Rheological Study Bringing New Insights into PET/PC Reactive Blends

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Summary: Extruded poly(ethylene terephthalate)/polycarbonate (PET/PC) blends, with/without cobalt catalyst and at different polymer ratios, were prepared. Rheological behaviour was discussed in terms of storage (G′) and loss (G″) moduli, loss tangent (Tan δ) and viscosity (η). Both G′ and G″ increased as a function of frequency for all blends. PET was the matrix in the blends with 80 and 50 wt% of polyester but in the PC rich-blend an inversion was observed. In all cases, lower Tan δ values were achieved at high frequencies. The viscosity behaviour showed a catalyst dependency. PET dictated the rheological properties of the blends without catalyst whereas PC governed blends with catalyst. Alcoholysis and acidolysis reactions plus a transesterification reaction occurred on the interface was dependent on the matrix component. These reactions seem to occur at higher extent in blends in which PET is the matrix but the inverse happened in the PC rich-blend.

Keywords: blends; catalyst; PET/PC; reactive blend; rheology

Introduction

Commercially successful thermoplastics with remarkable properties, included in the polyester family, poly(ethylene terephthalate) (PET) and polycarbonate (PC) can be employed as commodity or as engineering materials depending on the level of application. PET has good resistance to solvent and chemical reagents, possesses a large processing window but presents low mechanical and thermal properties expressed in terms of impact toughness and dimensional stability. Conversely, PC has the two latter characteristics in high degree but relatively poor solvent resistance and a narrow window of processability. During the last two decades, blends of the above have been developed in order to achieve a new material with their combined properties.[1–10] The majority of those studies have been focussed on the miscibility,[1–3] phase behavior[4–8] and on transesterification reactions which can occur during the blend melt mixing.[8–12] A series of possible reactions involving PET/PC reactive blending has been reported.[11–14] These kinds of reactions are strongly dependent on their initial compatibility and blending conditions. It is generally accepted that from the transesterification reactions the homopolymers are transformed in block copolymers and subsequently in a random copolymer, as block lengths gradually decreased.[15–17] The resultant copolymers can affect the homogeneity of the blend end-products.[18] The following reactions are largely accepted to happen in PET/PC melt blend: intermolecular ester-carbonate exchange reactions (transesterification); intermolecular reaction between PET hydroxyl terminals and PC carbonate groups (alcoholysis); intermolecular reaction between PET carboxyl-end groups and PC carbonate

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groups (acidolysis); intramolecular reaction for releasing cyclic ethylene carbonate from glycol-carbonate moiety (elimination reaction); intramolecular reaction for releasing carbon dioxide moiety from carbonate group (decarboxylation); scission reaction from PET-ester linkage (dehydroxylation).[10] Although the transesterification reactions have been focussing in the current literature on PET/PC reactive blending, data on rheology of that system are scarce. The rheological study has great importance in the polymer processing industry in that it assists in finding better polymer molding conditions for a given application.[19,20] The relationship between rheological properties and microstructure is expected to be one of the major factors in the control of the final blend properties.[20,21] The aim of this work was to investigate the rheological behavoiur of the PET/PC reactive blending taking into account, the blend composition, MFR of the components and the presence of catalyst.Each plays a role within the blend but the catalyst seems to have a distinguishable role on compatibility and therefore on the final properties.

Experimental Part

Materials

Commercial PET and PC were kindly supplied by Mossi & Ghisolfi Group and GE Plastics South America, respectively. The MFR and density of the neat PET were 33.0 g/10 min and 1.39 $g \cdot cm^{-3}$, respectively. The MFR and density of the PC were 2.5 g/10min and 1.2 $g \cdot cm^{-3}$, respectively. All data was provided by the manufacturers. Commercial cobalt acetylacetonate jj was produced by J.T. Baker Chemical Co. and was used as a catalyst for transesterification reaction.

Blending

Reactive blending of PET/PC at different weight fractions, with (0.05%) and without cobalt acetylacetonate II, was carried out in a co-rotating twin-screw extruder (L/D = 36 and 22 mm of screw diameter), equipped with vacuum system, at 190–255 °C and 150 rpm. A master of PET and catalyst was extruded for adding to the catalyzed blends. Before processing, both polymers were dried, at 120 °C, for 8 hours, in order to remove the water, avoiding hydrolysis during melt processing. The extrudate was cooled in water (30°C) and pelletized.

Rheology Measurements

The rheological measurements were carried out using a dynamic oscillatory rheometer, model Rheometrics AR2000, equipped with parallel plates (D = 25 mm, gap = 1 mm), in the frequency range from 350 to 10 rad $\cdot s^{-1}$, at 270 °C, under nitrogen. Before measuring, all materials were dried, at 120 °C, for 8 hours. Viscosity (η'), storage modulus (G′) and loss modulus G″ as function of the frequency were taken.

Morphology Analysis

The morphology of the 20/80 blend was investigated using a scanning electron microscope (JEOL, model JSM-5610LV) with an acceleration voltage of 17 Kv. The photograph was taken from the cryogenic fracture surface. Etching was performed on one of the sample pieces with chloroform, during 6 hours, in order to show whether PET or PC was the matrix.

Results and Discussion

Storage Modulus

Figure 1 and 2 show the variation of the G′ as function of the frequency for the neat homopolymers, uncatalyzed and catalyzed blends. There is a progressive increase of the G′ with the frequency for all materials. The storage modulus of the neat PC is higher than that of pure PET revealing difference in molecular structure, molar mass and its distribution. At lower frequencies, G′ of the uncatalyzed blends are located between the homopolymer ones but at higher frequencies lay close to the PET. For all catalyzed blends, G′ is always between those of the parent homopolymers but near the PC. The addition of the

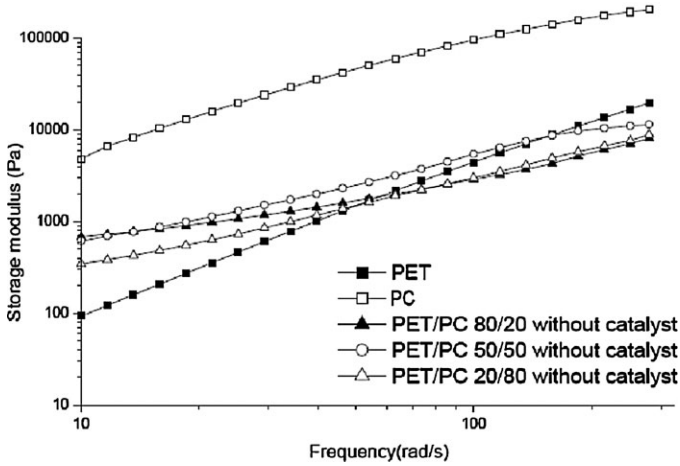


Figure 1.
Storage modulus of PET/PC blends without catalyst at 270 °C.

catalyst in the blends brought about an increase of the G′ over the entire frequency range which was understood as an increase of compatibility owing to the occurrence of the exchange and degrading reactions. The intermediate blend also exhibited the highest G′ value. The results seem to indicate that PET controls the G′ of the blends without catalyst and, after addition of the catalyst, the PC governs the G′.

Figure 3 and 4 show the behaviour of the storage modulus at low (10 rad/s) and high (100 rad/s) frequencies as function of the composition, for both blend systems.

Concerning the frequencies, G′ values of the catalyzed blend were higher than of the uncatalyzed one and highest values were reached for the blends with catalyst. There is a sharp dependency of G′ with the amount of PC. In all cases, G′ attained one maximum at the composition with 50 wt% of PC following a drop at highest content of PC. This evidence might suggest that a phase inversion has occurred. In fact, the

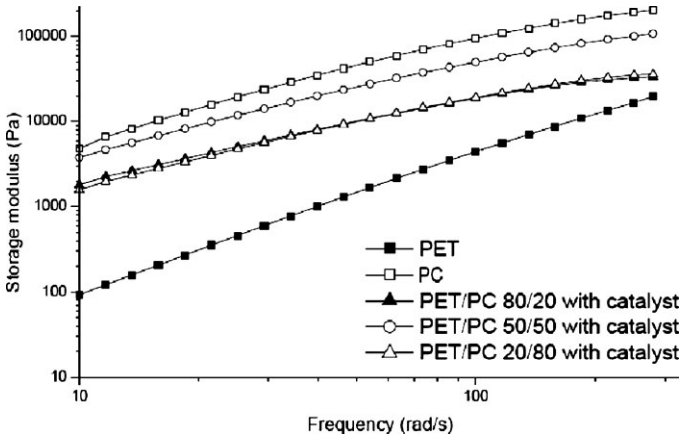


Figure 2.
Storage modulus of PET/PC blends with catalyst at 270 °C.

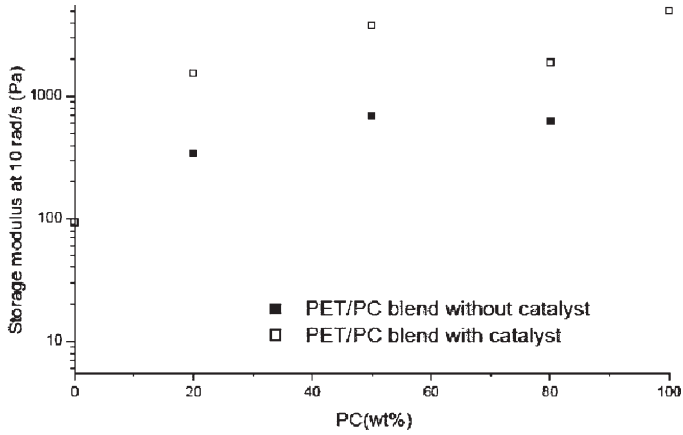


Figure 3.
Storage modulus at 10 rad/s of PET/PC blends at 270 °C.

SEM photomicrographs of the 20/80 blend (Figure 5), with and without catalyst,cryogenically fractured, after etching with chloroform, which has a good selectivity to etch PC without attacking PET, assist the discussion. Both blends exhibit a binary structure with spherical particles distributed throughout a continuous matrix. Those globular particles represent PET domains embedded in the PC matrix and were of smallish sizes in catalyzed 20/80 blend as a result of the decrease of interfacial tension between the polymers.

Rheological studies of PET/PC reactive blends were reported by Carrrot et al.[22] and Fraisse and co-workers.[23] Several aspects were contrary to those mentioned herein. Carrot employed iron acetate, lanthanum acetate and acetylacetonate as catalysts, dispersing them in the blends. Minor limit temperature and rotation speed were used. The G′ of neat PET was higher than that of PC and higher values of G′ were achieved for the uncatalyzed blends. Fraisse's group prepared blends from recycled PET and PC, without catalyst. The processing conditions and rheological results were not mentioned in detail, perhaps his work was focused on ageing properties. The controversial results might

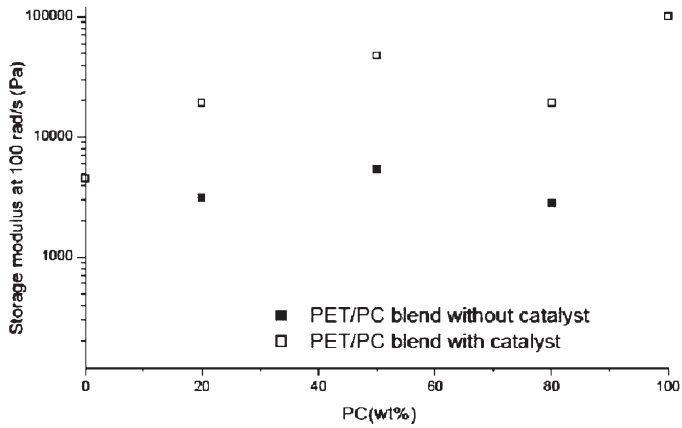


Figure 4.
Storage modulus at 100 rad/s of PET/PC blends at 270 °C.

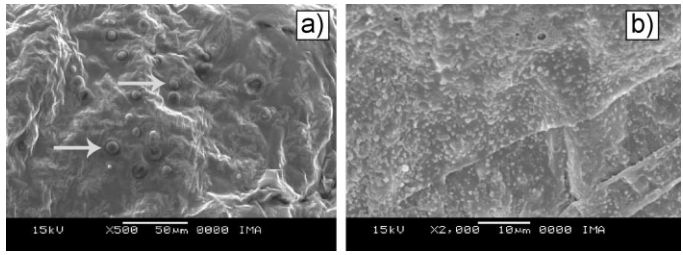


Figure 5.
SEM micrographs of cryo-fracture surface of PET/PC 20/80 blends without catalyst (a) and with catalyst (b).

suggest that the storage modulus could be governed by the homopolymer sources, typeof catalyst, processing conditions and so forth, playing an isolated or combined role. The morphological results of the 20/80 blend are in agreement with those reported by Nassar et al. [1] and Mbarek and co-workers.[24]

Loss Modulus

The variation of the G″ *versus* frequency for the neat homopolymers, uncatalyzed and catalyzed PET/PC blends are shown in Figures 6 and 7. Similar to storage modulus, a progressive increase of the G″ with frequency was noticed for all materials. Among all materials, PC showed the highest value of the G″. Generally speaking, G″ of the uncatalyzed blends showed curves close to and lower than PET, contrary to that which was reported by Carrot.[22] For catalyzed blends, all curves lay between those of the parent homopolymers being the highest value attained by intermediate composition.

The variation of the G″ versus frequency at 10rad/s (Figure 8) and 100 rad/s (Figure 9) is shown. An uneven behaviour was observed with respect to the presence of the catalyst. At low frequencies, higher G″ values were obtained for the catalyzed blends. At high frequency, G″ was around 10,000 Pa regardless of the composition. The tendency of the rich PC blend in showing lower modulus values remained but this trend seems non-existent in high frequency. The presence of the catalyst brought about an enhancement of the G″ but the composition also had influence on the loss modulus. Similarly the G′, PET

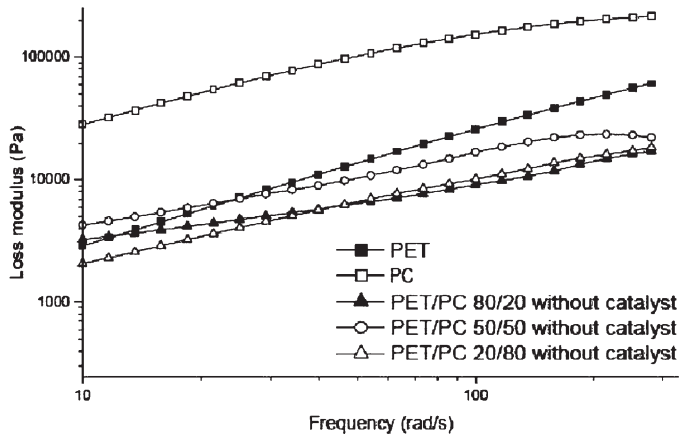


Figure 6.
Loss modulus of PET/PC blends without catalyst at 270 °C.

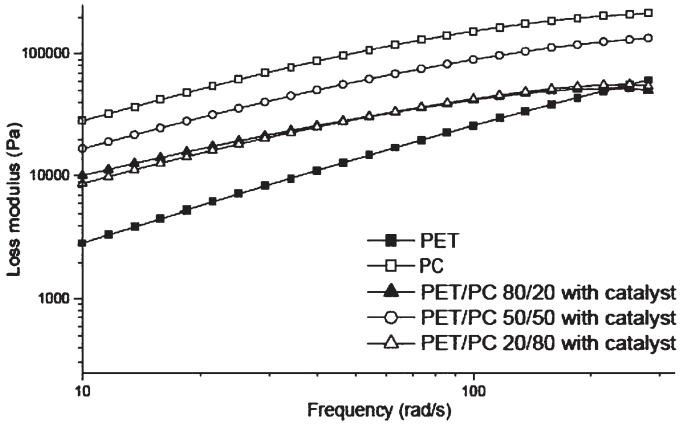


Figure 7.
Loss modulus of PET/PC blends with catalyst at 270 °C.

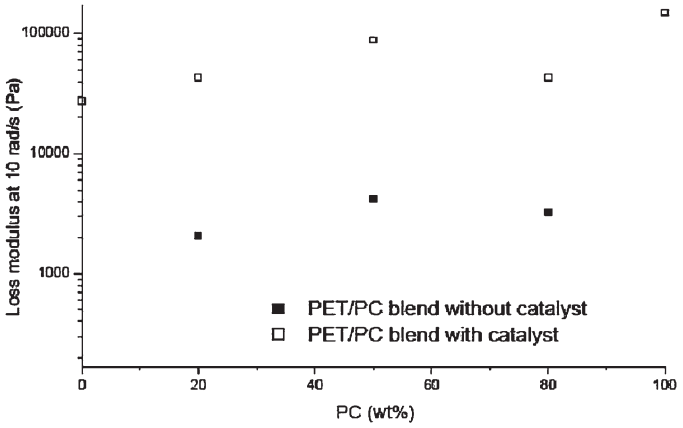


Figure 8.
Loss modulus at 10 rad/s of PET/PC blends at 270 °C.

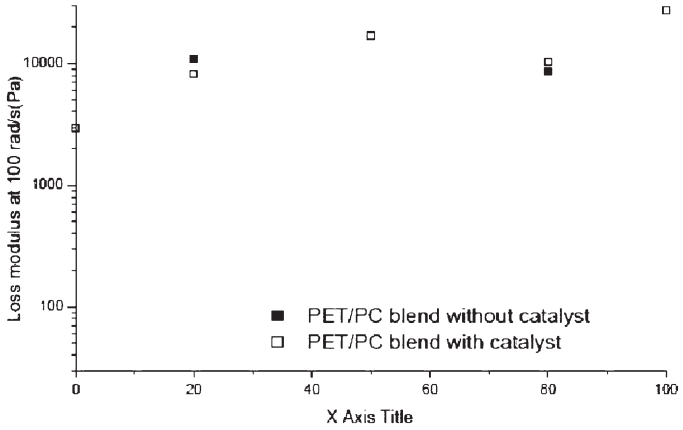


Figure 9.
Loss modulus at 100 rad/s of PET/PC blends at 270 °C.

material controls the G″ for uncatalyzed blends whereas PC manages that parameter in catalyzed ones.

The variation of G″ and G′ when catalyst is present in the blends could be explained in terms of the major reactions - alcoholysis, acidolysis and transesterification (exchange) - and of the phase structure (Schemes 1 and 2).

When PET is considered as disperse phase (Scheme 1), the alcoholysis and acidolysis reactions of the PET end-groups with carbonate linkages give rise to the formation of block copolymers (V and VI)which are attached to the PET domain and also the releasing of PC oligomers (IV) into the PC matrix, causing a diluting effect. The transesterification reactions take place at the expense of the break of ester and carbonate linkages and random copolymers arise from them. As the exchange reactions advance, a reduction of those reactions might be expected due to bulk hindrance of the copolymer on the surface of the PET phase. Further, the catalyst can also break the new ester linkages on the copolymers and its role is the reverse of that expected. Thus, the compatibility of the PET/PC blends is reduced when PC is the matrix and the moduli tend to decrease owing to the diluting effect of the PC oligomers.

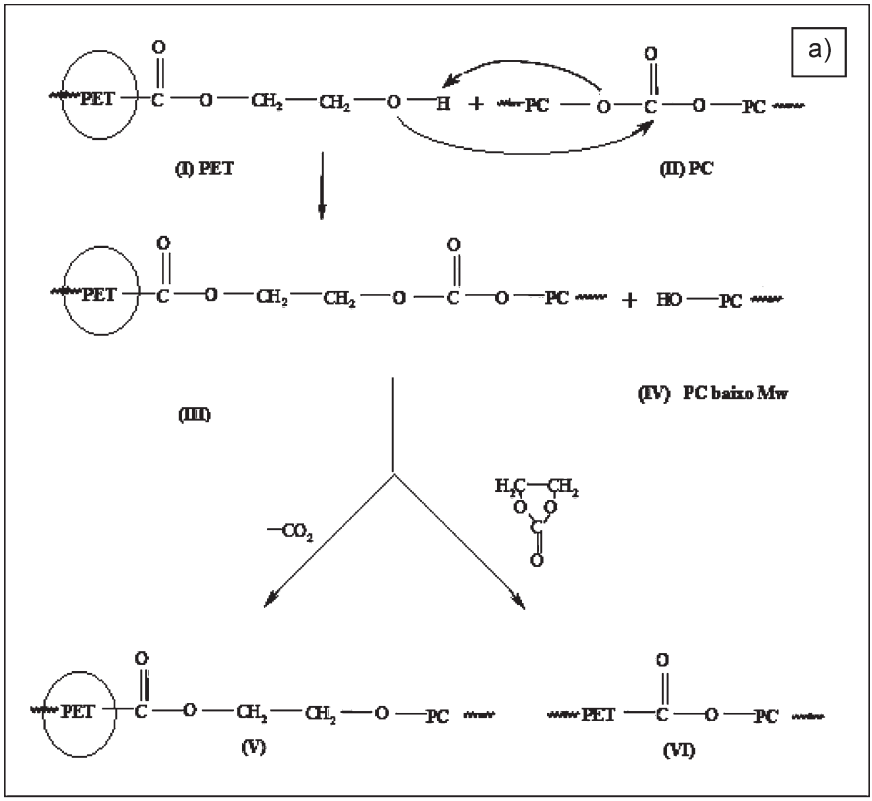
If PC is regarded as disperse phase (Scheme 2), block copolymers (V and VI) will be also formed.

They are available within the PET matrix leading the moieties of PC in the copolymers to be again attacked by the PET end-groups. PC phase continues being attacked by PET terminals producing domains with smallish sizes. Concomitantly, the catalyst promotes exchange reactions between the PC moieties on the block copolymer and PET molecules providing random copolymer and enhancing the blend compatibility. Thus, the catalyzed PET/PC blend, in which PET is the matrix, has better compatibility and higher moduli.

Summarizing, the presence of the catalyst had a distinguishable effect on the blend interface and of the moduli. It enhanced the compatibility through alcoholysis, acidolysis and transesterification reactions increasing the intimacy of the components, mainly when PET was the matrix. Hence, the load transfer from the matrix to the disperse domain was improved and sharply shows that the two moduli were strongly dependent on the blend microstructure.

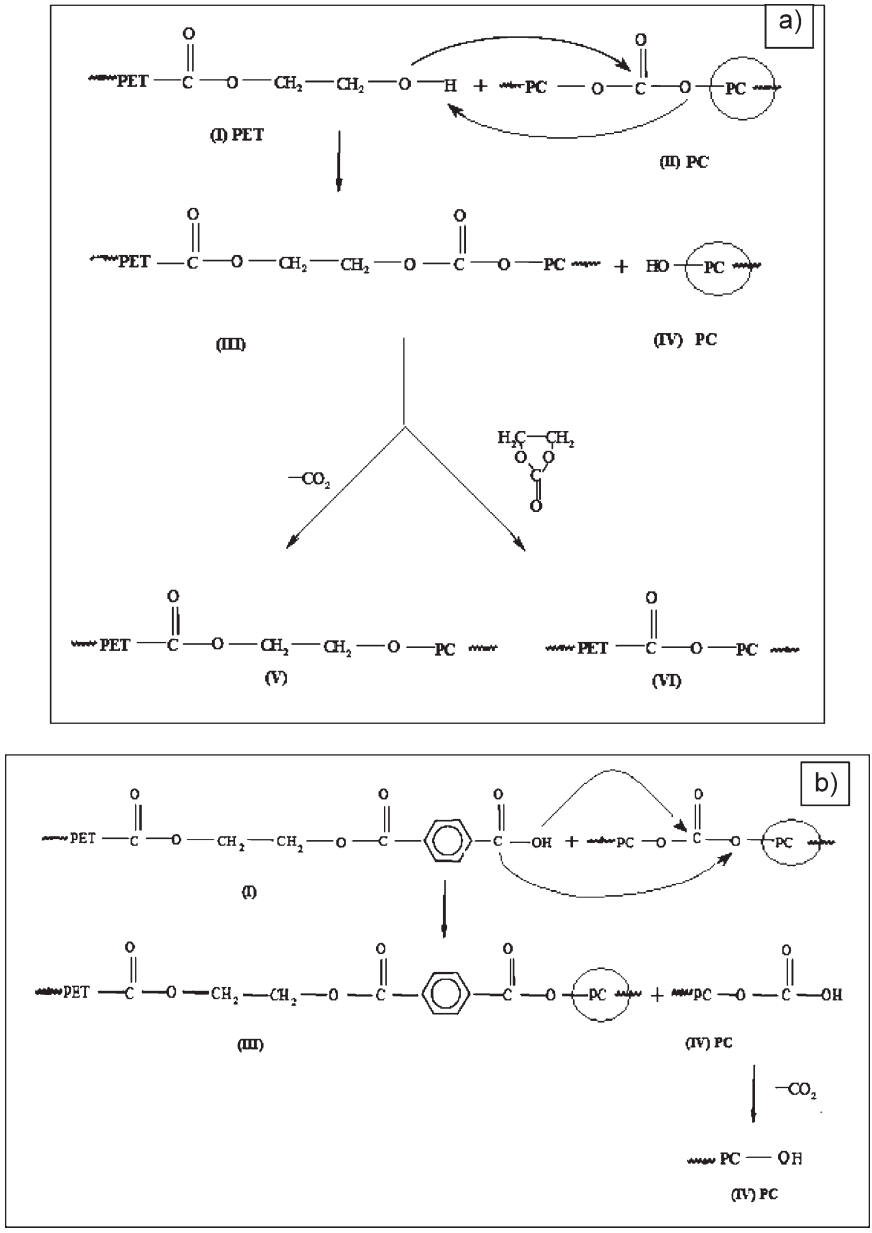
Figure 10 shows the variation of tan δ (G″/G′) with the composition, at low frequency (10rad/s) and high one (100rad/s), for all blends. It can be realized that, tan δ seems to be almost invariable with the composition, in all cases, and upper values were achieved at low frequency. The catalyst and test frequency seem to have influence on tan δ. At low frequency, the catalyzed blends showed tan δ higher than the uncatalyzed ones. If we consider the 80/20 blend at 10rad/s, it is possible to notice that the relative increase of G″ when catalyst was added is 2.3 but this value decreases to 1.85 when the same approach is made for G′. The viscous liquid behaviour of the catalyzed blend at 10rad/s could be also attributed to the alcoholysis, acidolysis and transesterification reactions. Thus, the ratio G″/G′ rose as function of the greater increase in G″ caused by those reactions. An expected behaviour of the tan δ was observed at 100rad/s, that is, the catalyzed blends showed lower values than uncatalyzed ones. This could be ascribed to the effect of the frequency on tan δ of the homopolymers. While G″/G′ of the neat PET at 10rad/s was around 30, the value lowered drastically at 100 rad/s (5.5). For the neat PC, the G″/G′ was 2.4 and 2.0, at 10 and 100 rad/s, respectively, being therefore practically unaltered. Thus, the change of the PET from viscous to elastic behaviour at high frequency overcame the catalyst action and the blends behave predominantly like an elastic material.

Figure 11 and 12 present the variation of the viscosity *versus* angular velocity for all materials. All materials presented pseudoplastic behaviour while newtonian behaviour was observed for the neat PET. The viscosity decreased with angular velocity for all material except for neat



Scheme 1.
PET/PC Alcoholysis and acidolysis considering PET as disperse phase (the circle around PET means disperse phase): (a) Alcoholysis; (b) Acidolysis.

PET. At any angular velocity, the blend viscosity rises as the amount of PC increases in blend. The viscosity of the neat PC is higher than that of PET. The viscosity of the uncatalyzed blends is situated between those homopolymers as reported by Carrot.[22] The blends with catalyst exhibited values lower than PET



Scheme 2.
PET/PC Alcoholysis and acidolysis considering PC as disperse phase (the circle around PC means disperse phase): (a) Alcoholysis; (b) Acidolysis.

although the 20/80 blend was that with the highest value of viscosity among the blends. A similar result was found by Nabar and collaborators[25] although they have only studied PET/PC (40/60) with tetra-n-butyl orthotitanate (0.1–0.2 w%).

The viscosity showed that the presence of the catalyst caused a decreasing of the molar mass of the components. The trans-esterification reactions occur at the expense of the scission of PET-ester and PC-carbonate linkages and the catalyst speeds

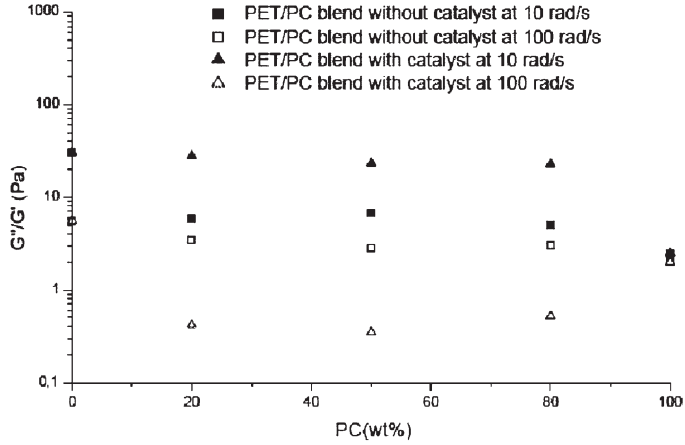


Figure 10.
G″/G′ (Pa) of PET/PC blends at 270 °C.

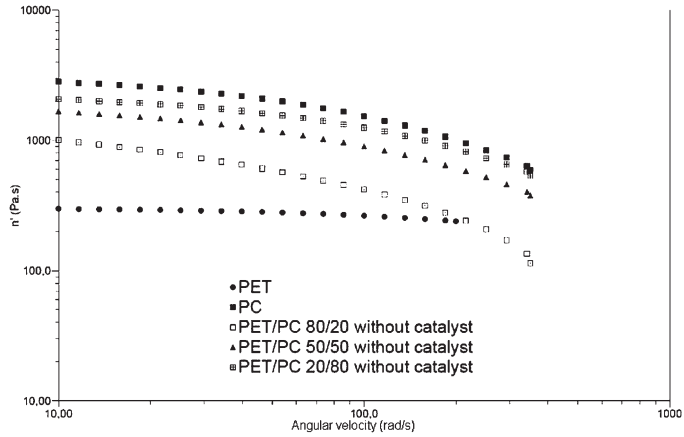


Figure 11.
Viscosity of PET/PC blends at 270 °C.

them up. The rate of degradation is higher than the recombination of the moieties of the PET and PC by transesterification reactions. This means that, in the processing conditions, the degradation rate was higher than that of transesterification. The new ester linkages obtained by the latter reaction and those produced by acidolysis/alcoholysis are indistinctly broken by catalyst action. In this way, the viscosity of the catalyzed blends tends to be quite lower than the parent homopolymers and for uncatalyzed blends.

Conclusion

Based on rheological results, it was realized that the PET/PC blend properties are dependent on the composition, phase structure and absence or presence of catalyst. The phase structure and catalyst seem to have a close relationship on the blend interface. Alcoholysis and acidolysis are reactions that naturally occur in PET/PC blend but when the catalyst is added a remarkable effect on the moduli is noticed. The additional transesterification reactions

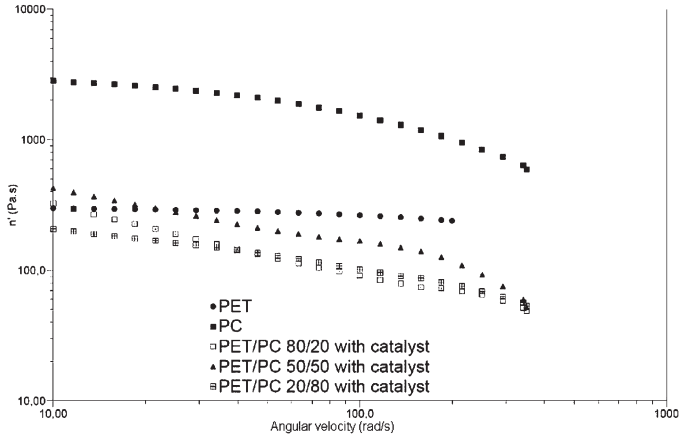


Figure 12.
Viscosity of PET/PC blends at 270 °C

lead to an increase of the moduli due to the lowering of the blend interface, in which mainly PET is the matrix. Hence, the load transfer from the matrix to the disperse domain was improved and sharply shows that the two moduli were strongly dependent on the blend microstructure.

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