Polypropylene/Nylon-66/Carbon Black Blends Processed at Temperatures Just Below the Nylon Melting: Anisotropy in Structure and Properties

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Summary: In-situ fibrillation of nylon (Ny) is obtained by compounding and processing its binary blends with polypropylene (PP) and ternary carbon black (CB) containing blends just below the melting temperature (Tm) of the dispersed, Ny phase, yet, above that of the PP. At such low temperatures the Ny behaves as an elastic solid deforming under the elongational flow of the molten PP matrix. Without the mediation of PP, Ny could not be processed or compounded at such low temperatures. This structured anisotropy in both binary and ternary blends resulted in anisotropy in the electrical and dielectric properties of the blends. Moreover, the dynamic electrical behavior was used as a powerful tool to study the CB dispersion mode in the polymer blends.

Keywords: blends; electrical behavior; morphology; nylon; polypropylene

INTRODUCTION

The spatial arrangement of immiscible polymer blend phases is governed by processing conditions. The morphological structuring of polymer blends during processing depends on the balance of compositional, rheological, and processing factors [1]. Several attempts to structure the morphology of the dispersed phase into fibrils were reported. In blends containing thermotropic liquid crystalline polymers (LCP) as the minor phase, the LCP droplets become elongated and oriented during melt flow. The structure is retained upon cooling, due to the LCP long relaxation time [2,3]. In thermoplastics blends, minor phase fibrillation was achieved through hot drawing [4] or the use of specially designed dies to generate high elongational deformations [5]. Minor phase fibrillation was reported in blends that were first melt mixed and then processed at temperatures below melting of this phase by means of capillary rheometers or injection molding [6,7]. The process of both compounding and processing below the melting temperature of the minor phase was studied on ethylene vinyl acetate (EVA)/PP [8] and EVA/Ny6 [9] blends. Melt elasticity and original size of the dispersed phase were found to affect the ability to fibrillate at certain blending conditions.

Carbon black (CB) containing composites are most extensively studied when moderate conductivity is required [e.g. 10]. CB is distributed non-uniformly in immiscible polymer blend due to their multiphase morphology [e.g. 11]. The preferential location of the CB within or on top one of the continuous phases decreases the percolation content and increases conductivity [e.g. 12]. Anisotropy in electrical conductivity was reported in films of carbon fibers embedded in a polymeric matrix [13] and for short graphite fiber reinforced epoxy [14]. The highest conductivity was measured parallel to the fiber axis alignment. Theoretical approaches, extending existing theories to the case of anisotropic composites

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are given by Carmona [14], Huang [15] and Munson-McGee [16].

Recent reports discussed the dielectric response of CB filled polymer composites [e.g. 17]. However, understanding of the internal structure and the role of interfaces, filler-matrix interactions and filler dispersion in controlling the dielectric properties is still lacking.

We have studied the process of *in-situ* fibrillation of a dispersed Ny phase during processing of binary PP/Ny and ternary PP/Ny/CB blends and its effect on the dielectric response [18]. The present article focuses on their processing-structure-performance relationships.

EXPERIMENTAL

Materials

The matrix polymer used in was Polypropylene (PP), T50E (MFI = 25 g/10 min, Tm = 170 °C), supplied by Carmel Olefins, Israel. The minor polymer phase used was PA-6/6 (Ny), PA100, having a relative viscosity of 2.7 in 1% solution of 96% H_2SO_4, Tm = 267 °C, supplied by Polyram Ram-On Industries, Israel. Ketjenblack EC-600 CB was used as a highly structured conductive filler, supplied by Akzo, Nobel Inc. The CB is characterized by a density of 1.8g/cm^3, BET surface area of 1250 m^2/g and electrical volume resistivity of 0.01–0.1 ohm*cm.

Preparation Methods

Prior to blending, the polymer pellets were ground in a Thoams Wiley grinding-mill using a 2 mm screen and the Ny was dried overnight at 80 °C in vacuum. Binary [PP/Ny] blends containing 30% wt Ny were compounded in a twin screw extruder compounder (TSC 42/6, Brabender) at 30 rpm and at several temperatures. The blend extrudates were ground and then injection molded using an Arburg 220/150 injection molding machine, equipped with an ASTM standard mold. All zones of the injection molding machine were maintained at the same temperature, and the mold at 50 °C. Three different processing temperatures were used: 275 °C, above the melting temperature of both components, and two temperatures below the Ny melting temperature but above that of the PP; 260 °C and 256 °C. The compounding and injection molding temperature were kept the same, unless stated differently.

Ternary blends were processed in two different compounding sequences. In the first all components were dry blended together and then compounded, referred to as [(70PP + 30Ny)/3 phr CB]. In the second sequence, PP was compounded with CB and the Ny was subsequently added in the injection molding stage. This sequence will be referred to as [(70PP + 3 phr CB)/30Ny]. The nomenclature used for ternary blends consist of the [binary blend]/filler ratio in phr (parts per hundred binary blend weight) and the binary blend composition given in weight ratios. A single blend composition was studied containing 3 phr CB and 30% wt Ny. The blend [(70 + 30)/3] consists of 3 phr filler, 70 wt% polymer 1 and 30 wt% polymer 2. Blend [(70 + 3)/30] has the same composition as the [(70 + 30)/3] one, but was prepared using the second mixing sequence.

Characterization

The blends morphology was studied on freeze fractured surfaces, using a Philips XL-30 scanning electron microscope (SEM) and a Zeiss LEO982 high resolution SEM (HRSEM).

Room temperature current-voltage (I–V) curves were carried out on injection molded bars. Silver paint was applied to minimize contact resistance. Samples ($12 \times 12 \times 3$ mm^3) were cut from the middle of injection molded bars and I-V measurements were performed in a 2-point apparatus perpendicular and in the flow direction using a MDC system equipped with a probe station, and a picoampermeter source voltage.

AC dielectric relaxation spectroscopy measurements of the complex permittivity and electrical capacitance were performed using a HIOKI 3531 Z HiTESTER instrument, operated at a frequency range of 1×10^3–4×10^6 Hz, under applied AC voltage of 1V. Measurements were carried at constant room temperatures parallel and perpendicular to the flow direction. The AC measurements were performed in a $C_p - R_p$ mode. Three specimens from each sample were taken and measured twice.

RESULTS AND DISCUSSION

Morphology

Figure 1 depicts the effect of processing temperature on the morphology of [70PP/30Ny] blends after extrusion compounding or injection molding. The morphology above the melting temperature of both

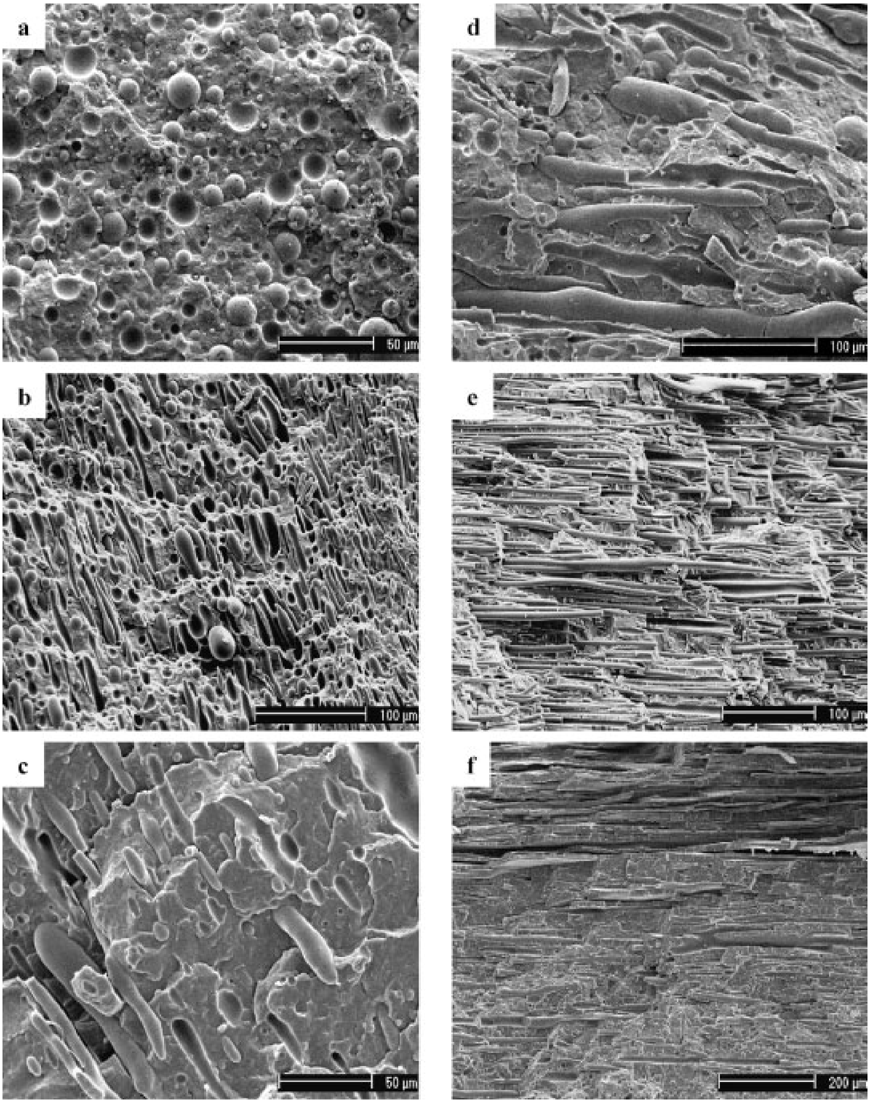

Figure 1.
Effect of processing temperature on the morphology of extrusion compounded blends (a–c) and injection molded blends (d–f) at: (a, d)-275 °C; (b, e)-260 °C; and (c, f)-256 °C.

blend components (275 °C) is distinctively different from that when processing is performed above the melting temperature of the PP matrix but below the melting temperature of the dispersive Ny phase (260 °C and 256 °C). The prior resulted in the common immiscible blends morphology of spherical Ny particle dispersed in the PP matrix (Fig. 1a). Upon reducing the compounding temperature Ny elongated fibrils were formed in the flow direction (Fig. 1b and Fig 1c). Interestingly, a higher extent of Ny fibrillation was observed for the 260 °C compounded blends than in the 256 °C ones. The Ny fibrils in the 260 °C compounded blends are of 70 μm in length and 6 μm in diameter, while the 256 °C compounded blends exhibited smaller fibrils, 40 μm in length and 10 μm in diameter.

We have shown that the morphology of these extruded blends can be explained by applying the mechanism of capillary instability, examining the relation between the time required for fibril break up according to this mechanism and the residence time in the die [18]. In the 275 °C processed blends the fibril breakup time was shorter than the residence time. Thus, fibrils formed at the entrance of the die were soon after broken into a chain of droplets. Upon reducing the processing temperature to 260 °C the fibril breakup time became longer than the time necessary to flow through the die. The shearing flow is not sufficiently long to cause fibril fragmentation and the distortion amplitude does not reach its bursting value; fibril breakup is stopped in mid action resulting in undulant fibrils. A further reduction in the processing temperature to 256 °C increased the fibril breakup time so that the disturbance leading to fibril breakup has no sufficient time to develop (considering the residence time in the die), resulting in smooth fibrils (Fig. 1c). Similarly to the extruded blends, reducing the injection molding temperature from 275 °C to the 260 °C also resulted in Ny fibrillar morphology (Fig. 1d and Fig. 1e, respectively). The 275 °C injection molded blend exhibited typical skin/core morphology, containing both Ny fibrils and spherical particles in the skin region (Fig. 1d) and Ny spheres in the core (not shown). The morphology of the 260 °C injection molded blends, on the other hand, did not exhibit skin/core morphology but rather highly elongated Ny fibrils oriented in the flow direction throughout the whole specimen's volume. A further reduction in the injection molding temperature to 256 °C reduced the extent of Ny fibrillation (compared to the 260 °C injection molded blends) and resulted in the appearance of a large skin comprised of Ny platelets while the small core was a mixture of short Ny fibrils and spheres.

The mechanism of capillary instability may be used to explain the fibril morphology in the injection stage. Considering the high mixing forces and the predeformation during extrusion, a higher extent of Ny deformation is achieved. As the material enters the mold, it is subjected to the known fountain flow causing further deformation through necking, resulting in the observed Ny fibril morphology. The lower extent of Ny fibrillation in the 256 °C processed blends can be related to the morphology of the extruded blends and the mechanism of fibril formation. Extrusion at 256 °C further increased the breakup time compared to the die residence time so that no disturbance was developed and, therefore, highly deformed Ny fibrils were formed. The further deformation of the Ny fibrils in the 256 °C injection molded blends resulted in either transformation to Ny ribbons or even fragmentation.

The fibril breakup time, $t_{breakup}$, is defined according to the theory of capillary instability as [19,20]:

$$t_{breakup} = \frac{2\eta_{matrix} R_0}{\sigma \Omega(\lambda, K)} \ln\left(\frac{0.8}{0.003}\right) \tag{1}$$

where η is the viscosity, K the viscosity ratio of the dispersed phase and the matrix,R_0, the initial droplet radius, σ interfacial tension and $\Omega(\lambda,K)$ is a function describing the growth rate of the distortion. We have shown that changing the parameters defining the breakup time affected the morphology of injection molded binary blends as follows; reducing the breakup time (by reducing Ny content or Ny pellet original size) resulted in the appearance of Ny fibrils and spherical particles throughout the whole specimen, while increasing the breakup time (by reducing the processing temperature or increasing the matrix viscosity) resulted in the appearance of Ny ribbons at the specimen skin and a mixture of Ny spherical particles and short fibrils at the core [18].

The extrusion stage has an important role in attaining the Ny fibrillar morphology. The Ny deformation starts at the extrusion stage, enabling further extensive elongation through necking at the subsequent injection molding stage (Fig. 2a). As was shown by Taylor [21], low deformations are the critical stage as they require high forces. This is clearly demonstrated in the morphology of the [70PP/30Ny] blend that was first extruded at 275 °C and then injection molded at 260 °C (Fig. 2b). Once the initial deformation is not achieved in the extrusion stage the extent of Ny fibrillation in the subsequent injection molding stage is severely deteriorated.

Addition of 3 phr CB to a [70PP/30Ny] blend altered its morphology: Ny formed an irregular continuous phase (Fig. 3a) rather than fibrils even after injection molding at 260 °C (below the Ny Tm). Yet, upon changing the processing sequence, adding Ny at the injection stage Ny fibrils were attained, while maintaining phase continuity (Fig. 3b). The CB location in these blends also differs. As can be seen in Fig. 3, CB is located within the Ny particles in the former blend, while, in the latter CB is located at the interface, coating the Ny fibril surface, leaving the interior free of CB. Although, the composition and compounding temperature of the 30 wt% Ny containing blends are identical, the different compounding sequences result in different structures of the feed for the injection molding [18].

Attempting to explain these morphological differences the theory of capillary instability was applied. Since the residence time of both blends was identical, the breakup time will be discussed. The feed in the [(70PP + 30Ny)/3phrCB] blend consisted of irregular shaped Ny particles, on the verge of continuity, dispersed in the PP matrix and CB appeared both upon and within these Ny particles [18]. On the other hand, the feed for the [(70PP + 3 phr CB)/30Ny] blend consisted of PP pre-extruded with CB mixed with 2 mm sized ground Ny pellets (at appropriate weight ratios). Examining Eq. 1 reveals that for the [(70PP + 30Ny)/3 phr CB], both interfacial tension and $\Omega(\lambda,K)$ are smaller than for the [(70PP + 3 phr CB)/30Ny], due to the different CB location. The presence of CB in the PP matrix in the former blend increases the interfacial tension compared to the

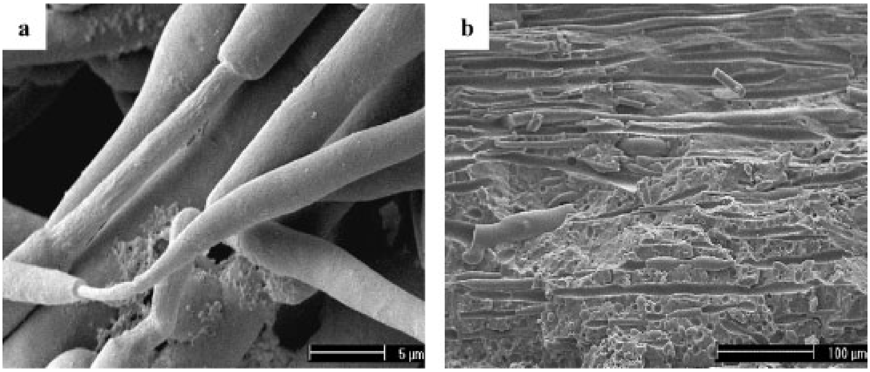

Figure 2.
SEM micrographs of (a)- the [70PP/30Ny] blend processed at 260 °C after PP extraction with xylene and of (b)- the [70PP/30Ny] blend following extrusion compounding at 275 °C and injection molding at 260 °C.

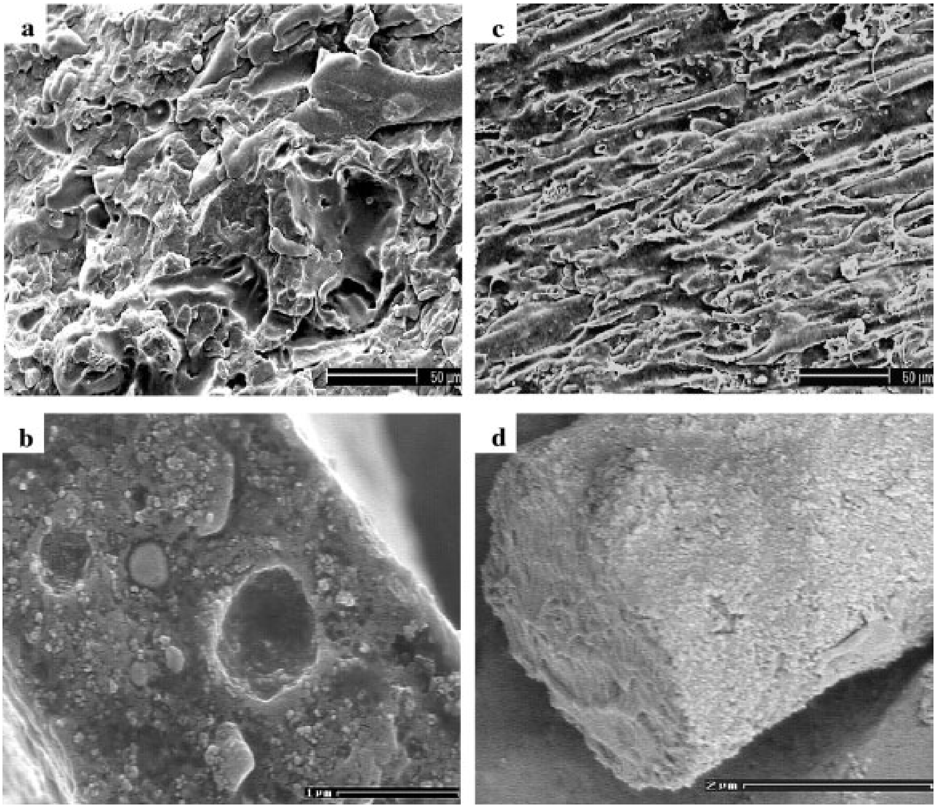

Figure 3.
Effect of compounding sequence on the morphology and CB location in 3 phr CB containing blends: (a, b)- all components compounded together; (c, d)- Ny added at the injection molding stage.

latter blend. Furthermore, the CB location changes the viscosity ratio, leading to $K_{[(70PP+3\,phr\,CB)/Ny30]} < K_{[(70PP+30Ny)/3\,phr\,CB]}$ and hence also to $\Omega(\lambda,K)_{[(70PP+3\,phr\,CB)/Ny30]} > \Omega(\lambda,K)_{[(70PP+30Ny)/3\,phr\,CB]}$. Turning to the nominator of Eq. 1, a larger nominator is displayed by the [(70PP + 30Ny)/3 phr CB] blend than that of the [(70PP + 3 phr CB)/30Ny], mainly due to the almost continuous Ny phase in the former. In over all the breakup time in the [(70PP + 30Ny)/3 phr CB] blend is higher than that in the [(70PP + 3 phr CB)/30Ny]. Thus, an opposite morphology is predicted according the theory of capillary instability. It can be concluded that in CB containing blends this theory can not be applied and the morphology attained is mostly governed by the different feeds for the injection stage and the different CB locations in them. The formation of elongated structures can be attributed to localization of CB upon the surface of the dispersed phase. This localization promotes stronger interactions between the CB coated dispersed particles and the matrix, better stress transfer, leading to elongated structures. Formation of rode like dispersed phase structure upon addition of CB has been also reported in HIPS/LLDPE and HIPS/EVA blends [22].

Resistivity

The effect of Ny fibrillation on the electrical properties is manifested in the [(70PP + 3 phr CB)/30Ny] and [(70PP + 30Ny)/3 phr CB] blends which are different in their morphology and, hence, in their electrical properties (Fig. 4). The random co-continuous morphology (CB is encapsulated by

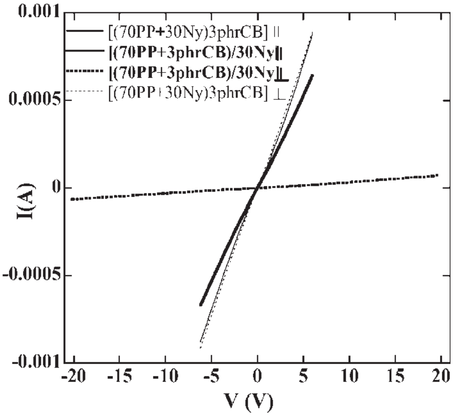

Figure 4.

I–V curves for injection molded blends measured perpendicular and in the flow direction.

the Ny phase) of the [(70PP + 30Ny)/3 phr CB] blend resulted in similar resistivity in both measuring directions. On the other hand, the [(70PP + 3 phr CB)/30Ny] blend, having fibril, continuous morphology is nearly insulating perpendicular to the flow direction, while relatively conductive in the flow direction (i.e. in the fibril direction).

The combination of CB preferred location upon the surface of the Ny fibrils and the Ny phase continuity lead to the formation of conductive pathways in the fibril direction, contributing to the electrical anisotropy. We have studied several additional compositions [18] and found that the CB location and the Ny phase morphology had a considerable effect on the electrical properties. The preferred localization of CB upon the Ny surface resulted in a tighter packing of the CB particles than within the Ny phase, exhibiting lower resistivity. The Ny continuity was found to be crucial for achieving conductivity, as required by the double percolation. However, this requirement can be relaxed if some aspect of the fibrillar morphology is maintained and CB is located upon the surface of these fibrils as well as in the PP matrix.

Dielectric Properties

The dielectric behavior of the 3 phr CB containing blends further highlights the differences between the blends (Fig. 5). The [(70PP + 30Ny)/3 phr CB] blends exhibited similar dielectric properties in both perpendicular and in the flow measuring directions, within experimental error. Constant AC conductivity and permittivity were observed until a critical frequency of 5×10^4 Hz was reached. Thereafter, the permittivity decreased while AC conductivity increased with frequency. The [(70PP + 3 phr CB)/30Ny] blend displayed anisotropy. In the flow direction, the dependence of the AC conductivity and dielectric constant on frequency was similar to that of the [(70PP + 30Ny)/3 phr CB]

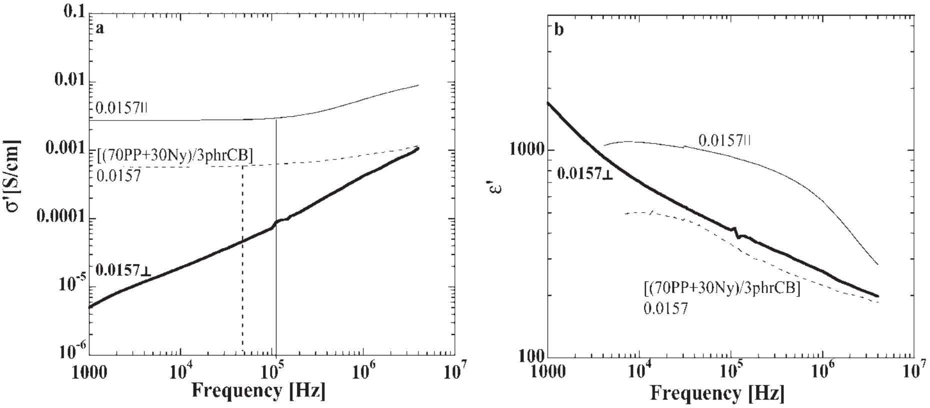

Figure 5.

Effect of compounding sequence and measuring direction on (a) AC conductivity and (b) dielectric constant of [PP70 + CB3]Ny30 and [PP70/Ny30]CB3 ($v_{CB} = 0.0157$). Vertical lines denote the critical frequency.

blend. That is, constant properties until a critical frequency are reached and at higher frequencies the AC conductivity increases concurringly with a decreasing permittivity. However, the value of critical frequency was 10^5 Hz, higher for the [(70PP + 3 phr CB)/30Ny] blend. On the other hand, continuous decreasing permittivity conjugated with ascending AC conductivity as frequency was increased were observed upon measuring the same blend but perpendicular to the flow direction.

The models of charge carriers' diffusion on percolating clusters (DCP) [23], and The RC model (intercluster polarization) [24], describing the dependence of dielectric properties on frequency in percolating systems, distinguished between these two behaviors. In case a percolating network exists, according to the DCP model, at low frequencies the overall conductivity is that of the network and its conductivity remains constant. At higher frequencies the material becomes sensitive to its fractal nature. Since the length scale scanned by the charge carriers is reduced as the frequency increases, more cluster parts will contribute to the AC conductivity which, therefore, increases with frequency. According to the RC model, at low frequency, the current through the sample is entirely carried by the backbone of resistors, the conductor fraction, as capacitive junctions (the dielectric medium) constitute very high impedance paths. However, above a critical frequency, the impedance of the capacitive junctions decrease and therefore the current finds more parallel paths and the AC conductivity increases. For systems below percolation threshold, the capacitive junctions predominate since the conductors are not connected. As the frequency increase, the impedance of these paths is reduced and conductivity increase.

Hence, it can be inferred that perpendicular to the fibrils direction, the [(70PP + 3 phr CB)/30Ny] blend is below percolation as exhibited by the low AC conductivity values and its continuous increase with frequency. Since the PP matrix creates an insulating barrier between the CB particles located upon these Ny fibrils. In the flow direction this blend is above percolation, i.e., a conductive network exists along the Ny fibrils. The [(70PP + 30Ny)/3phrCB] blend is also above percolation, however, a conductive CB network exists in both perpendicular and flow direction, owing to its random continuous Ny phase and the CB within it.

The [(70PP + 3phrCB)/30Ny] blend measured in the flow direction exhibited higher critical frequency and constant AC conductivity than the [(70PP + 30Ny)/3phrCB] blend (Fig. 5). That is in the former the conductive network is either tighter packed or constitutes larger CB clusters. The morphological arrangement of the CB affects the quality and size of the conductive network and hence the dielectric properties. In the former blend CB is located upon the interface of the Ny phase, while in the latter CB is located within the Ny phase.

CONCLUSIONS

Processing below the Ny melting temperature but above that of the PP matrix transforms the spherical Ny particles in the melt processed blends into highly elongated fibrils throughout the whole specimen cross section. This anisotropic morphology affected the behavior of the blends in all examined aspects. This unique morphology attained during extrusion compounding or injection molding can be explained by applying the theory of ''capillary instability''. The relation between the time required for fibril break-up and the residence time in the die determines the stability of the fibrils. The initial extrusion stage has an important role in attaining Ny fibril morphology after the following injection molding. In CB containing blends processing below the Ny melting temperature resulted in irregular co-continuous morphology. Ny fibrillation was achieved only upon changing the compounding sequence, i.e., PP and CB were first compounded and Ny was added in the subsequent molding stage. In the former CB is located within the Ny phase, while in the latter upon the Ny fibrils surface. The CB network formed upon the surface of the Ny fibrils is larger or tighter packed than that formed within the Ny phase. Electrical and dielectrical anisotropy were found in blends exhibiting a fibrillar Ny network covered by CB. However, once CB is located within the Ny the dielectric behavior is isotropic. Dielectric spectroscopy was found a mean to probe the CB percolating structure, to investigate the state of CB dispersion as well estimating the correlation length of the CB clusters.

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