Investigation of Thermal and Melt rheological properties of Linear Low Density Polyethylene/Cyclic olefin copolymer blends

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Abstract In this paper, Cyclic Olefin Copolymer (COC) was melt blended in various weight fractions (5%, 10%, 15%, and 20%) with Linear Low Density Polyethylene (LLDPE) using Haake extruder followed by preparation of samples in the form of sheets using compression molding press. Differential scanning calorimetery (DSC) was carried out on polymers and its blends to investigate effect of Cyclic Olefin Copolymer (COC) on melt temperature and percent crystallinity. It was investigated that melting (Tm) and crystalline temperature (Tc) of LLDPE was not affected by the presence of COC. Melt flow index was carried out to measure of the ease of flow of the melt blend. It was observed that there was an increase in MFI values of the LLDPE/COC blend with the rise of temperature which results in the decrease of viscosity at high temperature.

Keywords — Polymer blends, Differential Scanning Calorimeter, Melt Flow Index, Polyethylene.

I. INTRODUCTION

The commercial growth of new polymers appears to be everlasting. However, preparation of polymer blends from the already existing polymers would be economically feasible. In the past few years a growing scientific and technological attention come into sight towards the leeway of combination two or more polymers with properties different from those of the base polymer in order to produce new materials by simply mechanical mixing. [1-3]. Among polyolefin, linear low-density polyethylene (LLDPE), offers a wide range of properties so it is an ideal choice for a range of packaging applications. LLDPE is looked-for as a resin for films because of its relatively low cost, in combination with this low cost an excellent set of mechanical/physical/chemical properties such as tensile and tear strength, modulus, puncture resistance, elongation at break, etc. Cyclic olefin copolymer (COC) is an amorphous, transparent copolymer of ethylene and norbornene polymerized by using metallocene catalysts. Its property outline can be varied over a wide range by modifying the chemical structure during polymerization. These new materials exhibit an outstanding combination of properties such as high transparency and gloss, high stiffness and strength, good moisture barrier, outstanding biocompatibility and inertness resists hydrolysis, polar organics, acids and alkalis, which makes it suitable for the range of applications. [4-8]

Polyolefins, 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. It has been accepted that morphology of polymer blends plays a significant role in deciding their physical and mechanical properties. K. Lamnawar et al [9] studied the rheological, morphological, and heat seal properties of linear low density polyethylene and cyclo olefine copolymer blends and reported that partial phase miscibility/compatibility was proposed by means of Cole–Cole and equivalent plots and successively confirmed by an investigation of the blend morphologies using scanning electron microscopy. Complex viscosity of the linear low density polyethylene and cyclo olefine copolymer blends was slightly higher than that of neat LLDPE when the angular frequency was lower than 10 rad s^{-1}.

M. Ebrahimi et al [10] reported the effects of shear rate and organoclay on the morphology of polypropylene/cycloolefin copolymer (80/20 wt. %) blends by using a combination of rheological measurements, X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was found that the COC phase was converted to finely dispersed fibrils in PP matrix. The SEM micrographs of cryofractured surfaces of PP/COC blend at three different shear rates indicate that the droplet size decreases with increase in the shear rate. S. Taglialatela Scafati et al [11] studied barrier properties of monolayer cast films from blends of Polyethylene with Etyylene-co-Norbornene. SEM analysis reported good

dispersion and distribution of the COC domains in the PE matrix. The elastic modulus was five times higher than that of the PE matrix by adding only 5 wt % of COC.

Transparent thermoplastic blends were also formed from a thermoplastic urethane and a cycloolefin copolymer such as norbornene-ethylene. The norbornene-ethylene copolymers generally contain at least about 50 mole % ethylene and have a Tg of less than about 150° C. The indices of refraction of both components are similar so that a transparent blend is formed which can be utilized in various applications demanding transparency such as in electronic and semi-conductor packaging, hard disc drive constituents and packaging, optical devices and films, etc. [12]. H. A. Khonakdar et al. [8] studied dynamic mechanical characteristics, morphology and rheology of COC, POE and their blends. The SEM image exhibited immiscibility between blends. To investigate rheological behavior of the blends, melt viscosity, storage modulus and Han diagrams were used. The results showed that the storage modulus of neat COC was greater than that of neat POE, whereas the modulus of the blends was in between the modulus of the neat polymers. Dynamic mechanical analysis showed that COC/POE blends were immiscible which absolutely supported the morphological and rheological conclusions.

Cyclic olefin copolymer/poly(ethylene-co-vinyl acetate) blends were prepared by melt processing in a twin screw extruder equipped with a cast film haul-off unit and microstructural, rheological, mechanical, and viscoelastic properties of film with ratios 90/10, 80/20, and 70/30 blends were investigated by Ali Durmus [13], several tests performed in scanning electron microscope, rotational rheometer, dynamic mechanical analysis, and tensile test. It was observed that the films revealed distinguishing immiscible "matrix–droplet" or "co-continuous" blend morphology and poly (ethylene-co-vinyl acetate) addition into cyclic olefin copolymer reduced the Young's modulus and yield stress and increased the strain at break for the blends.

A. Dorigato et al [14] reported that increasing fraction of COC in the LLDPE blends increased the maximum load persistent by the samples in impact tests, but decreased the blend ductility. S. Sánchez-Valdes et al [15] reported Influence of modified polyethylene compatibilizer on filler dispersion and flammability characteristics COC blends containing flame retardant combination. The PEgDMAE compatibilizer enhanced the filler dispersion and increased the LOI. Because of a high fraction of ethylene units, COC is likely to be compatible with polyethylene and other polyolefins without addition of special compatibilizers [16]. The data on miscibility behavior in COC based blends and mainly on linear low density polyethylene and cyclo olefine copolymer blends

and its relation with thermal and morphological properties are very rare.

The objective of this work is to study thermal and melt rheological properties of the LLDPE and COC blend by adding 5, 10, 15 and 20 wt % of COC in LLDPE by melt blending using Haake twin screw extruder, which can be used to develop monolayer blown film for packaging application. Monolayer films created using blends are easy substitutes to multilayer co-extruded films.

II. MATERIALS AND METHODOLOGY

Materials

Linear low-density polyethylene (LLDPE), F19010 (MFI at 190°C and 2.16 kg = 0.90 g/10 min, density = 0.918 g/cm^{-3}), was procured from Reliance Industries Limited, and Cyclic olefin copolymer (COC), TOPAS 8007F (Tg = 78 ℃, MFI at 190°C and 2.16 kg = 1.9 g/10 min, density = 1.02 g/cm^{-3}), was generously donated by TOPAS Advanced Polymers.

Preparation of blends

The LLDPE/COC blends with different compositions (95/5, 90/10, 85/15, and 80/20 wt/wt) were prepared in a Haake Rheomix TW100 (Figure 1), Processing parameters were: screw speed 50 rpm, cylinder temperature profile: 210, 220, 230 ℃ and die exit temperature 230 ℃. After the melt blending, extrudate were quenched in a cold water bath and granulated. Granules were pre-dried for 24 hrs at 60 ℃ under vacuum oven. These granules were used to determine Melt flow index (MFI).

Figure 1: Preparation of LLDPE/COC blend using Haake Rheomix TW100.

Sample Preparation

The blends were compression molded in the form of sheet having thickness between 2.5-3 mm, at 250°C under a pressure of 200 kg/cm^2 for the time period of 10 min (Figure 2). These sheets were used for differential scanning calorimeter (DSC).
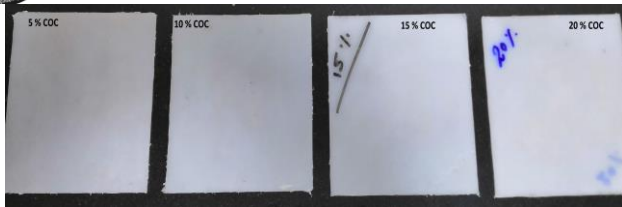
Figure 2: Sheets of LLDPE/COC blend using Compression molding press.

Sample characterization

The differential scanning calorimetry (DSC) (Model: (PERKIN ELMER, Diamond DSC) analysis was carried out under nitrogen purging rate at 50 ml/min. The samples were heated from 0 °C to 200 °C at 10 °C/min and then cooled down to 0°C at the same rate. A second heating run up to 200°C was then carried out under the same conditions as first run. In this way it was possible to evaluate the melting temperature of LLDPE in the blends and its %crystallinity (X_C) was calculated as the ratio of the melting enthalpy (ΔH_f), to the weight fraction of LLDPE in the blends (w_{ss}), and the reference value of the fully crystalline polyethylene (ΔH°_f) which was taken as 293.6 J/g. Equation (1) was used to determine the % crystallinity.

$$\%X_c = \frac{\Delta H_f}{w_{ss} \times \Delta H_f^\circ} \times 100 \qquad\text{..................}\ (1)$$

Melt flow index(MFI) of the blends was done as per ASTM D 1238 at 190º C and 230º C at 2.16 kg load. Five samples were used for each test and the average value was taken.

III.   RESULTS AND DISCUSSION

Figure 3-8 shows DSC thermograms of the LLDPE, COC and their blends, and the most relevant thermal properties are mentioned in Table 1. The intensity of the endothermic peak related to the melting of the crystalline regions of 100% LLDPE is higher than blend with COC. Melting (Tm) and crystalline temperature (Tc) of LLDPE is not affected by the presence of COC. COC is amorphous material because of cyclic structure of norbornene, addition of COC in LLDPE decreases the area under the curve and so enthalpy and crystallinity of the blend compared to 100% LLDPE.

Table 1: Values of Tm, Tc, ΔHm, and Xc obtained during heating scans of LLDPE/COC Blends.

Sample	Melting Temperature Tm [°C]		Enthalpy ΔH [J/g]		Crystalline Temperature Tc [°C]	PE % Crystallinity % Xc	
	1st Run	2nd Run	1st Run	2nd Run		1st Run	2nd Run
LL100 COC 0	122.49	124.45	59.19	44.34	110.20	20.20	15.13
LL95 COC 05	122.79	123.88	53.85	43.19	110.68	19.34	15.51
LL90 COC 10	121.71	123.95	47.84	41.26	110.48	18.14	15.64
LL85 COC 15	125.82	126.70	48.74	37.84	112.55	19.57	15.19
LL80 COC 20	125.16	125.70	44.99	38.95	111.58	19.19	16.36

Figure 8 indicates the glass transition of the 100% COC component at about 83°C. In which, the first run shows a change of slope at about 85°C due to the stresses built into the material as a result of processing, handling, or thermal history which are released when the material is heated through its glass transition [17].
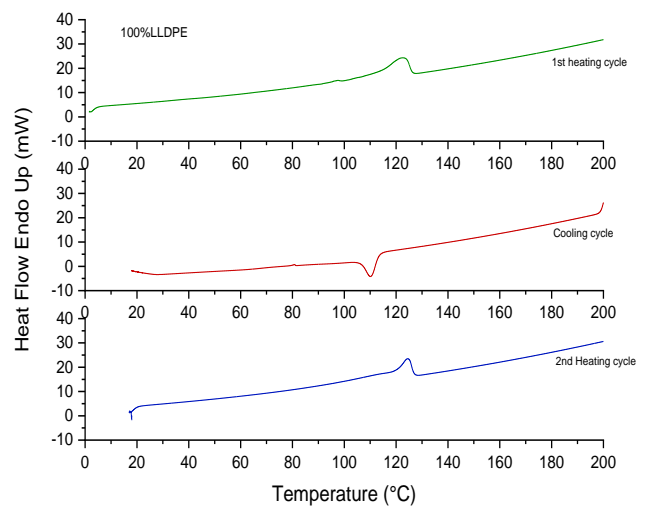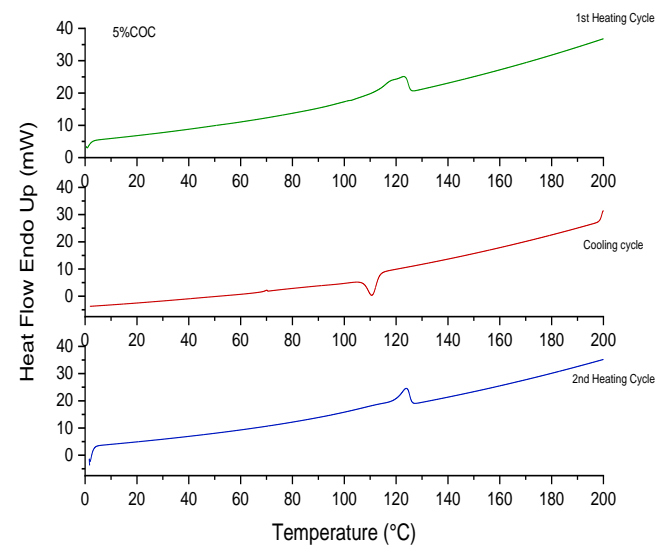

Figure 3: DSC thermograms of 100% LLDPE

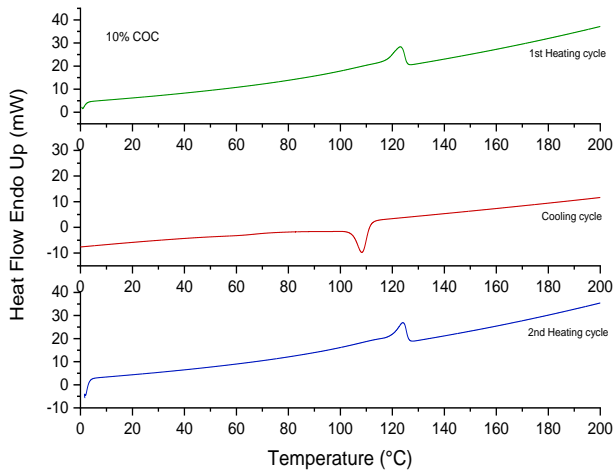Figure 4: DSC thermograms of 5% COC blend.
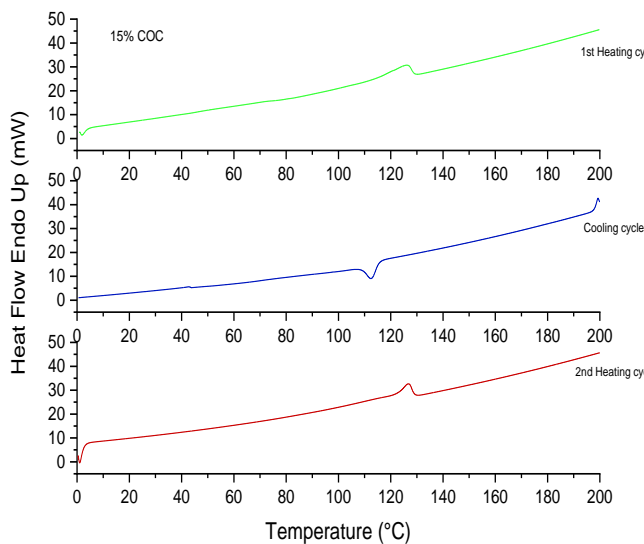
Figure 5: DSC thermograms of 10% COC blend.

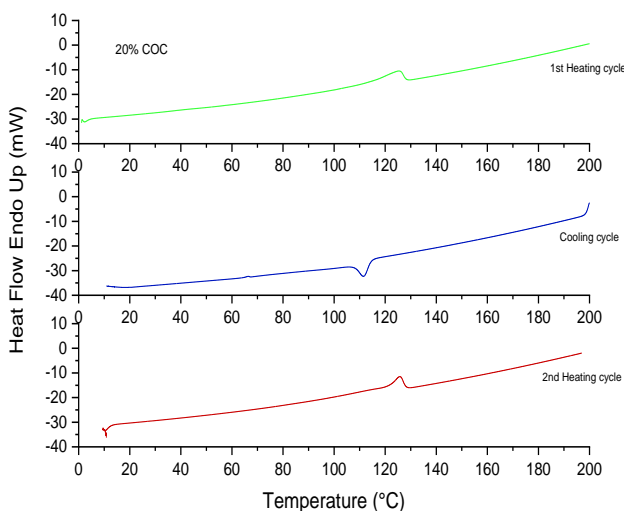Figure 6: DSC thermograms of 15% COC blend.

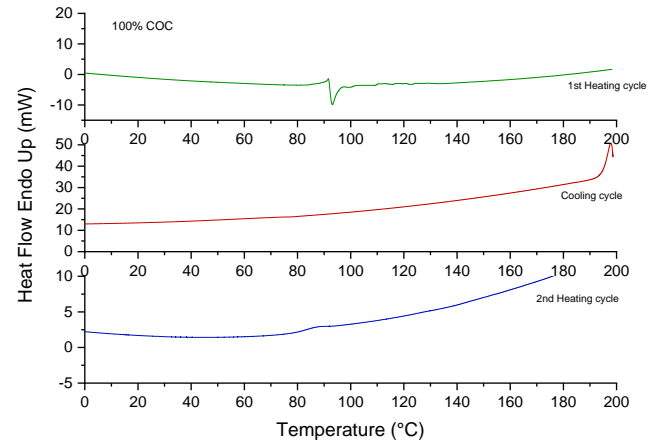Figure 7: DSC thermograms of 20% COC blend.

Figure 8: DSC thermograms of 100% COC.

During the quench cooling from 200°C to a temperature below, the thermogram does not show an exothermic signal associated with a crystallization phenomenon because COC is amorphous. The second heating run after the internal stresses were relieved; the graph shows a change on the flow energy manifested by the presence of the glass transition at around 83°C when the molecules go from a rigid to a flexible structure.

Melt flow index is (MFI) the weight of material in grams extruded in 10 min through a small orifice. It is useful for determining flow characteristics of a polymer. MFI and viscosity are inversely related and viscosity for polymer material depends on the applied force.

The melt flow index (MFI) is calculate by the equation,

$$MFI = 600 \times m / t \qquad \ldots\ldots\ldots\ldots(2)$$

Where,

m - The average mass of the cut-offs, in grams;

t - The cut-off time-interval, in seconds.

600- the factor used to convert grams per second into grams per 10 min (600 s);

Table 2 shows melt flow index (MFI) measured at 190 ºC and 230 ºC at 2.16 kg load of LLDPE, COC and its blends. When the minor component has higher viscosity than the major component, the minor component is coarsely dispersed. On the other hand, the minor component is finely dispersed when it has a lower viscosity than the major component [18]. Here COC acts as a minor component and it has lower viscosity than LLDPE. Due to its amorphous structure, the temperature dependence of MFI is higher for COC than LLDPE. COC becomes less viscous than LLDPE at higher temperatures, specifically at 230º C for 2.16 kg load. Melt flow rate increases slightly with the addition % COC (5%-20%) in LLDPE for both 190º C and 230 º C at 2.16 kg load as shown in figure 9.
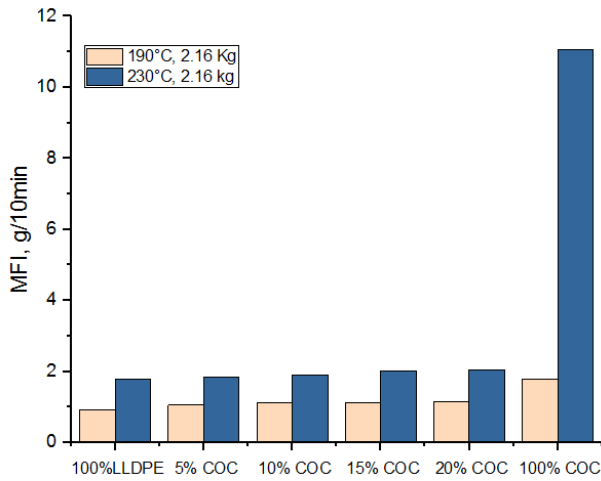
Figure 9: Melt flow index (MFI) of LLDPE/COC and its blends.

Table 2: Melt flow index value of LLDPE/COC blends.

Sr. No	Blend Ratio	MFI g/10min at 2.16kg load	
		190 °C	230 °C
1	100%LLDPE	0.93	1.54
2	5%COC	1.06	1.92
3	10%COC	1.11	2.01
4	15%COC	1.13	2.06
5	20%COC	1.15	2.14
6.	100%COC	1.8	11.06

IV. CONCLUSION

The effect of COC thermal and melt rheological properties of LLDPE blend was investigated using DSC and MFI tester. Crystallinity of LLDPE changed slightly with loading of 5%-20% COC, as the COC obstructs the nucleation and crystal growth geometries of LLDPE blends. Exothermic peak associated with a crystallization phenomenon was not shown by 100% COC because of its amorphous structure. Hence, COC is copolymer of ethylene and norbornene having amorphous characteristics because of cyclic structure of norbornene, addition of COC in LLDPE decreases slight crystallinity of the blend compared to 100% LLDPE. The MFI values of the LLDPE/COC blend increases with the rise of temperature showing the decrease of viscosity at high temperature. COC becomes less viscous than LLDPE at higher temperatures, specifically at 230º C for 2.16 kg load. MFI value of LLDPE/COC blends comes under acceptable range to process through blown/cast film extrusion.

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