Thermo-oxidative degradation study of melt-processed polyethylene and its blend with polyamide using time-resolved rheometry

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ABSTRACT: Time-resolved mechanical spectroscopy (TRMS) was conducted to study the thermo-oxidative degradation of linear low density polyethylene (LLDPE) samples with different thermal histories and their blends with a polyamide (PA6) in the melt state. Neat LLDPE was first melt-processed at 180, 220, 250, and 260 °C in an extruder and then pre-processed LLDPE samples were further extruded with PA6 at 260 °C to form various LLDPE/PA6 blends. TRMS measurements were conducted under an air atmosphere at 0.5% strain and a constant frequency of 0.1 rad/s for LLDPE samples and at a range of frequencies between 0.1 and 60 rad/s for LLDPE/PA blend samples, over a 1h period. In the case of LLDPE samples, time-sweep experiments were carried out at 190, 220, and 240 °C, whereas the temperature was fixed at 240 °C for the LLDPE/PA blend samples. The observed rheological behaviors revealed that the degradation resulted in an increase in the elastic moduli of the LLDPE and LLDPE/PA blends regardless of the thermal history. LLDPE processed at different processing temperatures produced different viscoelastic behaviors in cases where the LLDPE samples were processed at lower temperatures (180 and 220 °C) where a rapid increase in the modulus over a short period was seen. On the other hand, a change in the pre-processing temperature of the LLDPE had no effect on the rheological property of the corresponding LLDPE/PA6 blends. Cross-linking reactions during measurements under an air atmosphere could

be the main reason for the growth in the modulus as a result of thermo-oxidative degradation. It was found that degradation was only a function of the temperature and exposure time, not the frequency. The most important result of this study was that collecting data on the isochronal moduli at different scanning frequencies was a more accurate way to understand the degree of cross-linking compared to running conventional frequency sweep tests, where the molecular structure of the material was unstable as a result of rapid degradation.

KEYWORDS: Time-resolved mechanical spectroscopy, thermo-oxidative degradation, rheology, LLDPE, cross-linking

1. Introduction

Polyethylenes (PEs) are commodity polymers that are frequently used as packaging materials even though they exhibit poor barrier properties against certain chemical components. One way to overcome this drawback is blending with another polymer with good barrier properties along with superior mechanical strength such as a polyamide (PA) [1, 2]. It is well documented that both polymers are prone to thermal degradation when certain conditions are met, e.g., specific temperature ranges, oxygen content, and shear intensities [3-6]. During their degradation, polymers may undergo chain scission, crosslinking, or both simultaneously as competitive reactions, depending on the conditions and extent of the process [4, 7-9]. In such a scenario, the oxidation of the PE is initiated by carbon radical production (chain scission), which is followed by the recombination of these radicals (alkyl radicals) and their addition to carbon-carbon double bonds (CH_2=CH−vinyl groups), causing cross-linking [10]. On the other hand, the oxidation of PA6 leads to the formation of alkoxy radicals containing amide and carboxylic groups from the decomposition of hydroperoxides during the chain scission process, whereas further oxidation leads to a cross-linking reaction between amine groups (−NH_2) and other reactive groups such as aldehydes and amides [6, 11]. Alternatively, the degree of degradation (chain scission or cross-linking) could affect physical properties such as the viscosity and final thermal stability of the products. From another perspective, thermo-oxidative degradation can be used to initiate the biodegradation process by

reducing the molecular weight to the point where biodegradation can proceed [8, 12]. Therefore, it is important to study the effect of the thermo-oxidation process for polymers to develop materials with superior performance under optimized processing conditions.

Different techniques have been used to study the thermo-oxidative degradation of polymers, including thermogravimetric analysis (TGA) [7, 12, 13], differential scanning calorimetry (DSC) [7], Fourier transform infrared spectroscopy (FTIR) [5, 13, 14], size exclusion chromatography (SEC) [1], gas chromatography (GC) [7], oxygen uptake [6], chemiluminescence [6], and UV spectroscopy [5, 6]. One of the most reliable techniques to study the mechanisms of the degradation process is the melt-rheological methods because it is very sensitive to any small microstructural changes from chain scission to crosslinking [4, 15, 16]. Conventional frequency sweep tests are very common to study the dynamic of polymers with respect to their molecular structures and morphologies as they probe polymers within their linear viscoelastic regions where molecular structures do not change during the tests. Low frequency results are richer in information as they are associated with longer relaxation times related to the larger portions of the materials. However, the longer required experimental time related to the low frequency regions could surpass the degradation time of some of testing materials (e.g., transient polymers). Thus, the long relaxation time associated to the structure of the polymer might not be accurate as degradation has already interfered with the structure and hence the properties. It has been shown that for materials undergoing fast degradation, conventional frequency sweep tests may not be informative because the degradation can occur within a few seconds during the course of frequency sweep tests. Alternatively, Mours and Winter [17] proposed the use of Time-resolved mechanical spectroscopy (TRMS) as a convenient technique to monitor the properties, e.g., the elastic and loss moduli, of transient materials at a single frequency. TRMS is a technique to sequentially acquiring the frequency dependencies of materials by probing the dynamic mechanical properties of such materials within their linear viscoelastic regions (constant strain amplitude) over a specific measuring time and at a fixed frequency [9, 17-19].

The aim of this study was to observe the effect of the thermal history on the kinetics of the thermo-oxidative degradation of linear low density polyethylene (LLDPE) samples and their corresponding blends with PA via a time-resolved rheology technique. Different LLDPE samples were processed at different temperatures from 180 °C to 260 °C in an extruder. Then, in the next step, these differently processed LLDPE samples passed through another extrusion to be blended with PA at 260 °C. This research may help us to understand the degradation kinetics of blends in the melt state.

2. Experimental

2.1. Materials

The polymers used in this study were commercial products. LLDPE, designated as HF120, was purchased from Sasol, South Africa. According to the supplier, it has a melt flow index (190 °C/2.16 kg) = 1.0 g/10 min, density = 0.920 g/m^3, and recommended melt-processing temperature of 190 °C. Nylon 6 (PA6), which was designated as UBE nylon 1030B, was purchased from UBE industries, Ltd. According to the supplier, it has a density = 1.14 g/m^3 and melt range temperature = 215–225 °C. Its measured melt flow index (250 °C/2.16 kg) was found to be 4.56 g/10 min.

2.1.1. Sample preparation

Neat LLDPE and 80 wt% pre-processed LLDPE/20 wt% neat PA6 blends were processed using a TE-30 co-rotating twin screw extruder (Nanjing ONLY Extrusion Machinery Co. Ltd), with an L/D of 40. Four neat LLDPE samples were processed at different temperatures:

(i) Processed at 180 °C; the following zone temperatures were used: 120, 160, 180, 180, 180, 180, 180, 180, and 180 °C; the die temperature was 180 °C; and the screw speed was 200 rpm.

(ii) Processed at 220 °C; the following zone temperatures were used: 120, 180, 220, 220, 220, 220, 220, 220, and 220 °C; the die temperature was 220 °C; and the screw speed was 200 rpm.

(iii) Processed at 250 °C; the following zone temperatures were used: 120, 220, 250, 250, 250, 250, 250, 250, and 250 °C; the die temperature was 250 °C; and the screw speed was 200 rpm.

(iv) Processed at 260 °C; the following zone temperatures were used: 120, 220, 260, 260, 260, 260, 260, 260, and 260 °C; die temperature was 260 °C; and the screw speed was 200 rpm.

It is interesting to note that the residence time for LLDPE's processed at 180 and 220°C was about 1.10 min and it increased to 1.30 min for polymers processed at 250 and 260°C.

Blends of 80 wt% pre-processed LLDPE samples and neat 20 wt% neat PA were processed using the following zone temperatures: 120, 200, 260, 260, 260, 260, 250, 250, and 245 °C, with a die temperature of 240 °C and screw speed of 200 rpm. During processing we did not find any change in residence time and color of the blend samples.

The extrudate was further molded using an injection molding machine (model: ENGEL, e-mac 50) to produce samples for rheological measurements. The following temperature zones were used: 220, 230, 235, 240, and 36 °C (mold temperature).

2.2. Characterization

2.2.1. Rheological analyses

Rheological analyses were conducted using a Physica MCR501 rheometer (Anton Paar Austria) equipped with 25 mm parallel plates. Time resolved mechanical spectroscopy (TRMS) measurements were carried out under an air atmosphere and a strain amplitude of 0.5% (linear region) within a 1 h period. The selected frequency for the melt-processed LLDPE samples was 0.1 rad/s, whereas various LLDPE/PA blend samples were probed at different frequencies of 0.1, 0.3, 1, 3, 6.28, 10, 30, and 60 rad/s to cover the low, intermediate, and high frequency regions. The time evolution rheological properties of the LLDPE were determined at different temperatures of 190, 220, and 240 °C, whereas the temperature was fixed at 240 °C for the LLDPE/PA blends, which was equal to their mixing temperature during injection molding. Frequency sweep tests were performed under an air atmosphere and a strain amplitude of 0.5%, with frequencies varying from 0.1 to 100 rad/s.

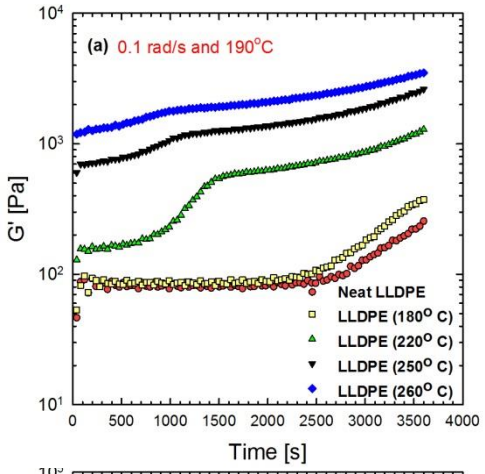
2.2.2. Morphology

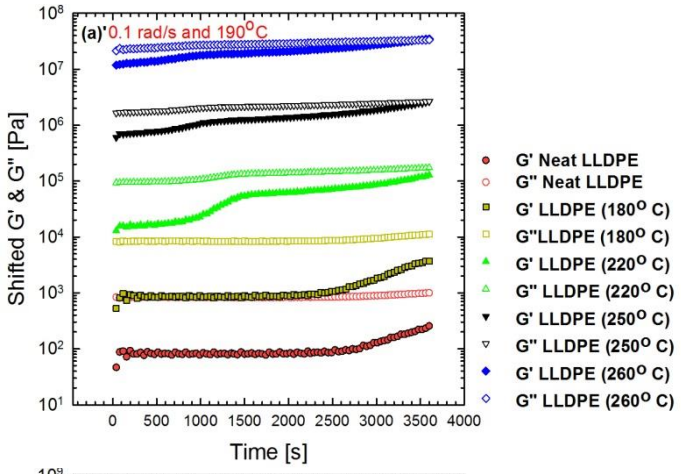
A Carl Zeiss (Germany) Auriga FE-SEM with a GEMINI column was used to image the cryo-fractured (using liquid nitrogen) surfaces of neat LLDPE/PA blends. The surfaces were coated by a Au/Pd alloy and viewed using an acceleration voltage of 3 kV.

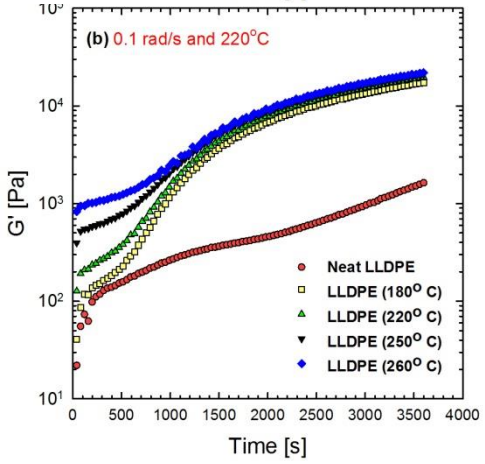
3. Results and discussion

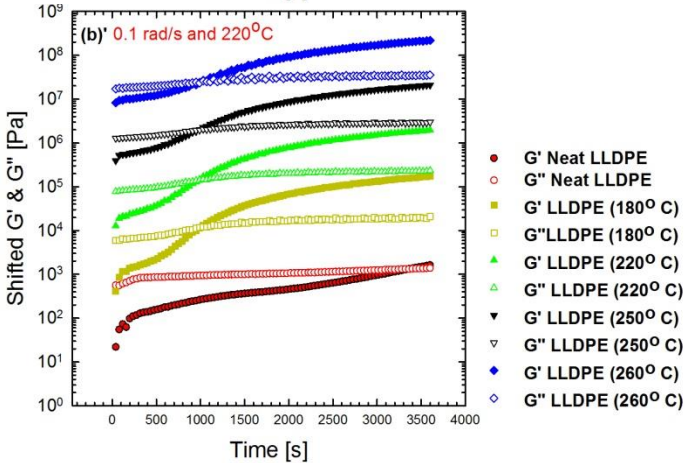
3.1. TRMS of LLDPE

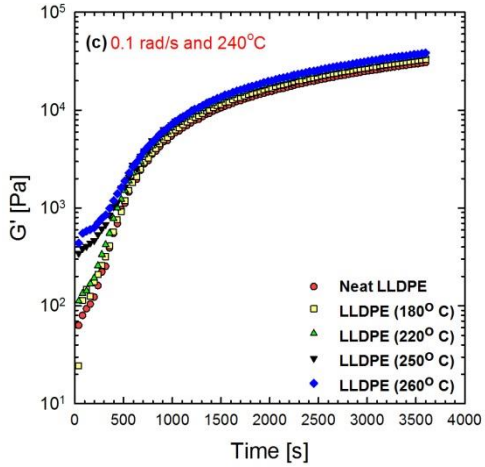
In order to understand the influence of the processing temperature on the thermo-oxidative degradation of LLDPE, the time evolution of moduli at a single frequency (0.1 rad/s) but different temperatures were recorded. The results acquired at different temperatures are plotted in Fig.1 (a−c) and their corresponding counterparts (a−c)' show the crossover behaviors. To gain a better understanding of the degradation kinetics, the elastic moduli of the materials were investigated at a low frequency of 0.1 rad/s as a function of time. The elastic modulus was more informative because it was more sensitive to changes in the molecular architecture [18] and low frequency as a result of being associated with a longer relaxation time (slower chain movements) because larger chains of polymers are involved [9, 19].


(a) 0.1 rad/s and 190°C
G' [Pa]
Time [s]
Neat LLDPE
LLDPE (180° C)
LLDPE (220° C)
LLDPE (250° C)
LLDPE (260° C)


(a)' 0.1 rad/s and 190°C
Shifted G' & G" [Pa]
Time [s]
G' Neat LLDPE
G" Neat LLDPE
G' LLDPE (180° C)
G"LLDPE (180° C)
G' LLDPE (220° C)
G" LLDPE (220° C)
G' LLDPE (250° C)
G" LLDPE (250° C)
G' LLDPE (260° C)
G" LLDPE (260° C)


(b) 0.1 rad/s and 220°C
G' [Pa]
Time [s]
Neat LLDPE
LLDPE (180° C)
LLDPE (220° C)
LLDPE (250° C)
LLDPE (260° C)


(b)' 0.1 rad/s and 220°C
Shifted G' & G" [Pa]
Time [s]
G' Neat LLDPE
G" Neat LLDPE
G' LLDPE (180° C)
G"LLDPE (180° C)
G' LLDPE (220° C)
G" LLDPE (220° C)
G' LLDPE (250° C)
G" LLDPE (250° C)
G' LLDPE (260° C)
G" LLDPE (260° C)


(c) 0.1 rad/s and 240°C
G' [Pa]
Time [s]
Neat LLDPE
LLDPE (180° C)
LLDPE (220° C)
LLDPE (250° C)
LLDPE (260° C)

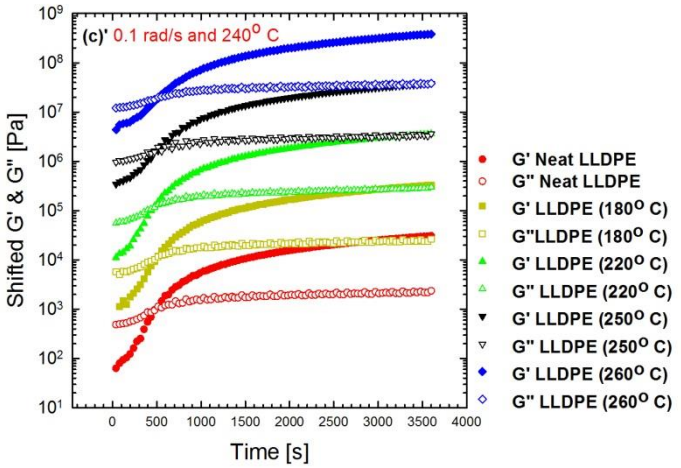

(c)' 0.1 rad/s and 240° C
Shifted G' & G" [Pa]
Time [s]
G' Neat LLDPE
G" Neat LLDPE
G' LLDPE (180° C)
G"LLDPE (180° C)
G' LLDPE (220° C)
G" LLDPE (220° C)
G' LLDPE (250° C)
G" LLDPE (250° C)
G' LLDPE (260° C)
G" LLDPE (260° C)

Fig. 1. (a−c) TRMS of elastic (storage) G' moduli of neat and processed LLDPE samples under air atmosphere at fixed frequency of 0.1 rad/s, strain amplitude of 0.5%, and different temperatures of (a) 190, (b) 220 and (c) 240 °C under air atmosphere. (a'−c'). Elastic (storage) and viscous (loss) moduli of the LLDPE samples. The moduli of the neat LLDPE and LLDPE processed at different temperatures of 180, 220, 250, and 260 °C, are artificially shifted by factors of 10^0, 10^1, 10^2, 10^3, and 10^4, respectively, for the sake of clarity.

Fig. 1 reveals a couple of phenomena that will be discussed below.

I. *Growth in moduli*

The first and most striking result is the growth in modulus *G*'(t) over time, specifically at shorter times. This growth in moduli over time is common for all samples studied here; however, the rates are different depending on the thermal history and measuring temperatures.

This is similar to the observations of Filippone et al. [9, 19], who found similar behavior for polyamide 11 (PA11) and PA11/clay. It was found that this phenomenon is related to changes in the

molecular architecture of the materials and that an upturn in the viscoelastic behavior of the polymer over time could be associated with the post-condensation reactions. However, the shape of curves shown here are a bit different with those reported by Filippone et al. [9, 17]. The slower growth rate at a shorter time [<500s, Fig.1(b)] than that of longer time of 1000s, and this is in contrast with other studies [9, 17], where the authors reported a sudden increase in G' at a shorter time and levelling off at higher times. In a recent study, Kruse and Wagner [18] also found that both chain scission and cross-linking can occur during the oxidation of polyethylene terephthalate (PET), where the extent of each process controls the viscoelasticity of PET during its time evolution. In other words, dominant cross-linking reactions at early stages of the tests could be responsible for the changes in the molecular structure for particular molecular weights and degrees of cross-linking, which produces a rapid growth in viscoelastic behavior. Peterson et al. [7] reported that chain scission and cross-linking can also occur concurrently in the case of PE. Knowing this, during the time evolution, the chain scission mechanism can equilibrate the molecular structures, which levels off or at least weakens the growth rate of the modulus. Therefore, it can be concluded that the growth rate could be due to the degree of cross-linking and its influence on moduli *G*'(t) of the polymers. Although some cross-linking is happening at shorter times [<500s, Fig.1(b)]; samples are not in gel form structures and cross-linking may not be significantly dominating chain scission reactions while near gel formation (vicinity of the cross-over point) the growth rate increases rapidly (t~1000s) indicating the dominating cross-linking reactions.

II. *Effect of processing temperature*

It is interesting to observe that LLDPE samples with different thermal histories responded differently to the degradation. Apart from neat LLDPE and LLDPE processed at 180 °C measured at 190 °C [Fig. 1(a)], which responded almost similarly, remaining unaltered for up to 2000 s, the growth rate decreased with an increase in the processing temperature of the LLDPE during extrusion. It can be said that these two particular samples with less intense thermal history require longer time to undergo structural changes at a lower temperature of 190 °C. Therefore, the unprocessed neat

LLDPE with no thermal history was exposed to the thermal treatment during measurement at 190 °C and the processed LLDPE (at 180 °C) with less structural modification during the processing are indicating the identical responses during measurement (a delay in increasing moduli G'). In other words, low temperature post-treatment condition (measuring temperature of 190 °C) has the same influence on the structure of neat LLDPE as the LLDPE processed at lower temperature of 180 °C. It can be suggested that the short residence time in the extruder and low processing temperature 180 °C were not enough to introduce outstanding cross-linking on LLDPE chains.

Moreover, the LLDPE processed at higher temperatures had higher moduli than those processed at lower temperatures in the following descending order LLDPE: (260 °C) > LLDPE (250 °C) >LLDPE (220 °C) >LLDPE (180 °C) > neat LLDPE. In other words, there had already been some alterations in the molecular architecture during processing, leading to preliminary cross-linking stages, where the LLDPE samples processed at higher temperatures had higher degrees of cross-linking. This in turn resulted in the higher modulus during TRMS.

III. *Effect of measuring temperatures*

Alternatively, it is worth noting the effect of the measuring temperature on the thermo-oxidative degradation mechanisms of the polymers via TMRS. It can be seen from Fig. 1 (a−c) that increasing the measuring temperature speeds up the modulus growth rate. This confirms the temperature dependency of the cross-linking reactions in LLDPE samples, which led to a gelation behavior when G' (t) intersected G" (t) within a few minutes of the measurements, as seen in Fig. 1 (a'−c'). Interestingly, as the measuring temperature increased, the differences in the moduli of the LLDPE samples with various processing temperatures became less significant, whereas at some point they converged into a single curve [see Fig. 1(c)]. In addition, the crossover points (gelation points) remained unchanged at high measuring temperatures, even for the unprocessed neat LLDPE. In other words, high temperature can minimize the thermal history of the polymers by balancing the molecular weights through rapid cross-linking reactions.

3.2. TRMS of LLDPE/PA blends

In the next step, the LLDPE samples processed at different temperatures were melt-mixed with 20% PA in an extruder at 260 °C. Test samples were injection molded at 240 °C. Therefore, we used similar time evolution rheological measurements to monitor the thermo-oxidative degradation of LLDPE/PA blends at a single temperature of 240 °C, which was similar to the injection molding temperature.

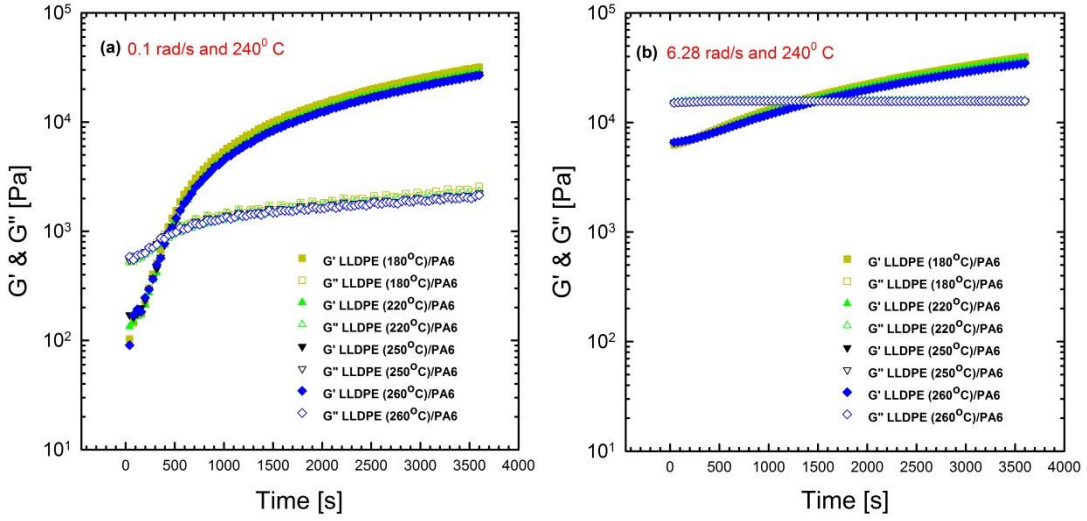


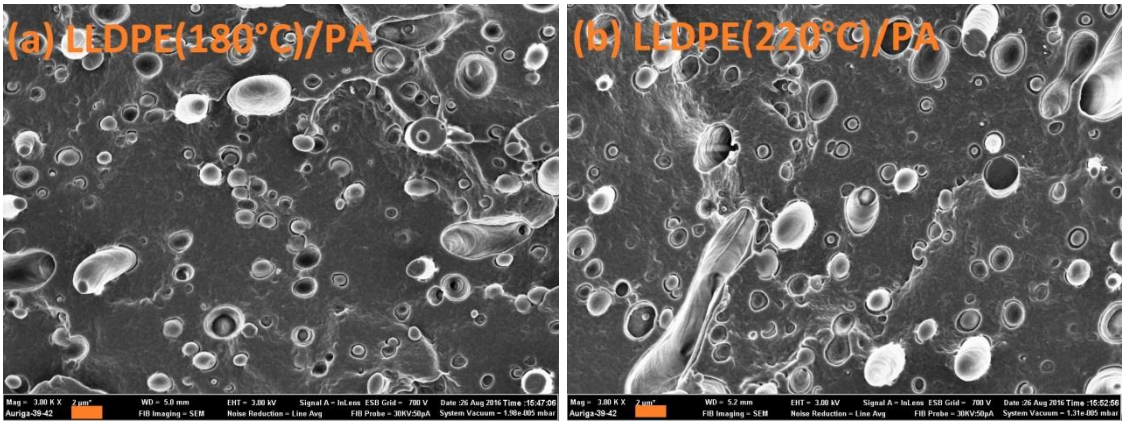
Fig. 2. TRMS results of elastic (storage) G' and viscous (loss) G" moduli of (80/20) LLDPE/PA blends at 240 °C and a strain amplitude of 0.5% under air atmosphere at frequencies of (a) 0.1 rad/s and (b) 6.28 rad/s.

Fig. 2 reveals that all the blends show the same response regardless of the thermal history of the LLDPE samples used in the blends. TRMS tests were conducted at two different frequencies to confirm that the LLDPE's thermal history did not play a role at different frequencies. This suggests that when the LLDPE underwent the second mixing process with PA at 260 °C, its molecular structure was balanced and blending them with the PA eliminated the previous processing temperature effects. SEM images of blends after extrusion [Fig. 3 (a−d)] also show that the morphologies of the blends with different LLDPE samples are identical, confirming that the thermal history of the LLDPE during processing has no influence during the second mixing process of blending with PA. Although the imposed strain amplitudes were too small (0.5%) to cause any droplet breakup or even coalescence; the possible cross-linking reactions at the interface between

LLDPE and PA during the course of TRMS test can induce some stabilization to the morphology of the blends against the coalescence of droplets during annealing. Therefore, it can be concluded that the progressive increase in the moduli and extension of the plateau modulus (we will discuss latter) is due to the increase in the molecular weights as a consequence of cross-linking reactions in individual polymers and possibly interfacial modifications between LLDPE and PA phases due to cross-links at the interface. It is known that the degradation of PE and PA6 can respectively yield alkyl and alkoxy radicals [10, 6] and these radicals can react to other carbon-carbon groups, amine and other active groups of the other polymers as well, hence creating a new copolymer at the interface. This maybe is the reason why the slow growth rate in moduli of the blends is no longer exist at short times compared to that of LLDPE [<500s, Fig. 1(b), (c)] due to dominant cross-linking reactions added in interface as well. Moreover, the convergence of the moduli at high frequencies is only a reflection of the chemical structures of a small portion of the polymers. Hence, it is not associated with long length scale changes in the polymers [18].

Hence, the LLDPE (180 °C)/PA blend was selected to investigate the kinetics of the thermo-oxidative degradation and will be referred to simply the LLDPE/PA blend.

Conventional frequency sweep tests were performed immediately after 1 h of TRMS measurements (frequencies of 0.1 and 6.28 rad/s) of the LLDPE/PA blend under an air atmosphere and at 240 °C.



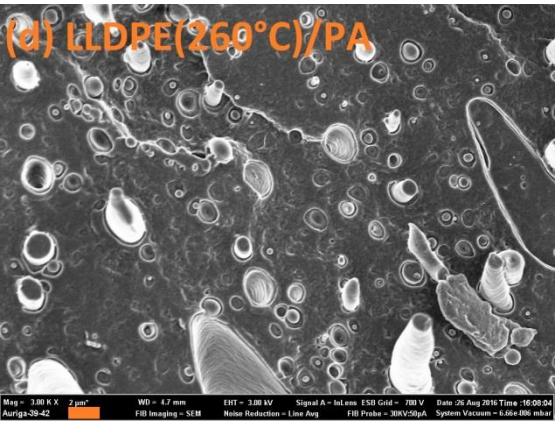


Fig. 3. SEM images of (a) LLDPE (180 °C)/PA, (b) LLDPE (220 °C)/PA, (C) LLDPE (250 °C)/PA and LLDPE (260 °C)/PA blends after extrusion (before TRMS). Scale bars are 2 µm in all images.

It can be observed in Fig. 4 that the elastic $G'(\omega)$ and viscous $G''(\omega)$ moduli of the blends obtained immediately after the TRMS measurements shown in Fig. 2a and 2b were exactly the same. This indicates that the thermo-oxidation was not a function of the frequency but a function of time and temperature. Moreover, dominant plateau elastic modulus $G'(\omega)$ over $G''(\omega)$ throughout the frequency range indicated the formation of a highly elastic network due to cross-linking reactions during the course of the TRMS test.

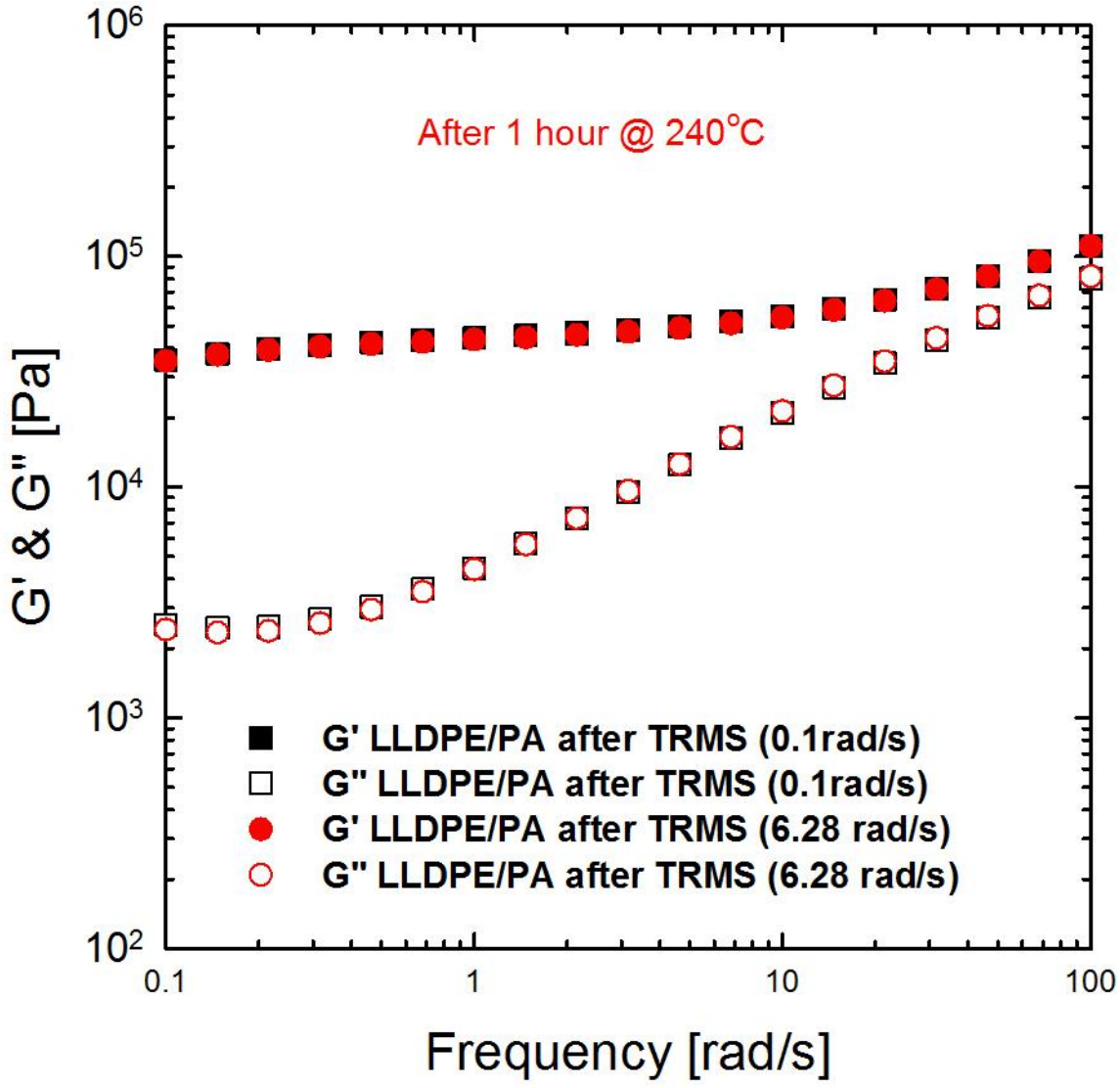


Fig. 4. Elastic, $G'(\omega)$ and loss, $G''(\omega)$ moduli of (80/20) LLDPE/PA blend after 1 h TRMS measurements at frequencies of 0.1 and 6.28 rad/s. A strain amplitude of 0.5% was maintained to ensure linear responses, and the frequencies were varied from 0.1 to 100 rad/s under 240 °C.

A more reliable way to monitor the degree of cross-linking due to the thermo-oxidative degradation was to record moduli at different times during the multiple-frequency TRMS tests at different frequencies (vertical lines in Fig. 5).

We will first discuss the frequency dependent behavior of the blend before any arguments on degradation are made.

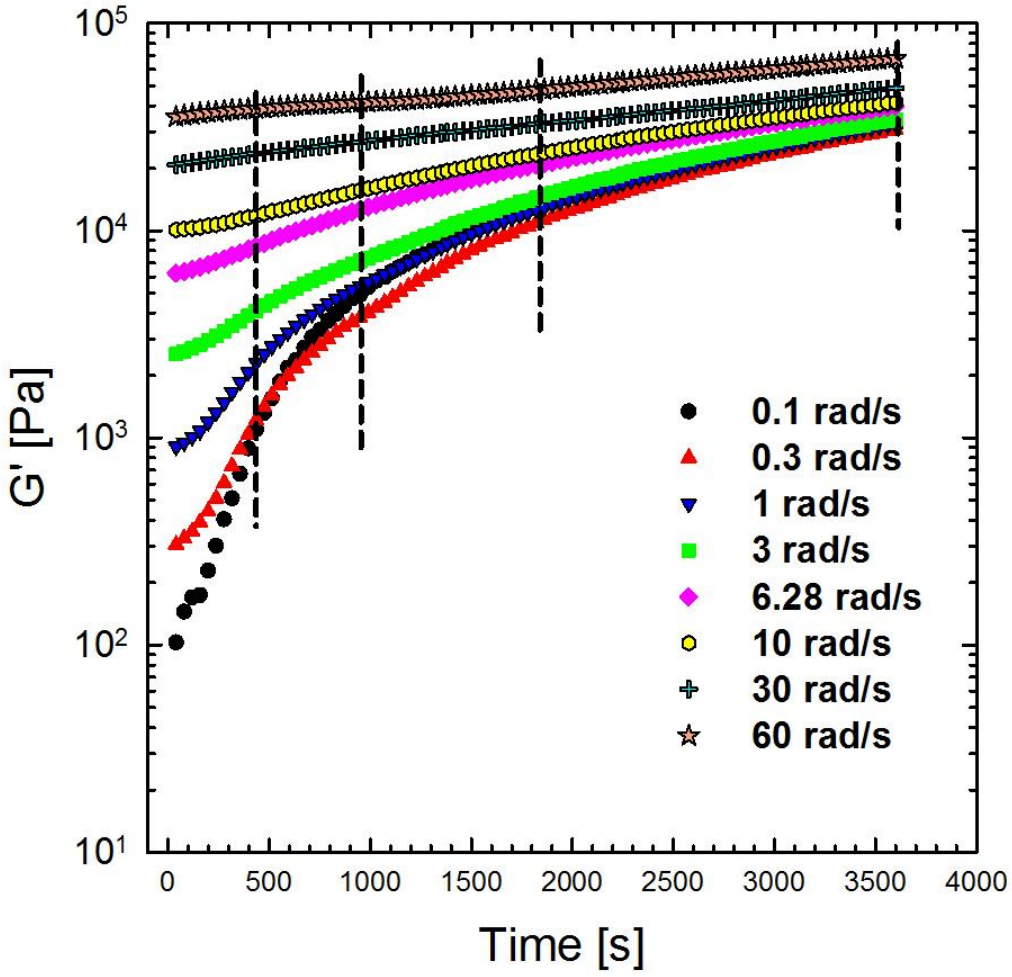


Fig. 5. TRMS results for elastic (storage) *G*'(t) of (80/20) LLDPE/PA blend at different frequencies, with fixed strain amplitude of 0.5% and temperature of 240 °C under air atmosphere. The dashed vertical lines indicate the times selected (7, 15, 30, and 60 min) to collect the moduli of the blend at different frequencies.

Fig. 5 reveals that the elastic modulus *G*'(t) of the blend increases when higher frequencies are used for the TRMS measurements. However, the lower frequency results are richer in information since a larger portion of the polymer is being probed for a longer time. Hence, elastic modulus *G*'(t) is growing more rapidly because it reflects changes in the molecular architectures more clearly, as previously discussed. On the other hand, smaller portions of the polymer are being stretched at high frequencies as a result of high-speed movements [9, 18]. Nonetheless, it could be useful for gathering data points at each frequency to plot the master curves at different times.

Because TRMS does not provide structural information at time zero, an extrapolation method was used to estimate the elastic moduli at time zero as follows [9, 18]:

$$\alpha_{1,2} = \frac{d \log G'}{dt} \cong \frac{\log G'(t_2) - \log G'(t_1)}{\Delta t_{1,2}} \qquad (1)$$

Therefore, the elastic moduli at time zero $G'(t_0)$ can be extrapolated using the following equation:

$$\log G'(t_0) = \log G'(t_1) - \alpha_{1,2} t_1 \qquad (2)$$

where, $\alpha_{1,2}$ is the interpolated slope between the elastic moduli at times $1\,G'(t_1)$ and $2\,G'(t_2)$ in a log-lin plot.

Fig. 6 shows the master curves of the isochronal elastic moduli $G'(\omega_t)$ of the blend recorded at different times during the TRMS course, as indicated by the dashed vertical lines in Fig. 5, along with the frequency sweep results for a fresh sample to monitor the extent of cross-linking from the thermo-oxidative degradation process.

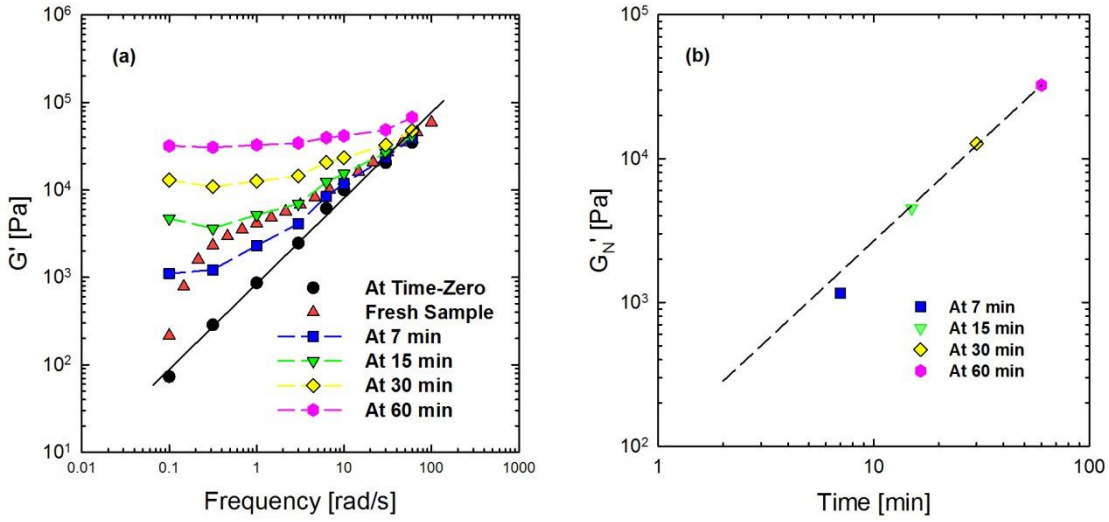


Fig. 6. (a) Isochronal elastic moduli $G'(\omega_t)$ of (80/20) LLDPE/PA blend collected at different times from multi-frequency TRMS tests under air atmosphere and temperature of 240 °C along with elastic modulus $G'(\omega)$ of fresh sample (as loaded) obtained from conventional frequency sweep test. (b) Plateau modulus of the cross-linked samples as a function of time obtained from Fig. 6(a).

Interesting results can be observed in Fig. 6. The modulus of the blend at time zero exhibits a power-law dependency at the different frequencies, indicating a terminal behavior. On the other hand, it shows that if a conventional frequency sweep test is performed, the results are completely different because the molecular structure is still changing during the frequency sweep test as a result of rapid degradation. It can be seen that at low frequencies, the modulus increases rapidly, and then the rate of change slows down, but with higher values than those obtained at time zero. A frequency sweep test (0.1~100 rad/s) takes about 12 min (720 s) and from Fig. 5 it is clear that the significant growth in moduli occurs at early times within 500 s.

This once again implies that a frequency sweep test may not be a suitable characterization method for such rapidly degrading materials. Further, a non-terminal behaviour (G'_N plateau modulus) at lower frequencies appeared after different periods of exposure to air under the TRMS test. This plateau modulus reached higher frequencies as the exposure time increased bcause the isochronal modulus of the blend at 60 min behaved almost like a plateau throughout the frequency range. The non-terminal behavior was indicative of a long relaxation mechanism for the blend associated with an increase in molar mass or cross-linking reactions during the exposure time to the air atmosphere under the TRMS test. The relationship between the plateau moduli at different times is plotted in Fig. 6(b). It can be seen that the plateau modulus, which is directly related to the degree of cross-linking, changes almost like a power-law manner with a slope of 1.4. This slope can be interpreted as the rate of cross-linking reactions. This cannot be mistaken for the stabilization effect of the droplets because the strain amplitudes are too small (0.5%) to cause any droplet breakup or even coalescence. Therefore, the only reason for the progressive increase in the moduli and extension of the plateau modulus is the increase in the molecular weights as a consequence of cross-linking reactions. Moreover, the convergence of the moduli at high frequencies is only a reflection of the chemical structures of a small portion of the polymers. Hence, it is not associated with long length scale changes in the polymers [18].

Thus, it can be reiterated that obtaining isochronal moduli at different frequencies from TRMS tests is a more accurate method for determining the degree of cross-linking due to thermo-oxidative degradation of the polymers. Now that it is believed that cross-linking reactions occur during the degradation, it would be also helpful to obtain a geometrical idea of this cross-linking in a parallel-plate fixture and how it can affect the rheological properties. Fig. 7(a−c) shows the side view and top view of the blend before and after the degradation.

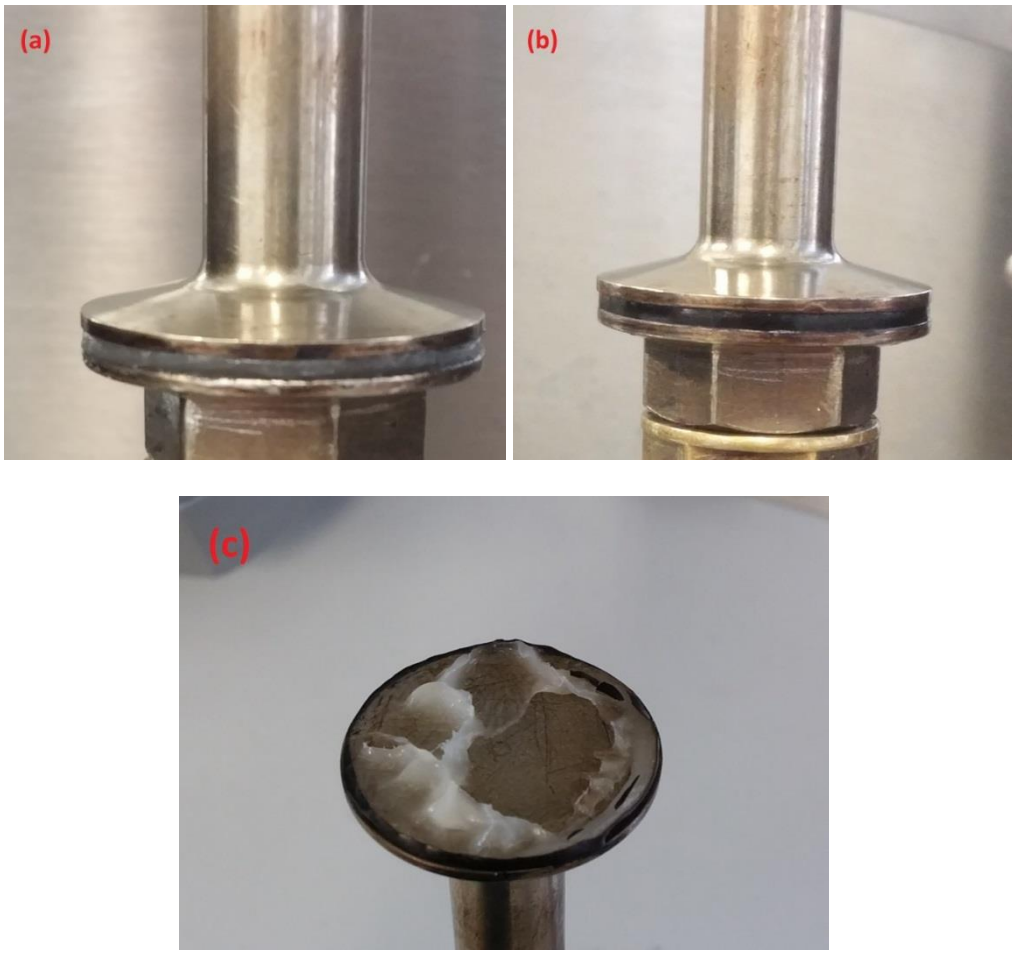


Fig. 7. Side views of (80/20) LLDPE/PA blend between parallel-plates (a) before starting test and (b) after 1h of TRMS testing, along with (c) top view of same sample after 1h of TRMS testing at 240 °C.

Fig. 7(a−c) shows that the oxidative degradation occurs at the edges where the material is in direct contact with air. This is shown by the color change from whitish to dark-brownish around the perimeter of the plates (a black strip is created around the sample at the edge part). It is possible to

determine how changes at the edges could have such a large influence on the rheological properties knowing that degradation has mainly occurred at the edges. It must be noted that shear rate distribution in the parallel-plate geometry is uneven, with the maximum at the edges according to the following equation [20]:

$$\dot{\gamma}_R = \frac{R\Omega}{H} \qquad (3)$$

where, R is the radial position, Ω is the angular velocity, and H is the gap height. Therefore, it can be inferred that any changes at the edge sections can have a significant effect on the rheological responses.

4. Conclusion

Thermo-oxidative degradation of LLDPE samples with different thermal histories and their corresponding blends was investigated using a time-resolved rheometry technique, where the time evolution rheological properties of the blends were probed using scans at different frequencies. It was found that the processing temperature had significant effects on the viscoelastic behavior and degradation of the LLDPE samples. However, it did not have any influence on the viscoelastic and morphological properties of the LLDPE/PA blends. The thermo-oxidative degradation led to discoloration at the edges of the samples where they were in direct contact with air. This in turn caused a significant upturn shift in the elastic modulus, especially at shorter times. It was concluded that dominant cross-linking reactions were the reason for the increase in the modulus and discoloration of the blends upon the thermo-oxidative degradation.

It was shown that the extrapolation of data points for such transient materials from TRMS tests at different frequencies was a more accurate method for acquiring the rheological properties as a function of the frequency compared to conducting conventional frequency sweep tests, which suffer from molecular architectural alterations due to rapid degradation mechanisms. Finally, it was suggested that the isochronal collection of data at different frequencies was a more convenient way to observe the degree of network formation as a result of degradation at different exposure times.

Although different mechanism routes were previously proposed for the degradation reactions (chain scission and cross-linking) of individual polymers (PEs and PA), the reactions at the interphase between LLDPE and PA are unknown and could be investigated in further studies.

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