

Rheological, Morphological, and Heat Seal Properties of Linear Low Density Polyethylene and Cyclo Olefine Copolymer (LLDPE/COC) Blends

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ABSTRACT: The rheological and morphological properties of linear low-density polyethylene/cyclo olefin copolymer (LLDPE/COC) blends were investigated, as were their peel seal characteristics when heat sealed to films of either polyethylene (PE) or polyethylene terephthalate (PET). Three blend systems, with COC volume percentages of 5, 10, and 15%, were melt blended in a twin-screw extruder. A partial phase miscibility/compatibility was initially suggested by Cole-Cole and equivalent plots of the dynamic rheological proper-

ties and subsequently confirmed by scanning electron microscopy. The investigation of the systems' heat sealing properties pointed out an interesting industrial potential for PET sheets covered with a fine layer of a LLDPE/COC blend before heat sealing to a PE film for packaging applications. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2015–2022, 2010

Key words: polymer blends; multilayer; coextrusion; dynamic rheological properties; morphology; heat sealing

INTRODUCTION

Polyolefines, such as linear low-density polyethylene (LLDPE), offer a broad spectrum of structures, properties, and processabilities, and therefore, they are widely used in industrial film applications. Cyclo olefine copolymers (COCs) belong to a new family of amorphous plastics having been subjected to recent investigations^{1–4} as a result of numerous valuable characteristics such as heat sealability, a very high transparency, and good barrier properties. Therefore, COC polymers are potential candidates for packaging applications.

Heat sealing^{5–7} is a technique that consists in welding two materials under the combined effects of three parameters: pressure, time, and temperature. In practice, the sealability is a key performance for all packaging applications for which the assembly of two extruded films is required. Numerous studies have been devoted to heat sealing of polymers^{5–8} and polymer blends.⁹ Jarousse et al.⁸ have reported that the temperature is the most influencing parameter among the three. In fact, the heat sealing process involves an interdiffusion of the macromolecules at the interface of the two materials to be welded.¹⁰ In

the case of semicrystalline polymers (with degrees of crystallinity higher than 30%), the heat sealing temperature has to be close to the melting temperature of the polymer crystallites to allow macromolecular mobility at the interface.

The interdiffusion at the interface can be associated to the reptation model, which considers a macromolecular chain in a virtual “tube” created by the adjacent chains.^{11,12} After a certain time, referred to as the “reptation time, τ ” ($\tau \propto M^3$), the macromolecular chain has moved out of the tube and crossed the interface several times.

To analyze the kinetics of seal formation in terms of established concepts of chain diffusion and entanglement, measurements under isothermal conditions, such as those achieved by longer contact times, are required. A time dependence of $t^{1/2}$ is reported for fracture energy of hot tack and welding of amorphous polymers.¹³ In these examples, the interfacial strength is determined primarily by the number of entangled chains that form connections across the interface. In heat sealing of semicrystalline polymers, the melted chains recrystallize as the seal is cooled to ambient temperature. Such rearrangements occurring at the interface during recrystallization must also be considered when evaluating the seal strength. The seal temperature determines whether the material becomes partially or fully molten. The residual crystallinity governs the number of chains available for diffusion as well as the amount of crystalline obstacles to diffusion. During cooling that

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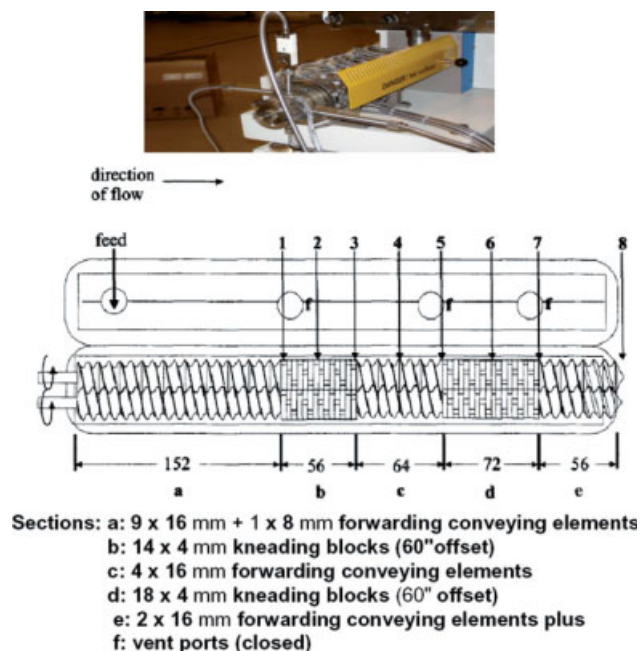


Figure 1 The 16 mm diameter corotating twin-screw extruder. The numbers 1–8 at the top of the extruder indicate the sampling positions. All dimensions are given in mm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

follows welding involved in the heat sealing process, the crystallization that takes place reinforces the interfacial area and particularly enhances the heat seal strength.

Heat sealing of blends of LLDPE and COC has been investigated by Jester et al.^{1,2} As a continuation, this study describes the evaluation of the rheological and morphological properties of LLDPE/COC blends when heat sealed to PE and PET films.

EXPERIMENTAL PART

Material and blend preparation

Linear low-density polyethylene (LLDPE), Dowlex 2106G (MFI = 3.3 g/10 min), was supplied by Dow Chemical Company, and cyclo olefine copolymer (COC), grade 8007 ($T_g = 78^\circ\text{C}$, MFI = 2 g/10 min), was generously donated by Topas.

A PRISM PTW 16/25D corotating twin-screw extruder with a screw diameter of 16 mm (Thermo Electron PolyLab System Rheocord RC400P) was employed for the preparation of three binary LLDPE/COC blends. The PRISM 16 mm twin-screw extruder (16 mm TSE) had a clam shell barrel design with a length to diameter ratio of 25 : 1 (Fig. 1). The maximum and minimum gaps in the 16 mm TSE are 0.2 mm and 3.3 mm, respectively. The screw configuration matched that in a larger 51 mm diameter twin-screw extruder used elsewhere. The extruder was run without a die since its presence may elon-

gate the dispersed phase domains. Samples can be taken at various locations shown in Figure 1 after the motor drive was stopped and the bolts removed.

The extrusion was carried out on premixed granules of the individual components at a screw speed of 100 rpm. The temperature profile in the extruder was set to 180, 210, 220, 225, and 230°C from the feed to the metering zone, respectively, which led to a melt temperature of 236°C in the die. The volume percentage of COC8007 in the blends was varied from 5 to 15% as indicated in Table I, and the samples were denoted M1, M2, and M3. These blends were also extruded into films with thicknesses ranging from 10 μm to 1 mm. The materials were rolled before heat sealing.

After the melt blending, each extrudate was quenched in a cold water bath and granulated. After a 12-h drying stage performed at 80°C under vacuum, the blend granules were molded into disk samples (diameter 25 mm, thickness 1 mm) to be used for the rheological measurements.

Sample characterization

Dynamic rheological measurements

The dynamic viscoelastic properties were determined using a strain-controlled rheometer: ARES (Advanced Rheometrics Expansion System, Rheometrics Co.) with a parallel-plate geometry ($\Phi = 25$ mm). The rheological experiments of the neat components as well as of their binary blends were performed at 240°C with angular frequencies ranging from 0.05 to 100 rad s^{-1} . All rheological measurements were carried out under nitrogen atmosphere and in the linear viscoelastic region of the samples (maximum strain level of 5%). The complex viscosity (η^*), the relaxation spectrum [$H(\lambda)$], the storage (G') and loss (G'') moduli of all the samples were recorded.

Morphological characterization

The morphologies of the LLDPE/COC blends were examined in an environmental HITACHI S-3500N scanning electron microscope (SEM). Before the SEM analysis, the samples were cryogenically fractured in liquid nitrogen. Cross sections parallel and perpendicular to the flow direction were systematically considered, but since spherical droplets were

TABLE I
LLDPE/COC Blend Compositions

Sample codes	LLDPE (vol %)	COC 8007 (vol %)
M1	95	5
M2	90	10
M3	85	15

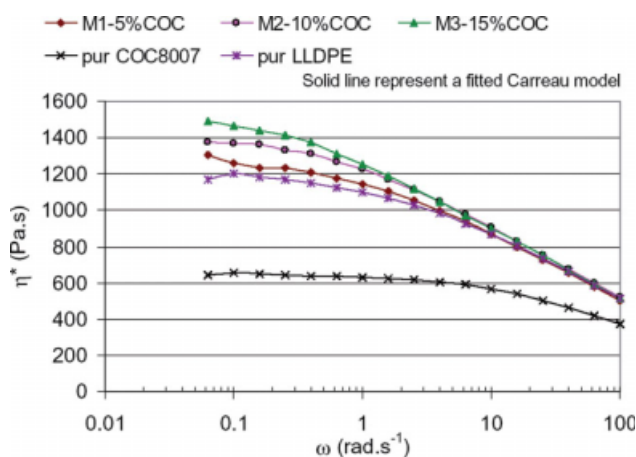


Figure 2 The angular frequency dependence of the complex viscosity (at 240°C) for the neat components (LLDPE and COC8007) and their blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed in all circumstances, only the transverse cross sections were ultimately analyzed.

Heat sealing and peel seal characterization

Before heat sealing, the extruded sheets of the binary LLDPE/COC blends (M1, M2, and M3) were placed in a cold atmosphere ($\sim 7^\circ\text{C}$) for 1 day in order for them to be subjected the same conditions as the materials used in industrial heat sealing applications. The sheets were then cut and placed on supports in industrial SEALPAC equipment to be heat sealed to films of either polyethylene (PE) or polyethylene terephthalate (PET). Optimal heat seal parameters were previously identified with the aim of generating the strongest possible peel seal strength in the samples. Thus, when the blends were heat sealed to a PE film, the SEALPAC equipment had the following setup: T

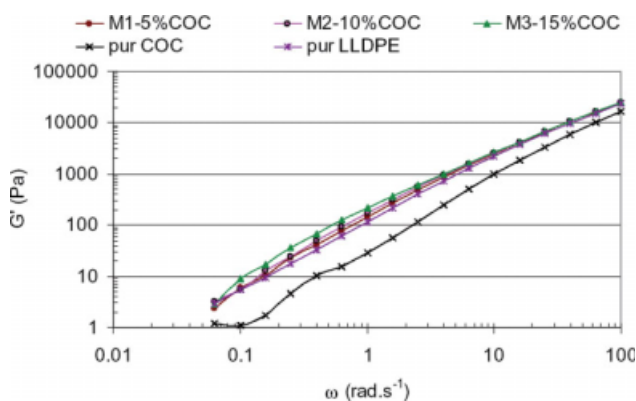


Figure 3 The angular frequency dependence of the storage modulus (at 240°C) for the neat components (LLDPE and COC8007) and their blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

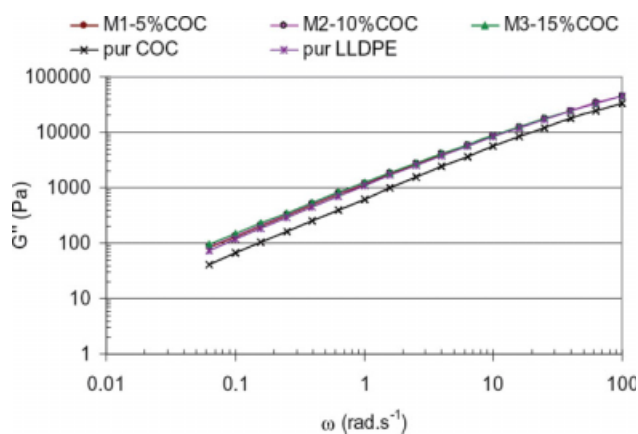


Figure 4 The angular frequency dependence of the loss modulus (at 240°C) for the neat components (LLDPE and COC8007) and their blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$= 145^\circ\text{C}$, contact time = 0.8 s, and pressure = 5 bar. In the case of heat sealing of the blends to a PET film, the optimum temperature was 215°C for a dwell time of 1.2 s under a pressure of 5 bars. The welds were 1.5 mm in width. The peel seal characterization was performed on a Chatillon TCD2000 equipment, using a pulling rate of 130 mm/min. These peel seal tests were carried out 1 day after the heat sealing to avoid aging effects on the weld. Approximately 20 samples were analyzed under identical conditions and subsequently averaged.

RESULTS AND DISCUSSION

Rheological properties

The angular frequency dependence at 240°C of the complex viscosity as well as of the storage and loss moduli for the neat components (LLDPE and COC8007) and their blends (M1, M2, and M3) are plotted in Figures 2, 3, and 4. Furthermore, Figure 4 gives the evolution of the torque of the mixing equipment as a function of the total mixing time in the Thermo Haake twin-screw (Fig. 1) extruder for the three binary mixtures M1, M2, and M3.

For a clearer overview, the torque data recorded for the three blends for mixing durations between 5 and 50 min was averaged, and the results are shown in Figure 5:

On the one hand, the torque data (Fig. 5) displayed a slight decrease when the volume fraction of COC8007 in the blends increased. This may reflect a blend effect during the mixing since the viscosity of neat COC8007 (Fig. 2) was found to be lower than that of LLDPE. It is important to note that the difference in torque values between the three blends is not clearly significant and that no clear conclusions can be drawn from the torque measurements.

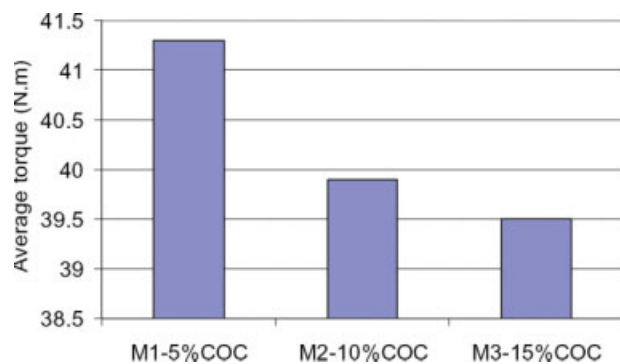


Figure 5 Torque data of the M1, M2, and M3 blends averaged between 5 and 50 min of mixing in the extruder. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

For the sake of clarity, only the rheological data is used to support the discussion. Indeed, the question of a higher viscosity but a lower torque of the blends is not the focus of this article. Because of the enormous complexity of this phenomenon (i.e., wall slip), no further attempts are made to explain it. Rather, the readers are encouraged to draw their own conclusions.

On the other hand, Figure 2 also showed that the complex viscosity of the three LLDPE/COC blends was slightly higher than that of neat LLDPE when the angular frequency was lower than 10 rad s^{-1} . At other frequencies, the two viscosities were equivalent.

This may result from miscibility/compatibility and/or interactions between the phases. By applying the Carreau model to the data presented in Figure 2, the Newtonian viscosity η_0 of the neat components and their blends can be extrapolated at low frequency sweeps. The resultant data is listed in Table II.

These values were then plotted (Fig. 6) as a function of the blend composition together with theoretical data obtained assuming the following blend model:

$$\ln(\eta_0)_{\text{blend}} = \sum x_i \ln(\eta_0)_i \quad (1)$$

where x_i is the volume fraction of component i (LLDPE and COC8007).

TABLE II
Newtonian Viscosities of the Neat Components and Their Blends as Obtained from the Extrapolation of the Carreau Model

Sample codes	Newtonian viscosity η_0 (Pa s) (from the Carreau model)
LLDPE	1221
M1	1347
M2	1445
M3	1654
COC8007	649

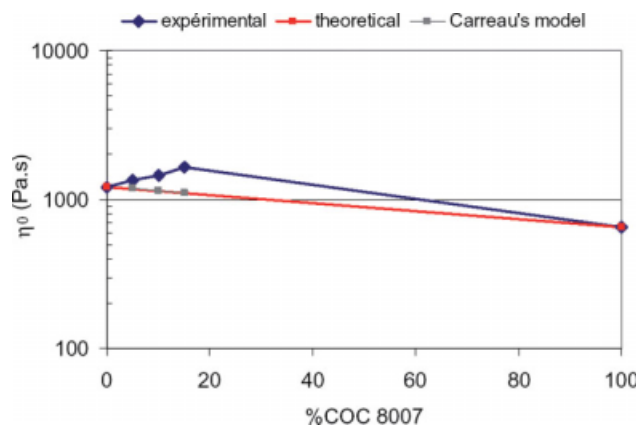


Figure 6 The experimental and theoretical Newtonian viscosity of the LLDPE/COC blends as functions of the blend composition. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Such a positive deviation of the experimental values from the theoretical ones has been reported^{14,15} as an indication of phase interactions.

The first explanation of the positive deviation involves a favorable energetic of mixing. In the presence of highly specific and favorable molecular interactions, polymer chains resist deformation. Since the blends are composed of a mixture of two nearly identical polymers, differing only in their content of branching, the enthalpy of mixing was assumed to be ~ 0 . Accordingly, this mechanism did not appear plausible for the present system.

The second explanation is related to the free volume of the polymer chains. Therefore, as the free volume increases, the viscosity decreases and *vice versa*. This suggests that the viscosity of the blends is higher than predicted by the log additive rule, since the free volume has decreased. The decrease in free volume within the blends may appear unrealistic, however, it must be kept in mind that degradation of the material during the conditioning period produces low-molecular weight species capable of affecting the free volume.

The dynamic rheological properties such as the storage and loss shear moduli (G' and G'') and the storage and loss viscosities (η' and η'') can also be used^{16,17,18} to evaluate the miscibility/compatibility between the phases in polymer blends.

Han et al.¹⁶ established a thermorheological criterion to determine the homogeneity of copolymers and polymer blends in the melt state. A linear correlation in the plot of $\log G'$ versus $\log G''$ was interpreted as an indication of a high level of homogeneity and compatibility in the multiphase system.

The rheological data can be analyzed in a Han plot ($\log G' - \log G''$) and a Cole-Cole plot. The Han plot has been used to investigate the miscibility of

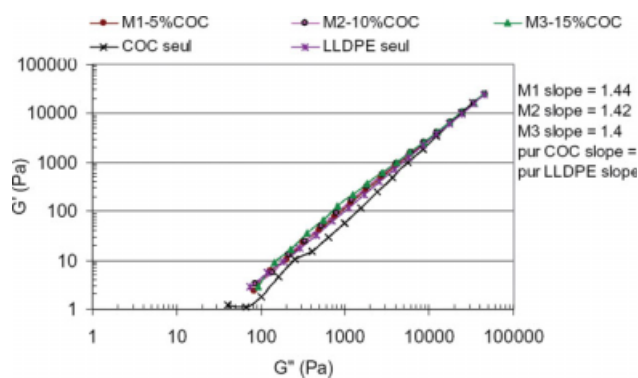


Figure 7 The storage modulus (G') versus loss modulus (G'') for the LLDPE/COC blends in the melt state (240°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymer blends. If a blend is miscible,¹⁷ the same slope is observed between the blend compositions and the pure component; otherwise, it is considered to be an immiscible or phase-separated blend.

The extent of the spread of the two curves in the log $G'/\log G''$ plots for a given polymer pair will depend on the extent of miscibility, polydispersity, and plateau moduli of the constituents.

Figure 7 displays such a plot for the neat components (LLDPE and COC8007) and their blends (M1, M2, and M3) where it can be clearly observed that the data described a single linear correlation with close slopes reflecting phase miscibility/compatibility in the blends (i.e., the slopes are, respectively, 1.44, 1.42, 1.4, 1.5, and 1.4 for M1, M2, M3, pure COC, and pure LLDPE).

This result may also be supported by the analysis of a Cole–Cole plot,^{19–23} in which the storage viscosity of a system is plotted against its loss viscosity.

It is also well known that a Cole–Cole plot can be used to analyze the miscibility of polymer blends. A smooth, semicircular shape of the plotted curves

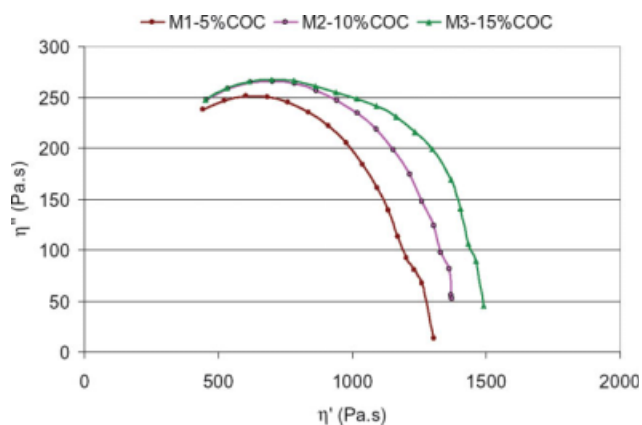


Figure 8 Cole–Cole plots for the three LLDPE/COC blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

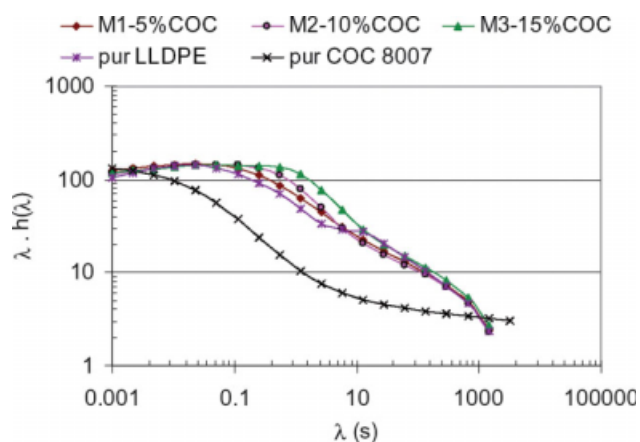


Figure 9 Relaxation spectra of LLDPE, COC8007, and their blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

suggests good compatibility, that is, phase homogeneity in the melt, and any deviation from this shape shows nonhomogeneous dispersion and phase segregation due to immiscibility.

The phase miscibility/compatibility was thus indicated^{18–24} by semicircular-shaped curves. The Cole–Cole plots for the three LLDPE/COC blends are given in Figure 8. The shapes of Cole–Cole plots are not ideally semicircular, which is correlated to the high polydispersity of the materials.

Each of the three Cole–Cole plots displayed only one arc which led to the conclusion that the phases of the three LLDPE/COC blends were to a certain extent compatible. Finally, Figure 9 shows the relaxation spectra of the neat components and their blends. The three blends displayed equivalent relaxation behaviors, which were also very much like that of the neat LLDPE. This was believed to be a clear indication that LLDPE acted as a continuous phase in the LLDPE/COC blends.

Morphological observations

The SEM micrographs of the three binary LLDPE/COC blends are displayed in Figure 10. Small COC8007 nodules (<1.5 μm) were found to be dispersed homogeneously in the continuous LLDPE phase. At the highest magnification, an interphase assuring the continuity between the dispersed and continuous phases was clearly identified. Such an observation, therefore, supported the conclusion of at least partial phase miscibility/compatibility in the LLDPE/COC blends, obtained from the investigation of their rheological properties.

A relatively good adhesion between the COC8007 nodules and the LLDPE matrix could also be reported since it was clear from the SEM micrographs that the failure did not occur at the interface but rather in the continuous phase.

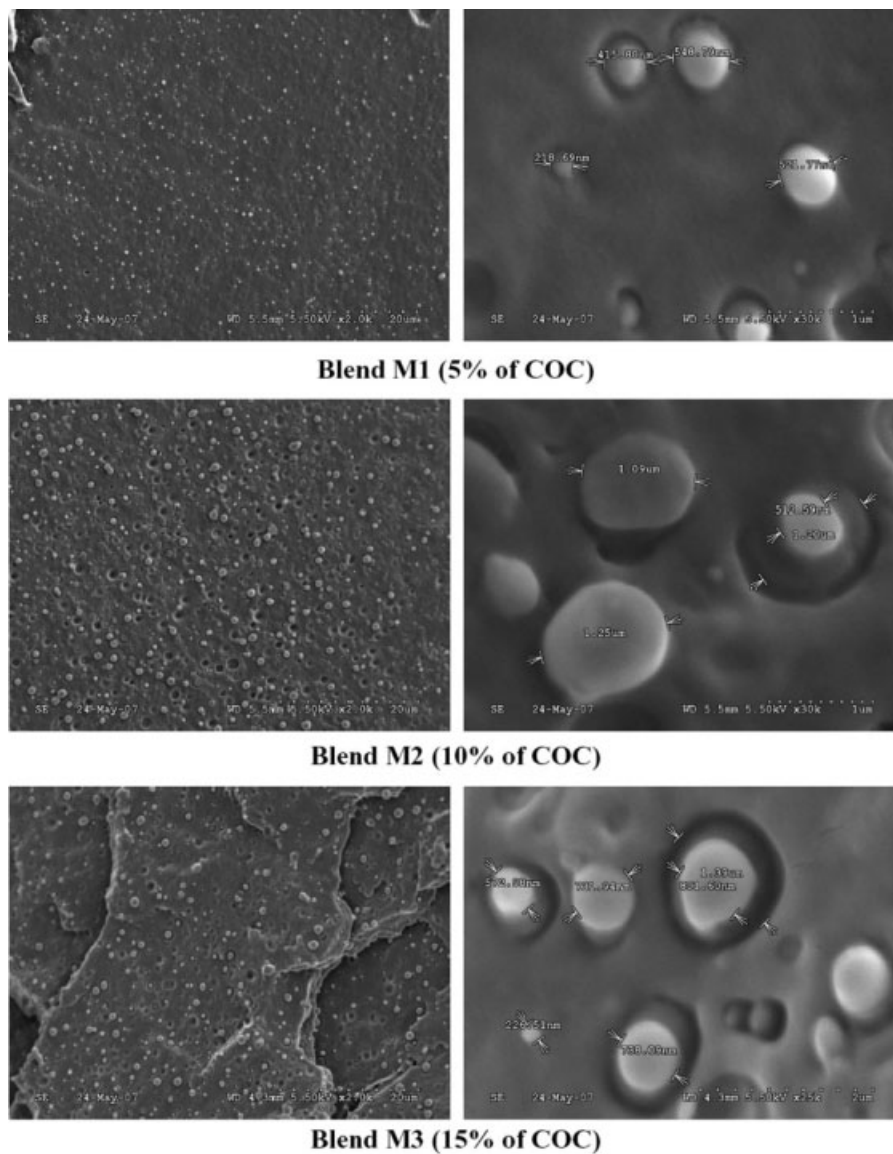


Figure 10 SEM micrographs of the LLDPE/COC blends.

Heat sealing and peel seal characterization

The heat sealing of the three blends to either PE or PET films was realized using industrial SEALPAC heat seal equipment. Peel tests were then performed to investigate the influence of the COC8007 and its concentration on the peel seal characteristics of the three systems. Seeing as PET tubs are traditionally used industrially, PE and PET films were first heat sealed on a PET layer to obtain PET/PET and PET/PE peel seal strengths to be used as a reference. Thus, the peel strength of PET/PET was measured as 1.37N/1.5 mm, whereas that of the PET/PE system was found to be equal to 0N/1.5 mm.

Two different configurations, based on the LLDPE/COC blends and two substrates (PE and PET), were utilized. Figures 11 and 12 show the average peel strengths that were measured for the

three LLDPE/COC blends as well as that of neat COC8007 heat sealed either to PE or to PET, respectively.

It was found that increasing the COC8007 concentration in the LLDPE/COC blends tended to offer a moderate increase in the peel strength of the systems. Indeed, a poor adhesion was clearly identified (Fig. 11) between the PE film and the neat COC8007. It can also be seen that the blend 2 (LLDPE with 10% COC) led to the best peel strength when compared with the other blends. This COC composition was thus thought to represent an optimum to promote adhesion with the PE film. Very likely, this blend was more compatibilized, which gave rise to enhanced adhesion properties. This result corroborated the rheological behavior and morphological observations described in the last paragraph.

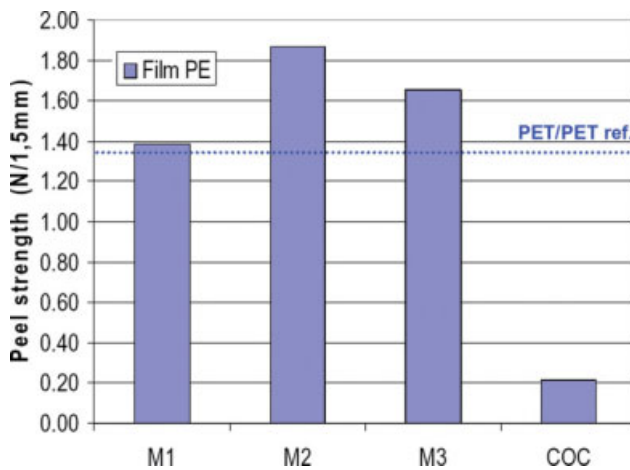


Figure 11 Peel strengths for the LLDPE/COC blends as well as that of COC8007 heat sealed to PE films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

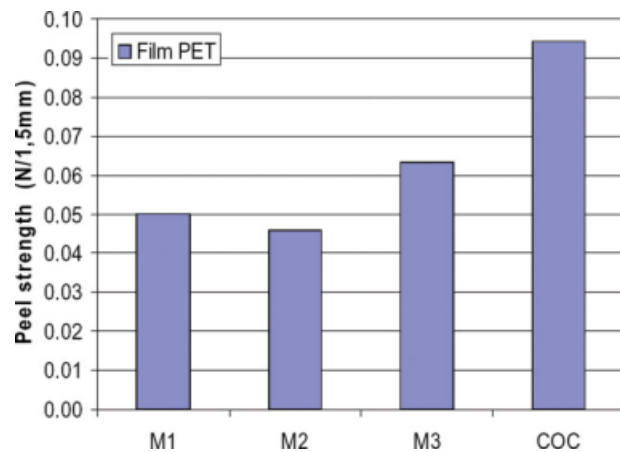


Figure 12 Peel strengths of the LLDPE/COC blends as well as that of COC8007 heat sealed to PET films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 12 also indicates that the peel strengths of LLDPE/COC blends heat sealed to a PE film were higher than that of the PET/PET (1.37N/1.5 mm) reference system. In Figure 12, it can be seen that an increase of COC in the LLDPE/COC blend favored the adhesion with the PET film but led to a low-peel strength with regard to the PE substrate. It seemed that higher the COC amount was, the higher was the peel strength. This was in contradiction to the results of adhesion with the PE film as given in Figure 11. Consequently, it is very important to choose a compromise with regard to the composition based on COC, as demonstrated by rheology and morphology.

According to the rheological characterization, the results of peel strength of the various blends with PE can be explained. Indeed, the partial miscibility revealed by the rheological and morphological characterization was coherent with the fact that these blends presented good adhesion with the PE film as a result of the polymer nature being the same.

This was based on COC 8007 ($T_g \sim 78^\circ\text{C}$) and PET having the same glass transition. Consequently, when these two polymers are heated, one can consider them to have the same molecular dynamics (the molecular mobility of PET and COC should be the same at a temperature corresponding to the glass temperature). The fact that these two polymers have the same molecular mobility during the glass

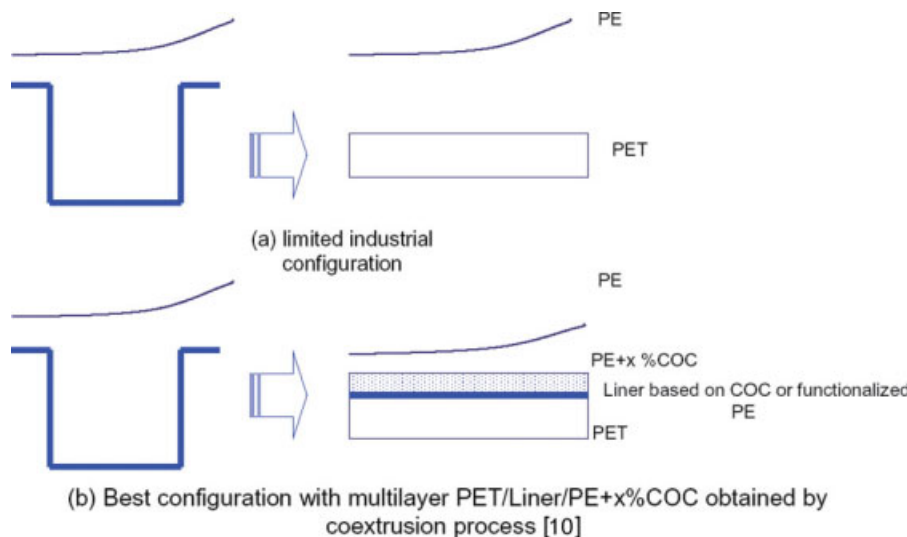


Figure 13 (a) A schematic of the actual limited configuration of PET tubs with PE heat sealing. (b) The proposed interesting configuration of multilayer structure with PET sheets covered with a thin layer of an optimized LLDPE/COC blend before heat sealing to a PE film for packaging applications. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

transition is thus believed to increase the probability of the formation of entanglements between them. This could explain that an augmentation of COC in an LLDPE/COC mix gave rise to an improved peel strength with a PET film.

Finally, the investigation of the systems' heat sealing properties pointed at an interesting industrial potential for PET sheets covered with a thin layer of an optimized LLDPE/COC blend in multilayer structure before heat sealing to a PE film for packaging applications [Fig. 13 (a,b)].

CONCLUSIONS

The focus of this article has been the assessment of the rheological and morphological properties of linear low-density polyethylene/cyclo olefin copolymer (LLDPE/COC) blends, as well as of their peel seal characteristics when heat sealed to films of either polyethylene (PE) or polyethylene terephthalate (PET) for packaging applications.

In a first step, the dynamic rheological properties of LLDPE/COC blends melt mixed in a twin-screw extruder were investigated in addition to those of their neat components. The compositional dependence of the zero shear viscosities, the Han-curves, the Cole–Cole plots, and the phase morphologies of the blends have been reported.

A partial phase miscibility/compatibility was suggested by means of Cole–Cole and equivalent plots and subsequently confirmed by an investigation of the blend morphologies using scanning electron microscopy. Moreover, the main motivation of this work involved the optimization of LLDPE/COC blend compositions as a function of final properties and especially the price of COC.

Secondly, the peel strength of PE films and PET films covered and heat sealed with thin layers of the LLDPE/COC blends were presented. The blends were heat sealed to either PE or PET films and the peel strengths of the resultant systems were characterized. The investigation of the systems' heat sealing properties pointed at an interesting industrial potential for PET sheets covered with a thin layer of an optimized LLDPE/COC blend before heat sealing

to a PE film for packaging applications. It would nonetheless be beneficial to investigate similar LLDPE/COC blends containing larger volume fractions of COC8007.

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