



# Rheological investigation of the influence of molecular structure on natural and accelerated UV degradation of linear low density polyethylene

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## Abstract

Metallocene and Ziegler–Natta (ZN) linear low density polyethylenes (LLDPEs) of different branch types and contents as well as linear high density polyethylene (HDPE) were exposed to natural and accelerated weather conditions. The degree of UV degradation of exposed samples was measured by rheological techniques and results were compared with unexposed polymers. Dynamic shear measurements were performed in an ARES rheometer in the linear viscoelastic range. The degree of enhancement or reduction in viscosity and elasticity was used as a measure of the degree of cross-linking or chain scission, respectively. The degradation results of LLDPE suggest that both cross-linking and chain scission are taking place. Chain scission dominated the degradation at high levels of short chain branching (SCB) and long exposure times. The degradation mechanism of m-LLDPE and ZN-LLDPE is similar; however, m-LLDPE showed a higher degradation rate than ZN-LLDPE of similar  $M_w$  and average SCB. ZN-LLDPE was found to be more stable than a similar m-LLDPE. Comonomer type had little influence on degradation. Dynamic shear rheology was very useful in revealing the influence of different molecular parameters and it exposed the degradation mechanism. © 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Degradation; Weathering; Molecular structure; Linear low density polyethylene; High density polyethylene; Cross-linking

## 1. Introduction

Polyethylene (PE) has been used for outdoor applications for many years. It has become a major concern for solid waste disposal as well as other environmental pollution due to its high degree of non-degradability [1]. In outdoor applications many simultaneous factors determine the degradation such as ultra-violet (UV) radiation, other solar radiation, temperature and thermal cycling, humidity, environmental pollutants, abrasion, rain, wind, etc. [2]. Of these factors UV is the most important cause of degradation of PEs [3]. Many studies [2,4–10] shown that degradation initiated by UV radiation follows different complex routes starting with free radical chain initiation, propagation, chain branching and termination.

As a matter of fact the deterioration of mechanical properties is the most evident consequence of the series of processes involved in photochemical degradation.

Linear low density polyethylenes (LLDPEs) prepared by metallocene catalysts possess narrow molecular weight distribution (MWD) in comparison with conventional Ziegler–Natta type (ZN-LLDPE). The rheological properties of these metallocene LLDPEs (m-LLDPEs) are directly influenced by their molecular structure such as branch type, short chain branching (SCB) and distribution; average molecular weight ( $M_w$ ) and MWD [11]. The author and co-workers have shown that most of these molecular parameters have a direct influence on mechanical properties; crystallization kinetics and melt rheological properties [11–13]. In addition, the rheological and mechanical properties of PEs may change due to thermo-mechanical or UV degradation [14,15]. The degradation and stabilization of polyethylene have attracted many

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researchers [5–8,15–26], very few of them on m-LLDPEs [15,17,24,26].

In a previous publication, we investigated the thermo-mechanical degradation of polyethylenes and its mechanisms by different techniques. These included NMR, GPC, differential scanning calorimetry, high performance liquid chromatography, temperature rising elution fractionation and rheology. Dynamic shear rheology, especially the low  $\omega$  data, was found to be the most sensitive technique. In that paper, we showed the link between cross-linking and formation of long chain branches in polyethylenes as confirmed by NMR. Hence, in this research we limit our testing tools to rheology only. The above fact about the sensitivity of rheology to structural modifications was reported by many other researchers [27–29]. The author and other researchers have reported cross-linking of HDPE caused by free radicals [14,28,30–32]. The mechanisms of polyethylene degradation were discussed in detail in an earlier publication [14] and references therein. It was reported that HDPE can undergo a chain scission or cross-linking depending on the type of residual catalyst [14,30]. For example, the HDPE produced by Phillips process, which uses a Cr-based catalyst, undergoes chain scission while that made by Ziegler–Natta catalyst goes through cross-linking [14].

However, all of the above research on the degradation of metallocene polyethylenes did not investigate the influence of molecular structure on the degradation of m-LLDPEs in natural and accelerated weather conditions. This finding motivated this research work. In the present work, metallocene copolymers of ethylene and 1-butene (m-EB), ethylene and 1-hexene (m-EH), and ethylene and 1-octene (m-EO) were used. The selected m-LLDPEs had similar  $M_w$  and MWD values. The objective was to investigate the influence of short chain branching (SCB); comonomer type and composition distribution on the degradability of LLDPEs. We understand that the multidimensional space of  $M_w$ , MWD, and SCB was explored via single lines. The main reason for this is the difficulty of finding commercial samples that fit the requirement of experimental design. One ZN-HDPE and conventional LLDPEs (ZN-LLDPEs) were also examined. The influence of SCB was studied by using m-LLDPE with SCB in the range 15–42 branches/1000 C. To explore the consequences of varying the comonomer type, butene and octene ethylene copolymers of selected SCB were used.

## 2. Experimental

### 2.1. Materials

Seven LLDPE samples of different short chain branching (SCB) and comonomer type as well as one HDPE (control) were used in this study. All samples were commercial resins in pellet form. Three commercial metallocene ethylene–butene (EB) LLDPEs of different BC (15–42) were used to study the influence of BC. Another two commercial ethylene–octene (EO) resins were tested to examine the influence of comonomer type at low and high SCB levels. The EO

LLDPE samples were selected such that  $M_w$ , MWD and SCB were similar to those of EB resins. On the other hand, two ZN-LLDPEs were selected for a comparison with m-LLDPE. Here, the objective is to investigate the influence of composition distribution while other molecular parameters were kept very similar. All samples are commercial resins produced by Exxon-Mobil except ZN-EB25 which is produced by Nova Chemicals of Canada.

Commercial resins were melted in a Carver press at 190 °C. Sheets were formed under a controlled thermo-mechanical history. In all cases, PE samples obtained from the melt blender were given a controlled thermo-mechanical history (moulding) before introduction into the rheometer for shear testing. The moulding operation, in a Carver press, produced flat discs (25 mm diameter, 2 mm thick) for insertion between the rheometer platens. Moulding was conducted at 170 °C after pre-heating for 4 min. The loaded sample was then placed under 3 tons pressure for 5 min, followed by an increase to 7 tons for 4 min. After the mould was water-cooled for 10 min, the PE disk was removed at room temperature and inserted between the rheometer platens. Table 1 provides characterization data for all of the eight samples such as  $M_w$ , MWD as determined by GPC and SCB as determined by  $^{13}\text{C}$  NMR. Density and melt index (MI) data were provided by the manufacturer. The sample name reflects its catalyst type (metallocene or Ziegler–Natta), comonomer type (EB or EO) and contains a number that indicates its SCB as branches/1000 C. Details of GPC and NMR characterization are given elsewhere [33].

### 2.2. Exposure

The moulded sheets were exposed to natural weathering for a period of 4 months at Dhahran, Saudi Arabia during the period mid-February to mid-June 2006. Dhahran has extreme weather conditions with high UV radiation. Details about this site were described by Hamid and co-workers [6,34,35]. Samples were withdrawn every 2 months for testing. In addition, exposure trials were conducted under accelerated conditions in a weatherometer for 250 and 500 h.

### 2.3. Rheological testing

Specimens for shear rheological testing were prepared from as-received resins and exposed samples by moulding discs,

Table 1  
Polymer characterization

Resin	Density (g/cm <sup>3</sup> )	MI (g/10 min)	$M_w$ (kg/mol)	$M_w/M_n$	SCB <sup>a</sup>
ZN-HDPE	0.9600	4.00	827	3.42	00.00
ZN-EB13	0.9180	1.00	113	2.55	13.00
ZN-EB25	N/A	N/A	137	13.26	25
m-EB15	0.9100	1.20	108	1.95	14.50
m-EB37	0.8880	2.20	87	2.10	36.62
m-EB42	0.8800	0.80	126	1.81	42.00
m-EO16	0.9020	1.10	93	2.13	16.32
m-EO33	0.8820	1.10	112	2.82	32.67

<sup>a</sup> CH<sub>3</sub>/1000 C.

about 2 mm thick, designed to match the platen diameter employed in the rheometer; this process is operated in a Carver hydraulic press. The ARES rheometer was used in the dynamic mode to study linear rheological properties for each sample as a function frequency,  $\omega$ . A strain sweep of 10% was used following a strain sweep test. Linear dynamic properties were measured in order to preserve the microstructures of the samples. A 25 mm cone-and-plate was used. All tests were conducted at 190 °C with nitrogen as the heating medium to avoid degradation during testing.

### 3. Results and discussion

The influence of SCB, comonomer type and composition distribution (catalyst type) on the degradation of LLDPEs was studied by rheological tools. A comparison of m-EB15, m-EB37 and m-EB42 will reveal the effect of SCB. On the other hand, a comparison of m-EB15 and m-EO16 and m-EO33 will indicate the influence of comonomer type at low and high SCB levels. Finally, the impact of catalyst type (Ziegler–Natta vs. metallocene) or composition distribution will be assessed by comparing m-EB15 vs. ZN-EB13 and ZN-EB25. The results for each molecular parameter are discussed below.

#### 3.1. Influence of short chain branching

The first sample to be considered in studying the influence of SCB is ZN-HDPE which was tested in a similar fashion as LLDPEs and used as a control sample since it has no branches. Results of natural weathering (NW) along with the data for artificial weathering (AW) for the ZN-HDPE sample are shown in Fig. 1. The dynamic shear viscosity,  $\eta'$ , and elastic modulus,  $G'$ , are given in Fig. 1a and b, respectively. The rheological data suggest that the natural exposure of the linear HDPE showed low levels of cross-linking as indicated by the increase in viscosity at low  $\omega$ . However, the AW experiments at 250 and 500 h resulted in similar or higher degrees of cross-linking of HDPE.

In AW, the enhancement in viscosity [14] increased with the increase of exposure time by  $\sim 30\%$  indicating increased intensity of cross-linking. Also,  $\eta'$  for samples exposed to 250 h of accelerated weathering and 4 months of natural exposure showed similar rheology. The results of  $\eta'$  are supported by  $G'$  data. It should be noted that 4 months of NW are equivalent to 1440 h of AW based on 12 h of sunshine per day in Dhahran. However, the current results suggest that the overall degradation of HDPE is very slow with 250 h of AW resulting in the same effect on the polymer as 4 months of NW. It is known that  $G'$  is more sensitive than  $\eta'$  and this is evident in  $G'$  data at low  $\omega$  which showed an increase of more than 50% when exposure time to AW was doubled. Hence, for the HDPE sample with zero branches the degradation is very slow and dominated by cross-linking. The impact of SCB on degradation of m-LLDPEs is discussed below.

For the low SCB m-EB15, results of  $\eta'$  and  $G'$  are given in Fig. 2a and b, respectively. The unexposed (control) sample showed a Newtonian plateau that extended over three decades of frequency. Results are typical for m-LLDPEs with narrow MWD [11]. The 2 months of NW resulted in a sharp increase of more than one order of magnitude in  $\eta'$  at low  $\omega$ . This is a clear indication of cross-linking which leads to the broadening of MWD as suggested by the sharp decrease in  $\eta'$  at high  $\omega$ . However, m-EB15 showed a similar shear thinning behavior after 4 months of NW. But at longer times of exposure (4 months)  $\eta'$  at low  $\omega$  was reduced by more than an order of magnitude (see Fig. 2a) suggesting chain scission. This suggests that chain scission is dominant in the relatively long NW experiment while cross-linking is dominant over the short exposure period of AW tests. The same conclusion can be drawn from  $G'$  data (see Fig. 2b) where the elastic modulus went through a marked increase of  $\sim$ three orders of magnitude followed by a decrease by more than one order of magnitude in the AW experiment. Similarly, data of both  $\eta'$  and  $G'$  at low  $\omega$  suggest that exposure to 250 h of AW leads to cross-linking. In addition, cross-linking continues at 500 h where  $\eta'$  at low  $\omega$  was observed to be above the Newtonian plateau. The conclusions from AW experiments are in agreement with results

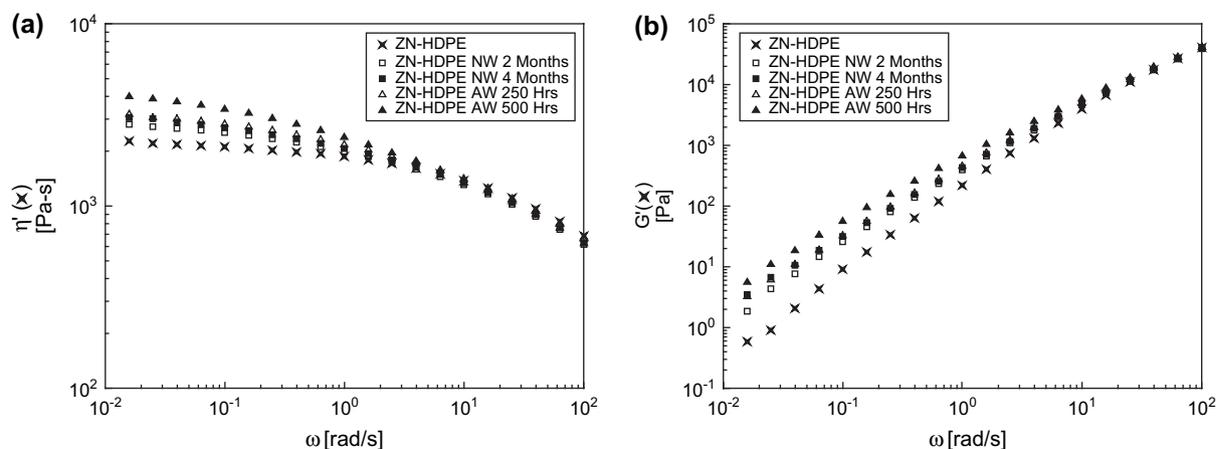


Fig. 1. (a)  $\eta'(\omega)$  for ZN-HDPE exposed to natural and accelerated weather conditions, and (b)  $G'(\omega)$  for ZN-HDPE exposed to natural and accelerated weather conditions.

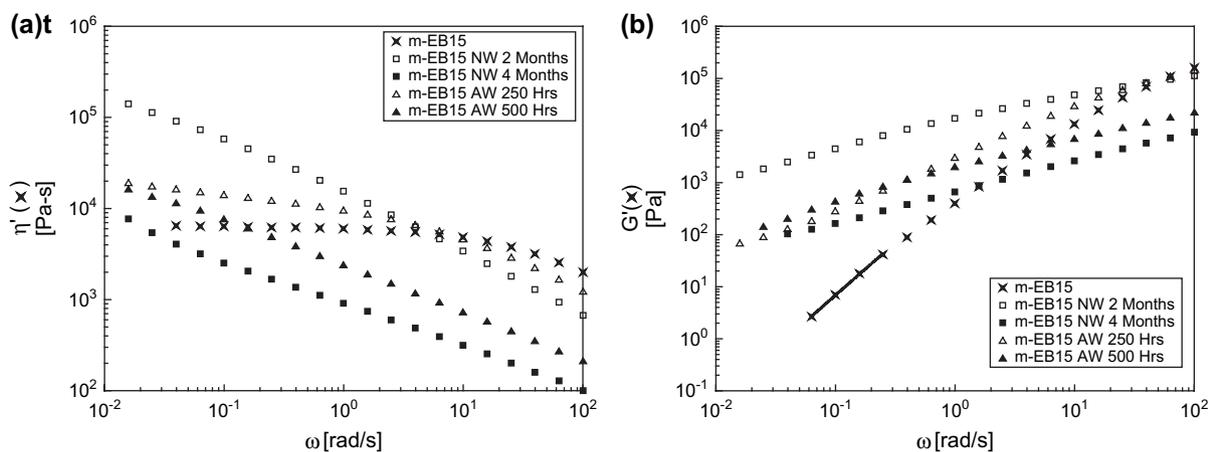


Fig. 2. (a)  $\eta'(\omega)$  for m-EB15 exposed to natural and accelerated weather conditions, and (b)  $G'(\omega)$  for m-EB15 exposed to natural and accelerated weather conditions.

obtained for samples exposed to 2 months of NW. The fact that the 500 h of AW are equivalent to less than 2 months of NW supports the agreement of the findings from both NW and AW tests.

In further analysis of the rheology data the slopes of  $\log G'$  vs.  $\log \omega$  were calculated using ARES software and the results for m-EB15 are shown in Table 2. The slope for the unexposed sample was found to be 2 which is a typical value for amorphous melts. A slope of 2 at low  $\omega$  is predicted by a simple Maxwell model. This slope showed a continuous decrease from 2 to 0.5 for NW and AW samples. If we examine the set of data collected for NW and AW vs. exposure time, it is clear that there is a general trend of a decrease in the slope of  $\log G'$  vs.  $\log \omega$  suggesting a broader MWD and cross-linking even when chain scission dominates at longer exposure times. However, the slope of  $\log G'$  vs.  $\log \omega$  is in the range of 0.5–0.8 and is insensitive to exposure time. These values of  $\log G'$  suggest that even after 4 months of natural exposure the chain scission is not complete and degraded samples contain cross-links.

In general, the degradation in the branched m-LLDPE is more severe than that of the linear HDPE as suggested by the magnitude of increase or decrease in  $\eta'$  and  $G'$ . In addition, during the specified exposure period, the degradation mechanism of m-EB15 is a combination of cross-linking and chain scission while that of HDPE is dominated by cross-linking. Results of both  $\eta'$  and  $G'$  for m-EB15 exposed to AW and NW support the dominance of cross-linking for short exposure times and chain scission over long exposure times (4 months). It should be noted that the degradation of branched

metallocene LLDPE (m-EB15) is faster than linear HDPE and chain scission dominated in a 4 months period.

For highly branched m-LLDPE, two samples were tested m-EB37 and m-EB42. The results for the two samples are similar; hence  $\eta'$  and  $G'$  for m-EB42 only are shown in Fig. 3a and b. The data of  $\eta'$  and  $G'$  at very low  $\omega$  was omitted for samples exposed at 4 months of NW since the torque signal is lower than the sensitivity range of the rheometer. At low  $\omega$ , the degree of increase in viscosity due to NW is much less than that of m-EB15. After 4 months of exposure to NW, the decrease in  $\eta'$  is more than one order of magnitude and indicates a strong chain scission. These results manifest that highly branched m-LLDPEs are more susceptible to UV degradation. In addition, the results for m-EB42 suggest domination of chain scission unlike low SCB m-LLDPE of similar  $M_w$  and MWD. For AW tests, short exposure times proposed a cross-linking mechanism that is reduced at prolonged exposure times. For the AW tests, m-EB42 is more sensitive to degradation than m-EB15 as displayed by the magnitude of the decrease in  $\eta'$  at low  $\omega$ . The same conclusion can be drawn from  $G'$  data. A simple example is the data for samples exposed to 4 months of NW.  $G'$  at 100 rad/s has dropped by about two orders of magnitudes for m-EB42 where that of m-EB15 dropped by about one order of magnitude at the same frequency. Therefore, both NW and AW tests of m-LLDPE lead to degradation of m-LLDPEs with chain scission dominating at high SCB or long exposure times.

A comparison of the results of  $\eta'$  and  $G'$  for ZN-HDPE, m-EB15 and m-EB42 suggests that the tendency of branched m-LLDPEs to degradation increases with increased short chain branching (SCB) in m-LLDPEs. Further, the degradation shifts from cross-linking to chain scission dominated with increased SCB. The results for m-EB37 are not shown here since they deliver the same message as that of m-EB42.

The tentative explanation for the above observations is that the susceptibility to oxidation increases with the increase in the number of branch points. At those points where branching occurs in the backbone chain, hydrogen is attached to a tertiary carbon atom. The bond between the carbon and the hydrogen

Table 2  
Slopes of  $\log G'$  vs.  $\log \omega$  for m-EB15

Sample	Slope of $\log G'$ vs. $\log \omega$
m-EB15	2.01
m-EB15 AW 250 h	0.73
m-EB15 AW 500 h	0.83
m-EB15 NW 2 Months (~720 h)	0.62
m-EB15 NW 4 Months (~1440 h)	0.52

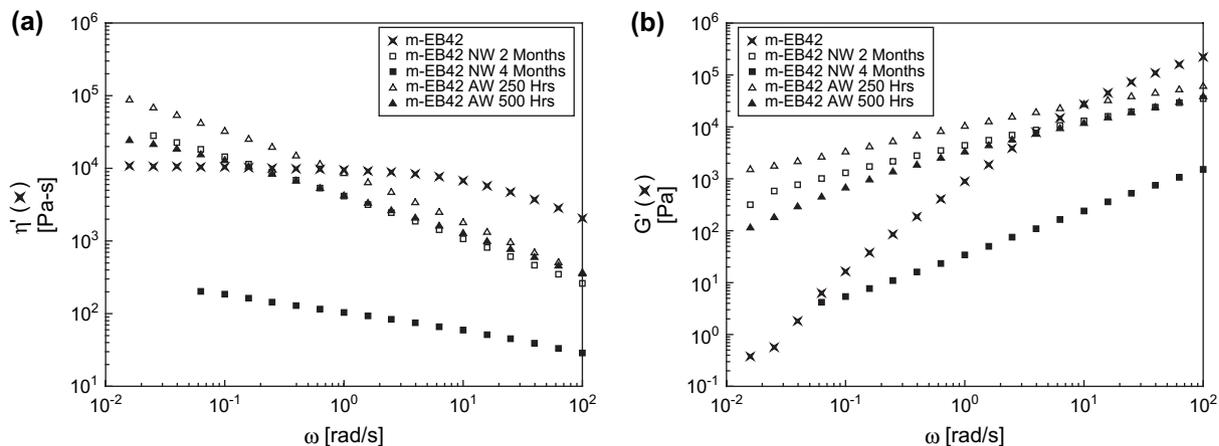


Fig. 3. (a)  $\eta'(\omega)$  for m-EB42 exposed to natural and accelerated weather conditions, and (b)  $G'(\omega)$  for m-EB42 exposed to natural and accelerated weather conditions.

at these branch points has lower dissociation energy than that between hydrogen and carbons in the methylene groups along the unbranched sections of the chain. These weak hydrogens are likely points for initiation of autoxidation and consequently LLDPE is more susceptible to oxidation than linear PE (see figure 108 of [36]). This tentative explanation and degradation mechanism are discussed elsewhere [30,14 and references therein]. This explanation suits our observations at long exposure times or results obtained for samples with high SCB. However, it does not provide explanations for the initial cross-linking shown by three different commercial PE samples. This observation needs further investigations.

### 3.2. Influence of comonomer type

Fig. 4a and b show  $\eta'(\omega)$  and  $G'(\omega)$  for m-EO16 which has similar  $M_w$ , MWD and SCB as m-EB15 but a different comonomer (octene in m-EO16 vs. butene in m-EB15). Results of  $\eta'$  and  $G'$  at low  $\omega$  were omitted since the torque reading is lower (0.34 g cm) than the sensitivity range of ARES rheometer. Results of  $\eta'(\omega)$  and  $G'(\omega)$  for AW tests are qualitatively and quantitatively very similar. Also, the general trends of  $G'(\omega)$  for both resins are similar. At low  $\omega$ ,  $\eta'(\omega)$  for both

resins show a shear thinning behavior with  $\eta'$  of naturally exposed samples approaching the zero shear viscosity of the control sample. However, m-EO16 has shown somewhat a higher degree of degradation as manifested in the higher drop in both  $\eta'(\omega)$  and  $G'(\omega)$  over a wide range of  $\omega$  in comparison with control sample. It is likely that chain scission at long exposure times is more pronounced in octene rather than butene m-LLDPE. The observed difference in degradation could be a result of chain scission in the side branch; however, this assumption needs further verification. Yet, the influence of comonomer type is generally weak. These observations are in agreement with our previous reports that comonomer type has little or no influence on the miscibility, mechanical and thermal properties of m-LLDPEs and their blends [11,33,37].

### 3.3. Influence of composition distribution

Here, a comparison between m-EB15 and ZN-EB13 is expected to reveal the influence of composition distribution or catalyst type since other molecular parameters are very similar (see Table 1). Results for ZN-EB13 are given in Fig. 5. Only the viscosity data are shown. The NW experiments at 2 and 4

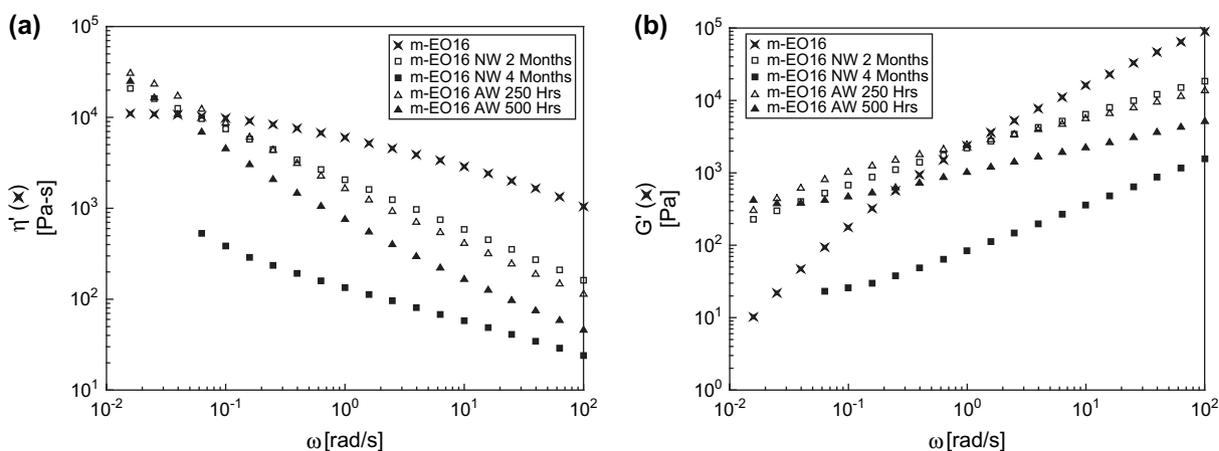


Fig. 4. (a)  $\eta'(\omega)$  for m-EO16 exposed to NW and AW conditions; and (b)  $G'(\omega)$  for m-EO16 exposed to NW and AW conditions.

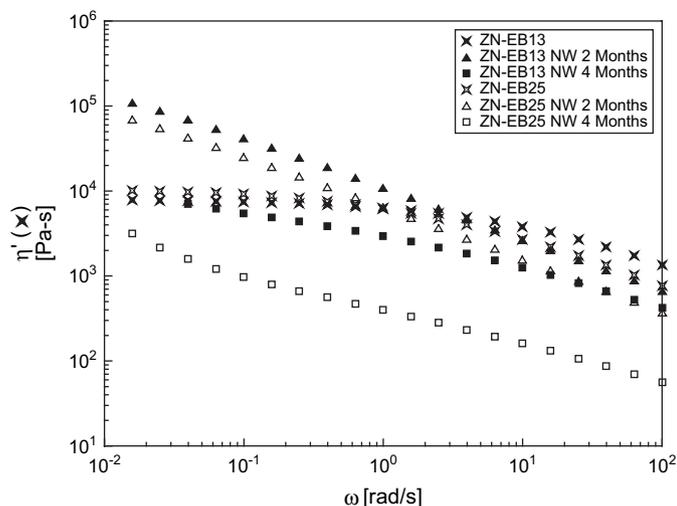


Fig. 5.  $\eta'(\omega)$  for ZN-EB13 and ZN-EB25 exposed to NW and AW conditions.

months showed the stability of ZN-EB13 in comparison with m-EB15. This is manifested in the following observations:

- After 2 months of natural exposure,  $\eta'$  at low  $\omega$  increased by  $\sim$ one order of magnitude while it has increased by more than that in the case of m-EB15.
- After 4 months of natural weathering,  $\eta'(\omega)$  for m-EB15 was much less than that of ZN-EB13 over a wide range of  $\omega$ .

The stability of ZN-LLDPE in comparison with m-LLDPE can be explained as follows: ZN-LLDPE is known to have heterogeneity in composition with long molecules being mainly linear and short molecules having high degree of branching [38]. The above results on ZN-HDPE suggested the stability of the linear molecule vs. branched m-LLDPEs. Therefore, it is likely that the linear molecules in ZN-LLDPE were generally stable and the consequences of chain scission in the small molecules had less impact on the rheology of ZN-LLDPE. Hence, UV has a stronger effect on the degradation of the uniformly distributed branches in m-LLDPE rather than ZN-LLDPE where the branches are concentrated in small molecules or at the end of a linear chain [38].

However, the results for both m-EB15 and ZN-EB13 suggest that the degradation goes through a combined cross-linking and chain scission processes with domination of chain scission at long exposure times. In addition, ZN-EB25 of a higher SCB was also tested and results shown in Fig. 5 displayed similar trends as ZN-EB13; however, the increased SCB has resulted in a higher degree of degradation. This observation supports the previous findings on m-LLDPE with high SCB. Therefore, increasing the SCB of both ZN-LLDPE and m-LLDPE accelerates the degradation of LLDPE.

#### 4. Conclusions

In general, the degradation in the branched LLDPE is more severe than that of the linear HDPE as suggested by the

magnitude of increase or decrease in  $\eta'$  and  $G'$ . During the specified exposure period, the degradation mechanism of m-LLDPE is a combination of cross-linking and chain scission while that of HDPE is dominated by cross-linking. For m-LLDPE, the cross-linking dominates at short exposure times while chain scission controls over long exposure times. The susceptibility to degradation accelerates with increased short chain branching (SCB) of ZN-LLDPE or m-LLDPE. Degradation shifts from cross-linking to chain scission dominated process with increased SCB. Hence, increasing the SCB of both ZN-LLDPE and m-LLDPE accelerates the degradation of LLDPE. The branch length (or comonomer type) had little influence on the degradation process with the possibility of chain scission in the short branches. The ZN-LLDPE was found to be more stable than m-LLDPE of similar molecular parameters. The results were explained in view of the dominance of linear chains on the rheology of ZN-LLDPE. In general, the degradation results of LLDPE suggest that both cross-linking and chain scission are taking place with chain scission more dominant at high SCB and long times of exposure with ZN-LLDPE being more susceptible to degradation.

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