 8. Variation of the viscosity ratio with temperature at $\omega = 1$ rad/s. EVA/PBT and EVA/PC blends.

a finite processing time: break-up and coalescence equilibrium including the mechanisms of deformation and crystallization of fine morphology in dispersed media. The development of the morphology can be imagined as following: with decreasing the temperature of the blend system under shear and elongational flow superposed, the crystallization takes place into PBT domains at transient state of the deformation. Consequently, the shape of the PBT morphology results in a transient freeze mechanism. When a crystallite is formed in a transient PBT domain, the crystallite is then undeformable, but the other parts of the PBT domains can deform and crystallize later in the PBT domain which has changed, between these two stages, of shape and/or has been exchanged (coalescence and break up) with other PBT domains. Assuming such a transient freezing process of the dispersed phase, a coral structure can be so generated. The deformation of the solids PBT structure, for example the finest structure with a high aspect ratio as shown in Fig. 5c, can be also considered. A control of this particular structure of PBT domains would require a perfect control of the type of flow field and the temperature gradient applied at the blend system. For the moment, this seems to be a utopia to want to control the development of such a specific morphology inside the extruder. However, development of fibrillar morphology from an elongational flow applied at the die exit of the extruder [5,6] or lamellar morphology from a specific design of the die [8–10] can be viewed as particular controlled case of the dynamic quenching process.

Fig. 6a and b shows the viscoelastic properties for the 20 and 30% PBT composites at $T = 180°C$. A secondary equilibrium modulus of the storage modulus is observed in the low frequency region. The magnitude of this plateau (G'_p) increases with the PBT content. This secondary plateau, named also in the literature pseudo-equilibrium plateau, is attributed to inter-particular interaction. Similar behavior was already observed with several multiphase systems [5,27–32]. This plateau modulus is found to depend on the particles content, the shape or the aspect ratio of the particles, the molecular weight of the matrix, as well as the degree of dispersion of the particles in the system. In the present case, the secondary plateau can be attributed to

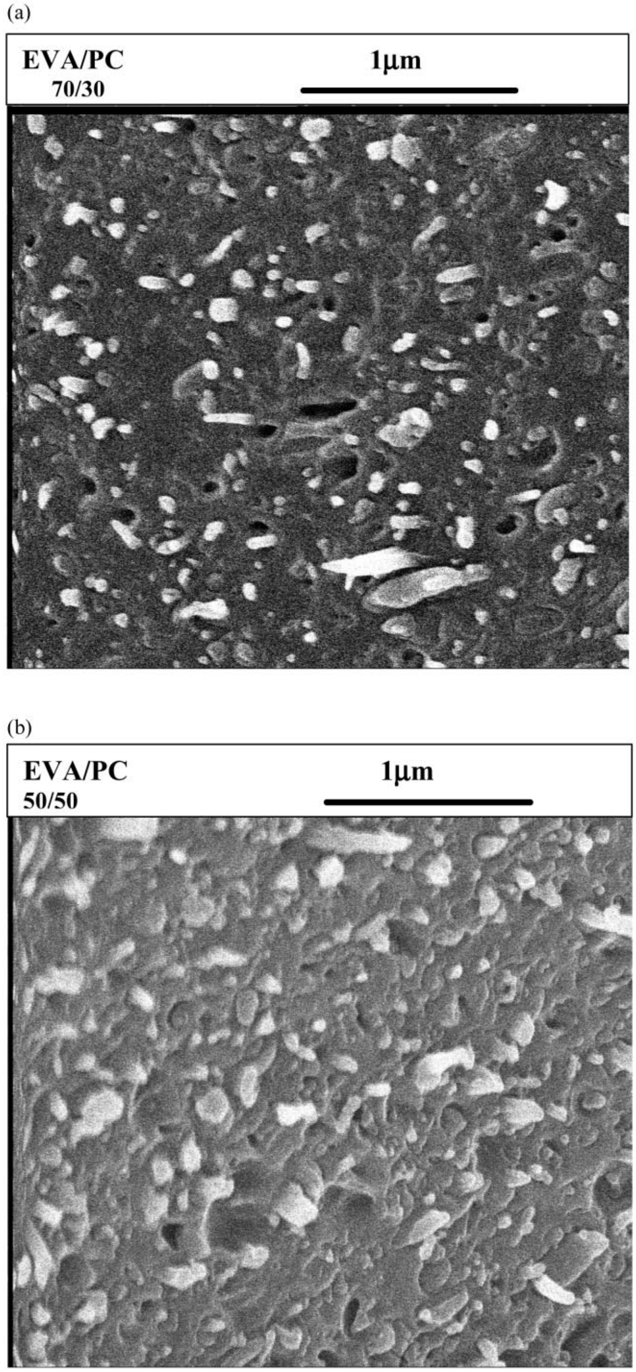


Fig. 9. Morphology of EVA/PC blends elaborated from the dynamic quenching process, rod particles. SEM pictures (a) 30% PC, (b) 50% PC.

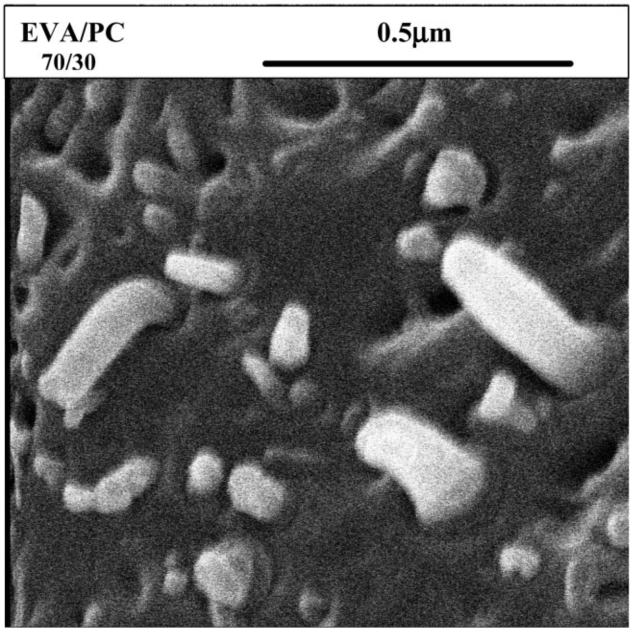


Fig. 10. Rod particles of PC, 30% PC, magnification 20,000.

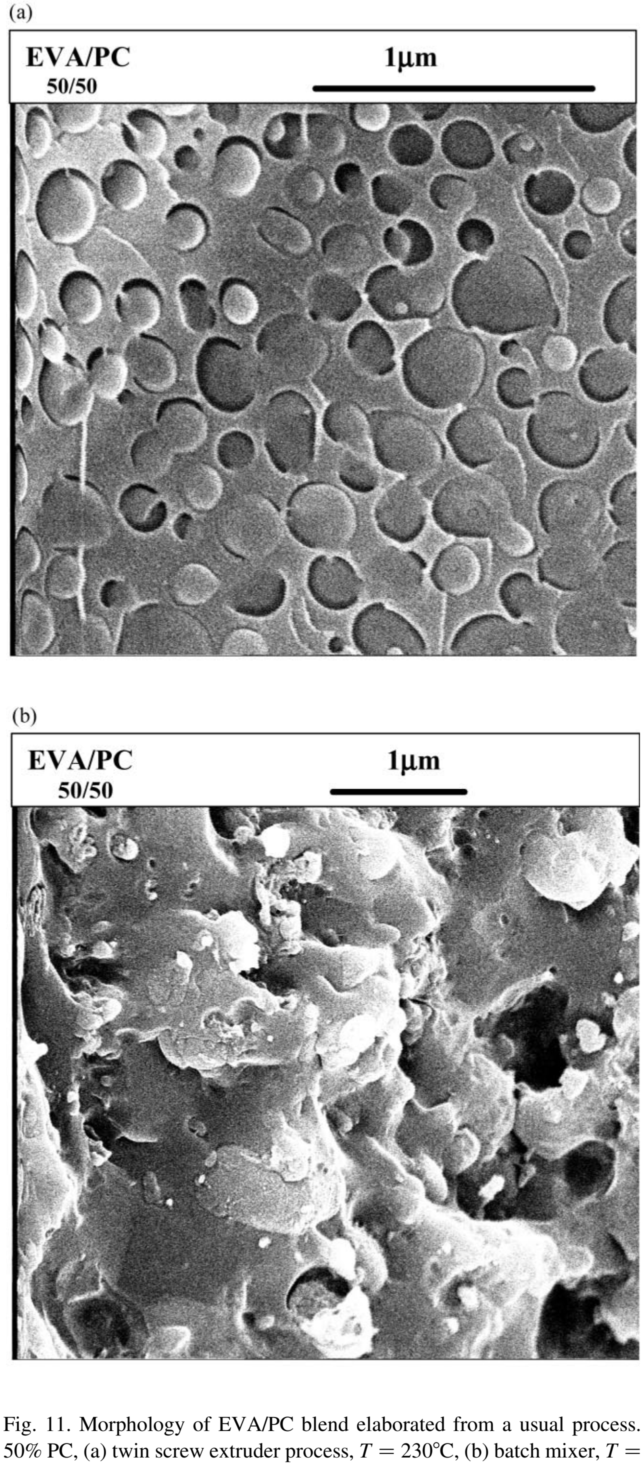


Fig. 11. Morphology of EVA/PC blend elaborated from a usual process. 50% PC, (a) twin screw extruder process, $T = 230°\text{C}$, (b) batch mixer, $T = 230°\text{C}$.

the shape of the PBT morphology. The PBT domains dispersed in the EVA matrix forms a three-dimensional physical network, which percolates through the coral structure. This network-type structure confers to the material an yield stress behavior. However, Bousmina and Muller [32] found, in polymer/rubber blends, that the value of the secondary plateau on G' corresponds to a critical stress above which the morphology of the dispersed particles becomes anisotropic whenever the blend is submitted to large deformation flow. From a material point of view, the yield stress property confers to the blend of the behavior of a physical crosslink polymer. Above the critical yield stress, ($\tau_c \equiv G'_p$) the blend can be processed but under τ_c, the creep behavior of the melt EVA reinforced with PBT is considerably reduced. Fig. 7 shows that the yield stress properties are conserved at all the temperatures to the melting temperature of the PBT phase.

4.3. EVA/PC blends

Polycarbonate is an amorphous polymer ($T_g = 150°\text{C}$) and therefore it can be expected as a quite different evolution of the morphology in the dynamic quenching process. Considering the EVA/PBT system, the variation of the viscosity from high temperature to crystallization temperature of PBT is very low ($\lambda \approx 1$ for $T_c < T(°\text{C}) < 250$) whereas in the EVA/PC blend the variation of the viscosity ratio increases considerably with decreasing temperature to T_g as shown in Fig. 8. On the other hand, the viscoelasticity of the PC phase gradually changes from a viscous behavior at high temperature to an elastic behavior (rubbery zone) with decreasing temperature to T_g. As described in the literature, the droplet elasticity seems to have much more control on the droplet deformability [33,34]. In a shear flow, the critical shear rate and the break up time have been found to increase with increasing elasticity ratio. The elasticity ratio k', defined as the ratio of the relaxation time of the dispersed phase to the relaxation time of the matrix ($k' = \lambda_d/\lambda_m$), increases considerably from 250°C to T_g of the polycarbonate. The deformation of an elastic PC droplet (near T_g) is less than the deformation of a newtonian PBT droplet (near T_c) but the time of break up of the deformed PC particle is much higher than the time of break up of the newtonian PBT particle so that a rod morphology of PC can be expected.

Fig. 9a and b shows the morphology of the EVA/PC blends, obtained from the dynamic quenching process, for 30 and 50% (by weight) of polycarbonate, respectively. A fine dispersion of nano-scale PC rods can be observed. The mean length of the rods is about 300 nm with a mean diameter of 100 nm. This new particular morphology is well defined by a magnification of 20,000 in Fig. 10. However, it is important to point out that a fine nodular morphology of PC can be obtained in a usual process at a high concentration of PC. Fig. 11a shows the morphology of 50% PC dispersed in EVA matrix by using an extruder regulated at the temperature of 230°C. Nevertheless, this morphology is not homogeneous in volume as some zones of the sample present a co-continuous morphology. Furthermore, the PC morphology considerably depends on the processing conditions. For example, Fig. 11b shows the morphology of such EVA/PC blends prepared in batch

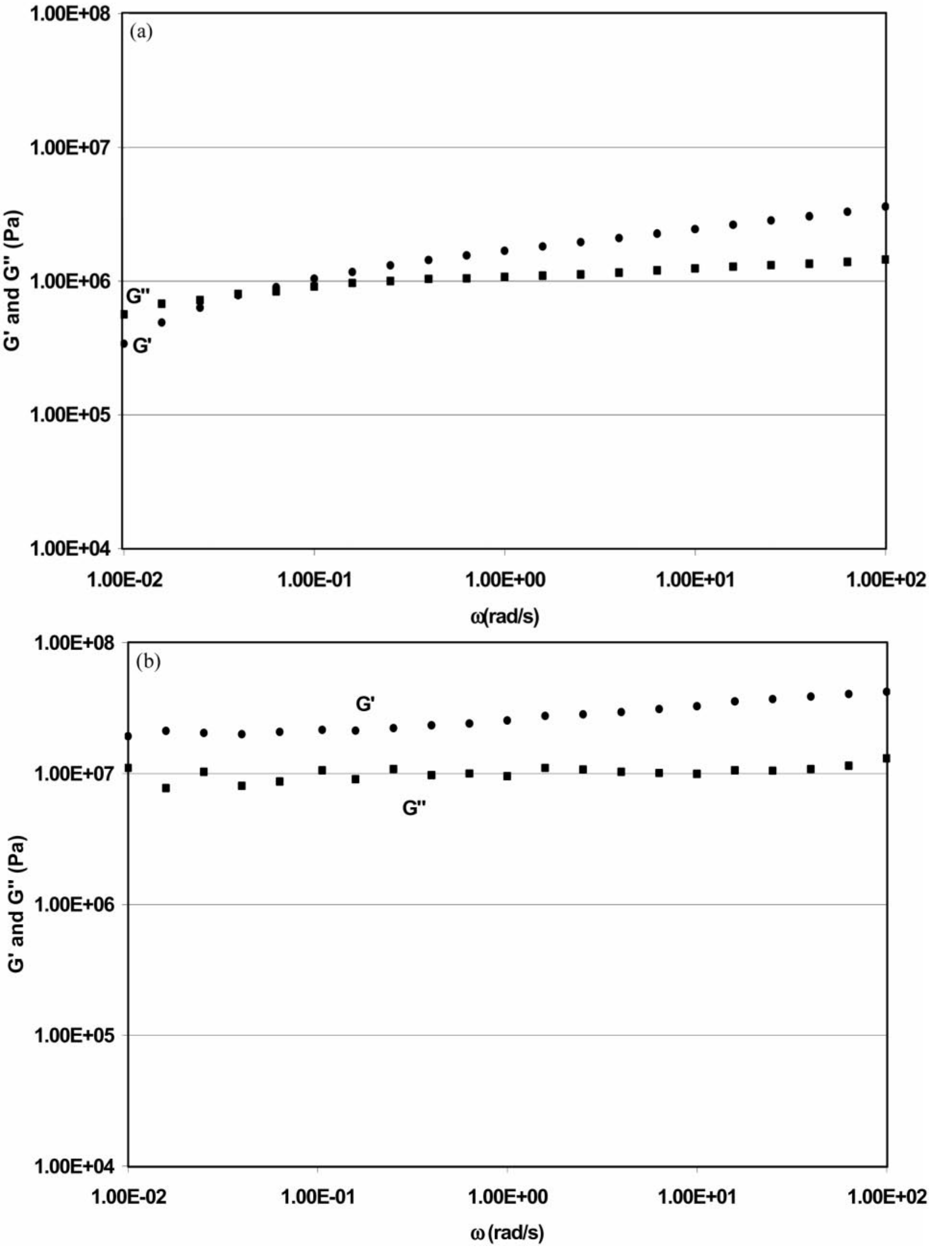


Fig. 12. Viscoelastic behavior of EVA/PC blends, 50PC, $T = 120$°C, (solid PC particles) (a) nodular morphology (see Fig. 11a), (b) co-continuous morphology (see Fig. 11b), (c) rods PC particles (see Fig. 9b).

mixer. A co-continuous morphology is observed with apparent brittle properties of the samples. As EVA and PC polymers have a low interfacial tension ($\cong 2.5$ mN/m) one can expect a fine dispersion of PC in EVA matrix. Reactions of transesterification between ester groups of the two polymers cannot be excluded at high temperatures ($T > 230$°C). However, at high concentration this morphology is not stable as the phenomenon of coalescence becomes predominant. In the present case, the dynamic quenching process is a way to control and to form a rod morphology at high concentration of PC. This new process can be then used as a way to reinforce elastomers matrix by finely dispersed amorphous polymers. Fig. 12a–c shows the viscoelastic behavior at $T = 120$°C (EVA: viscoelastic liquid, PC: solid elastic) of EVA matrix reinforced by 50% PC. Fig. 12a shows that a high concentration of fine nodular PC particles dispersed in the EVA matrix (see Fig. 11a), the flow behavior at low frequency is still conserved whereas Fig. 12b shows that a co-continuous morphology (see Fig. 11b) gives a solid elastic behavior of the blend. Fig. 12c shows an intermediary viscoelastic behavior of an EVA matrix reinforced by rods PC particles (see Figs. 9 and 10), characterized by the yield stress property of the blend.

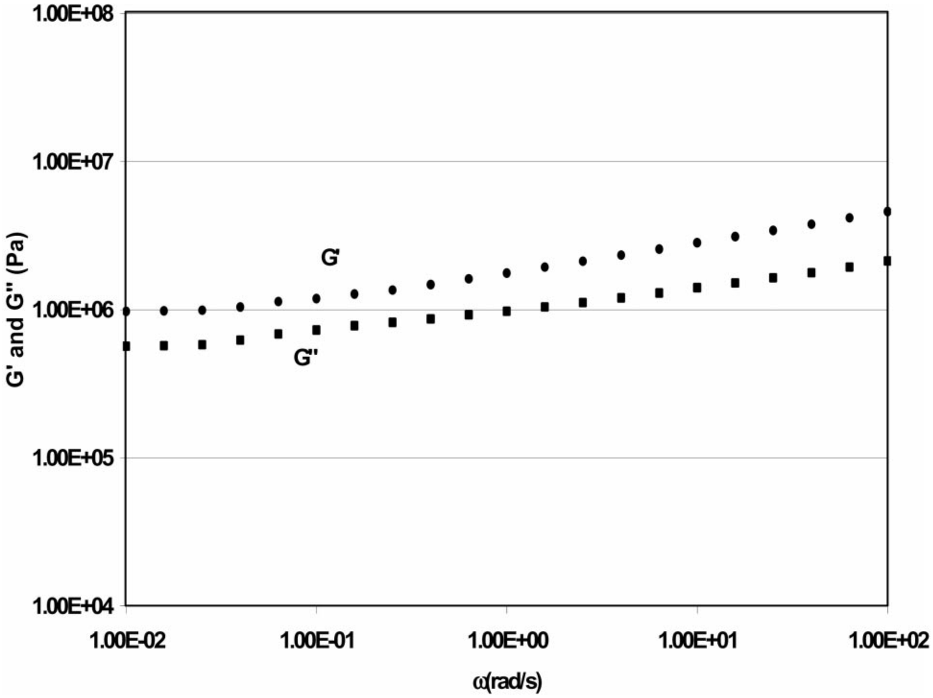


Fig. 12. (*continued*)

5. Conclusion

The present paper describes new morphologies in immiscible polymer blends obtained in twin-screw extruder by a new process named dynamic quenching. Two polymer systems have been investigated. An EVA matrix reinforced by a semi-crystalline polymer constitutes the first one and the second is based on the same EVA matrix reinforced by an amorphous polymer. The main conclusions are the following:

- *EVA/PBT blends*: A coral structure of the PBT domains has been elaborated. This new original morphology confers to the blend yield properties at low concentration of PBT. The development of the morphology during processing was qualitatively discussed in terms of crystallization under shear or elongational flows of fine PBT droplets dispersed in a melt EVA matrix.
- *EVA/PC blends*: Fine nanoscale PC rods have been elaborated by the new process. Rods of $100 \times 300\ \text{nm}^2$ have been generated and dispersed in an EVA matrix at high concentration of PC ($<50\%$). The mechanism of the morphology development is different from the one described in the EVA/PBT system. As PC is an amorphous polymer, the viscosity ratio and the elasticity of the PC phase considerably increases with decreasing temperature to the PC glass temperature. Consequently, the mechanisms of deformation, break up and coalescence of PC particles changes considerably under shear or elongational flow. When the melt temperature reaches the glass temperature of PC, the shape PC particles then freeze under flow.

Furthermore, the morphologies of these blend systems can be preserved in a second reprocessing step owing that the temperature of the material does not exceed the melting temperature of the semi-crystalline dispersed phase or the softening temperature of the amorphous dispersed phase.

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