

Impact of Branching on the UV Degradation of metallocene LLDPE

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Abstract

The effect of UV degradation on metallocene linear low density polyethylenes (LLDPEs) of different branching characteristics was studied. The samples were exposed to natural weather condition. The extent of the degradation on these LLDPEs was measured by Mechanical, FTIR and GPC testings. This paper addresses the structural modifications due to UV degradation of metallocene LLDPE (m-LLDPE). The results suggested that Z-N HDPE is very stable. Carbonyl absorbance and degradation of mechanical properties of m-LLDPEs increased with increasing branch content of the polymers. For short exposure times, the results suggested increase in the degree of cross-linking of m-PEs with the increase in BC leading to brittle behavior. However, at high exposure times chain scission dominates and it is branch content dependent. Most of the mechanical properties show a sharp rate of drop at branch contents less than 20 branches/1000 C followed by a slow drop rate. The results of the mechanical properties correlate very well with the carbonyl absorbance. GPC results confirmed that chain scission leading to a broader MWD is dominant at high exposure times and for LLDPEs with high branch contents. Branch type did not show any influence on mechanical properties.

Keyword: Degradation; Linear low density polyethylene; High Density polyethylene; Weathering; Branching content; Cross-linking, mechanical properties

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1. Introduction:

Polyethylene (PE) has been used for outdoor applications for many years. In recent years it has become a major concern for solid waste disposal as well as other environmental pollutions due to its high degree of non-degradability [1]. In outdoor applications many simultaneous factors determine the degradation such as Ultra-violet (UV) rays, other solar radiations, temperature and thermal cycling, humidity, environmental pollutants, abrasion, rain, wind, etc. [2]. Out of these factors UV is the most important cause of degradation of Pes [3]. Many studies [2; 4-9] shown that degradation initiated by UV radiations 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.

PE produced by Metallocene catalysts believed to have homogeneous composition distribution and narrow molecular weight distribution (MWD). This is significant in producing linear low-density polyethylene (LLDPE), which has high tensile strength and high clarity, appropriate for agricultural and packing films application. Metallocene LLDPE (m-LLDPE) due to its controlled structure attracted many researchers to investigate the micro structural properties [10-17]. In our previous works [18-20] we have seen that branch content (BC) has significant influences on the structure and morphology of m-LLDPEs. Therefore, it is expected that branching will influence the degradation of m-LLDPE. Consequently, the degree of branching in m-LLDPEs might affect the degradation mechanism and the degradation in mechanical properties. A large amount of work can be found in the literature [4-7; 21-32; 42-43] regarding the degradation and stabilization of polyethylenes, very few of them on m-LLDPEs [20; 29; 30-32]. The recent work of Hoang et al. [32], studied thermo-oxidative degradation and concluded that the degree of branching (0-15 CH₃/1000 C) plays a major role in the initiation stage of

oxidation of m-LLDPEs in the solid state and linear polymers are more stable. Also, the recent work of Hussein [20] studied the influence of branching characteristics on the UV degradation of m-LLDPE using rheological techniques. The current study is a continuation to the previous investigation. Here, the impact of UV degradation on the mechanical properties is studied and the influence of branching is assessed. The authors are not aware of any previous study that addressed the influences of branch content and co-monomer on the UV degradation of m-LLDPEs and its impact on the mechanical properties.

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 BC and comonomer type on the degradability of m-LLDPEs. One HDPE (ZN-HDPE) and one ZN-LLDPE were examined for comparison purposes. The influence of BC was studied by using m-LLDPE with BC in the range 14-42 branches/1000 C. To explore the consequences of varying the comonomer type, butene; hexene; and octene ethylene copolymers of selected BCs were used.

2. Experimental

2.1 Materials and Characterization

Twelve commercial polyethylene samples from ExxonMobil were used in this study. Eleven LLDPEs and one HDPE (control sample) were selected. Out of the eleven LLDPE samples one ZN-LLDPE was used for comparison with m-LLDPE. The m-LLDPE samples were of different branch type and content. Four metallocene ethylene-butene (m-EB) LLDPEs were used (BC= 15-42) to study the influence of BC. Another four metallocene ethylene-hexene resins (m-EH) with branch content in the range 12-32 were tested. The other two m-LLDPEs were

ethylene-octene (m-EO) with low and high branch content. The m-EO and m-EH samples were examined to study the impact of comonomer type at low and high BC levels. The EO LLDPE samples were selected such that Mw, MWD and BC are similar. On the other hand, the ZN-LLDPE was used for comparison with m-LLDPE of similar Mw, MWD and BC. Table 1 provides characterization data such as density at room temperature, melt index (MI) at 190°C as provided by ExxonMobil for all of the twelve samples. The number (Mn) and weight average (Mw) molecular weights and molecular weight distribution (MWD) in table 1 were determined using Waters Alliance GPC 2000 system. Two mixed bed columns (Plgel 10 μ m, Polymer laboratories) were used at 150°C. The solvent used in the sample preparation was 1, 2, 4 trichlorobenzene. A sample solution of 0.075 to 0.100 % by weight was prepared. The resulting solution (200 μ L) was injected into the GPC system. The total run time was 30 minutes. The chromatogram data were acquired and analyzed using millennium 32 software. The instrument was calibrated using narrow molecular weight polystyrene standards. The polystyrene based calibration curve was converted to universal calibration curve using the Mark-Houwink constants (k and α values). The k and α values are 0.000121 and 0.707 respectively for polystyrene and 0.000406 and 0.725 respectively for polyethylene. Nuclear magnetic resonance spectroscopy (^{13}C NMR) was used to evaluate the amount of branches in all the polyethylene samples [44]. Polymer sample (0.255g) was taken in 10 mm NMR-tube, and 1mL of 1,2,4-trichlorobenzene was added. The NMR-tube was thereafter placed in an oil bath at 150°C for 2h, allowing the polymer to dissolve in the solvent. Then 0.005g of iron (III) acetylacetonate, $\text{Fe}(\text{acac})_3$ was added as nuclear spin relaxation agent. Then a few drops of deuterated benzene was added before being run at 130°C on ^{13}C NMR spectrometer operating at 500 MHz carbon resonance frequency. The summary of ^{13}C NMR results is given in Table 1.

The sample name reflects its catalyst type (metallocene or Ziegler-Natter), comonomer type (EB, EH or EO) and contains a number that indicates its BC. For example, m-EB15 indicates that the m-LLDPE has an average branch content of 15 branches/1000 C. These LLDPEs were selected from the commercially available resins in such a way that BC will be the main variable. We did our best to match the Mw and MWD since it correlates with most of the mechanical properties. The Mw was chosen to be in the range of 100 kg/mol.

2.2 Natural and Accelerated Weathering

As-received commercial resins were melted in a Carver press at 190°C. Sheets were formed under a controlled thermo-mechanical history. The molding operation, in a Carver press, produced flat discs (25 mm diameter, 2 mm thick) for insertion between the rheometer platens. Molding was conducted at 190°C after preheating for 4 min. The loaded sample was then placed under 3 ton of pressure for 5 min, followed by an increase to 7 ton for 4 min. After the mold was water-cooled for 10 min, the PE disk was removed at room temperature and inserted between the rheometer platens.

Sheets were then exposed to natural sunlight weathering at Dhahran, Saudi Arabia. The details about Dhahran exposure site are given elsewhere [5]. Samples were exposed for natural weathering for 4 months and withdrawn every two months for testing. In addition, exposure trials were conducted under accelerated weather conditions in a Xenotest Beta-LM equipped with Xeno Chrome 300 with Suprex outer cylinder. The standard followed was ISO-4892-2 method A (outdoor) with spray. The chamber temperature was 38°C with 50% humidity. A wavelength of 300-400 nm and a rate of 60 W/m² were used. The duration of exposure was 250 and 500 hours.

2.2 Mechanical and FTIR Testing

The mechanical testing was performed in an Instron Universal Testing machine, Model 4301. All tests were conducted at room temperature according to ASTM D-882. Exposed and control samples were tested. A cross-head speed of 100 mm/min was used. At least, three samples were tested for each mechanical testing. The Infrared spectra were recorded using a Perkin-Elmer FTIR Spectrometer Model 1700. Carbonyl absorbance was monitored in the region of 1700-1740 cm^{-1} .

2.3 Differential Scanning Calorimetry (DSC)

Samples of 6-10 mg were sliced from the as-received pellets, and then they were compressed into non-hermetic aluminum sample pans for testing in a TA Instruments DSC (Model # Q1000) with modulated option. The instrument was blanketed with nitrogen gas to protect the samples from oxidation. A modulation period of 40 seconds, a heating rate of 2°C/min and amplitude of $\pm 0.2^\circ\text{C}$ were used. Temperature scan rates were varied, in the range of 2° - 6°C/min to study the influence of cooling rate on crystallization. Each sample was heated to 160°C to remove the thermal history, and then was cooled at a fixed cooling rate to 5°C.

3. Result & Discussion

3.1 FTIR Analysis

FTIR is a very sensitive technique in detecting degradation products [34]. As a matter of fact, all degradation products containing the carbonyl group, i.e. carboxylic acids, ketones, and esters absorb in the range of 1650-1850 cm^{-1} , and therefore the intensity of the peak centered in this interval of wavelengths can be followed, giving a measure of degradability [35]. Ram et al. suggested that the mechanical parameters could be well correlated with the carbonyl index [36].

The polymer samples containing carbonyl index higher than 0.3 become completely useless [35]. The changes of carbonyl index with increasing BC of m-EB and m-EH at various exposure times are presented in Figure 1 and Figure 2, respectively. In both Figures, HDPE was used as a reference with zero branching. It was reported in the literature that the branched PE is more readily oxidized than the linear polymer [38] and the rate of oxidation increased as the BC increased [39]. In Figures 1 and 2 HDPE, even after 4 months of exposure, remains unchanged. m-EB & m-EH having BC less than 20 branches/1000 C degraded but did not lose their mechanical properties completely until after 2 months, and copolymers with BC more than 20 branches/1000 C immediately lost their mechanical properties. So, it is clearly evident in the present work that the rate of degradation increases as BC increases. This observation is in agreement with the conclusions of our previous rheological study [20]. It is believed that the degradation of mechanical properties of polymers is attributed to the chain scission and cross-linking reaction in the polymer matrix [40, 20]. This is likely due to the increase in the amount of tertiary hydrogen atoms that are suggested to initiate the degradation process [37]. Furthermore, the results shown in Figures 1 and 2 manifest that the rate of carbonyl absorbance increases with the increase in BC up to 20 branches/1000 C and then it slows down.

3.2 Mechanical Properties

Influence of BC

The ultimate performance of polymer is its mechanical strength, which is of significance for practical applications. The elastic modulus and yield strength of m-EBs as a function of BC and the exposure time to the natural weathering were presented in Figures 3a and 3b, respectively. The elastic modulus and yield strength are directly related to the initial crystallinity of the polymers [18]. At longer exposure time, the samples undergo a chemical degradation

process and become brittle. However, for the period of exposure of 4hrs, there is a very small increase in the modulus and very small decrease in the yield strength as observed in Figure 3, which may still be due to direct consequence of cross-linking. **A sharp drop in the modulus with increasing BC is observed. Both the modulus and the yield strength decrease exponentially with increasing BC.**

As mentioned in the experimental part the Mw of these resins was selected to be around 100 kg/mol. As shown in Table 1, m-EB42 has the highest Mw and still has the lowest modulus and yield strength. . The elastic modulus and yield strength are directly related to the initial crystallinity of the polymers as discussed in our previous work [18]. **The reason for the low modulus and yield strength behavior of m-EB42 is the polymer crystallinity which decreases with increasing BC as shown in Figure 4 despite different cooling rates.** Therefore, BC is the most dominant factor that affects the mechanical properties. For the exposed samples, the slight increase or decrease in the value of the modulus is the result of the crosslinking and chain scission in the polymer chain. The explanation of crosslinking and chain scission was supported by the increase and decrease in G' as reported in our previous publication [20]. For the yield strength, the long exposure times and the high BC lead to the small decrease in the yield strength.

In the study of degradation of polymers one of the most important mechanical properties is the elongation at break because it can provide an early indication of mechanical failure. Moreover, elongation at break is more sensitive to the degradation process than ultimate tensile strength [41]. Figures 5a and 5b show that the elongation at break and ultimate tensile strength decrease as the time of exposure increases for all m-EBs, which is a result of the brittle nature of the exposed samples. The ultimate strength of all m-EB unexposed samples was in the of 40-50

MPa independent of BC. However, the exposed samples showed a marked drop in ultimate strength that drops very fast for BC in the range of 20 branches/1000 C and then the drop slows down. Longer natural exposure times (4 months) resulted in major drops in ultimate strength especially at high BC. For the strain at break, the results are interesting. For short exposure times (2 months) the strain at break increased increasing BC. This suggests that network structure was formed by crosslinking and the increase in branching points (crosslinking sites) resulted in the formation of more network structures [37]. Eventually the strain at break undergoes a significant drop at longer exposure times (4 months). Therefore, ultimate strength drops with increasing BC and exposure time. However, strain at break can increase with increasing branch content for short exposures (2 months). Nevertheless, the strain at break eventually drops at longer exposure and the drop is correlated with BC.

Influence of comonomer and catalyst types

Influences of co-monomer types are summarized in Figures 6 and 7. Comparisons were made among co-monomer types and composition distribution. Mechanical properties of low BC (BC around 15 CH₃/1000C) LLDPEs are shown in Figure 6. If for example, the elongation at break (see Fig. 6b) is considered for different co-monomer types, it is observed that aside from m-EH12 which showed slight increase at 2 months; other samples did not show any effect for the branch type. Similarly, a comparison of m-EB15 and ZN-EB13 of similar branch content but of different composition distribution (catalyst type is different) did not results in any noticeable difference. So, it can be said that co-monomer type and catalyst type (ZN vs metallocene) did not show any significant influence on the degradability; rather observed variation was due to the slight difference in BC. Similar results were found in highly branched LLDPEs (Figure 7). These

observations are in agreement with our previous reports that co-monomer type has little or no effect on the mechanical properties of LLDPEs [19].

Moreover, our results are in agreement with the recent work of Hoang et al., [32] that studied thermo-oxidative degradation of m-LLDPEs and linear polymers in the solid state and concluded that the degree of branching plays a major role in the initiation stage of oxidation and HDPE is more stable than m-LLDPE. Also, Luzuriaga et al. [42] concluded that for photo-oxidation of LDPE and HDPE cross-linking prevails in the early stage of irradiation; however, with increasing time of exposure HDPE undergoes chain scission while LDPE shows signs of cross-linking. This explains the cross-linking behavior of LLDPEs in the early stages of exposure and then the chain scission of the molecules which explains all of the above reported results.

4. Conclusion

Commercial m-PEs of different branch contents were exposed to sunlight under natural weather conditions for a period of four months. Also, linear HDPE was used as a reference. The results suggest the stability of the linear polymer without any change in mechanical properties. However, branched m-LLDPEs showed increase in carbonyl absorbance with increasing BC as indicated by FTIR. Also, the degradation of mechanical properties increased at higher BC. For short exposure times, the results suggested increase in the degree of cross-linking of m-PEs with the increase in BC leading to brittle behavior. However, at high exposure times chain scission dominates and it is branch content dependent. Most of the mechanical properties show a sharp drop at branch contents less than 20 branches/1000 C followed by a slow drop rate. The results of the mechanical properties correlate very well with the carbonyl absorbance.

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Table 1: Polymer Characterization

Resin	Density (g/cm ³)	MI (g/10min)	M _w (kg/mol)	M _w /M _n	BC *
ZN-HDPE	0.961	0.70	122	2.34	00.00
m-EB15	0.910	1.20	108	1.95	14.50
m-EB19	0.900	1.20	110	1.78	18.50
m-EB37	0.888	2.20	87	2.10	36.62
m-EB42	0.880	0.80	126	1.81	42.00
ZN-EB13	0.918	1.00	118	3.07	13.20
m-EH12	0.918	2.50	94	1.40	12.02
m-EH20	0.902	2.00	95	2.06	19.74
m-EH24	0.895	2.20	92	1.85	23.60
m-EH32	0.883	2.20	97	2.02	32.17
m-EO16	0.902	1.10	90	2.04	16.32
m-EO33	0.882	1.10	95	1.99	32.67

* (CH₃/1000C)

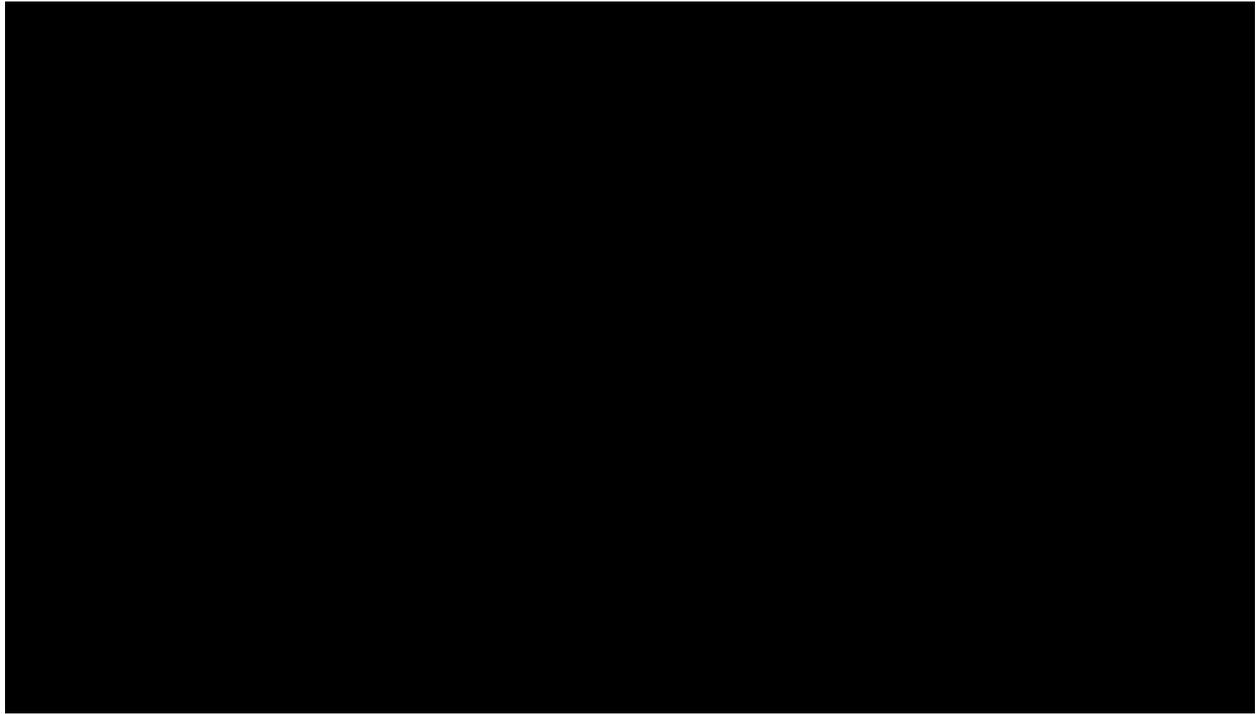


Figure 1: Carbonyl Index of m-EBs as a function of BC for different exposure times.

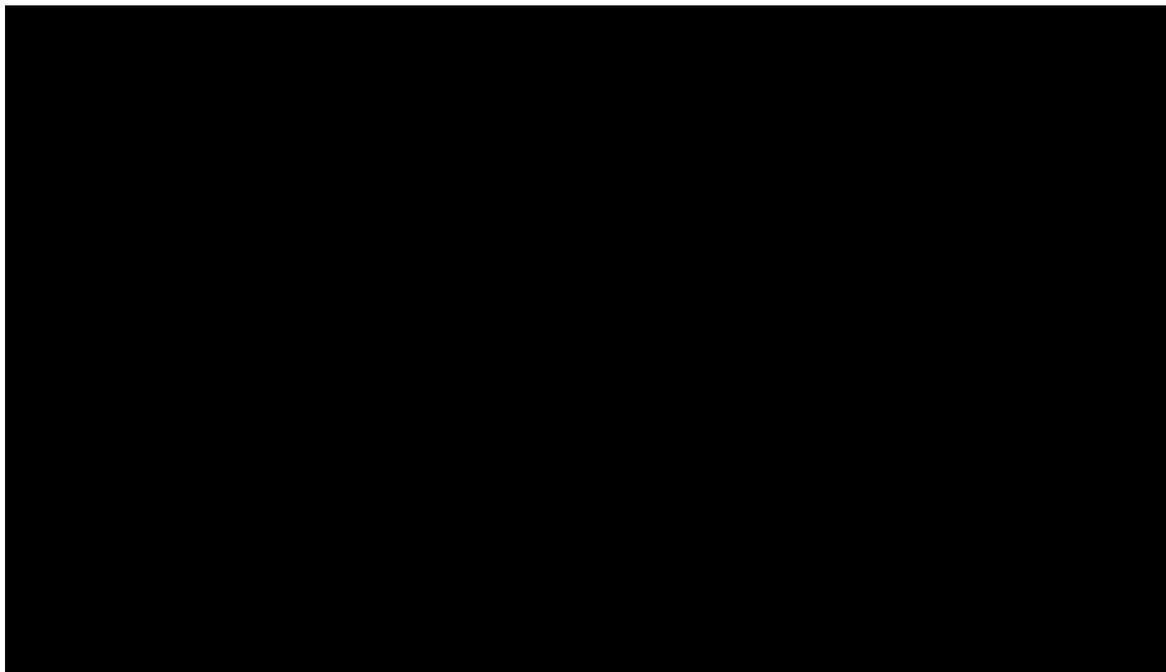


Figure 2: Carbonyl Index of m-EHs as a function of BC for different exposure times.

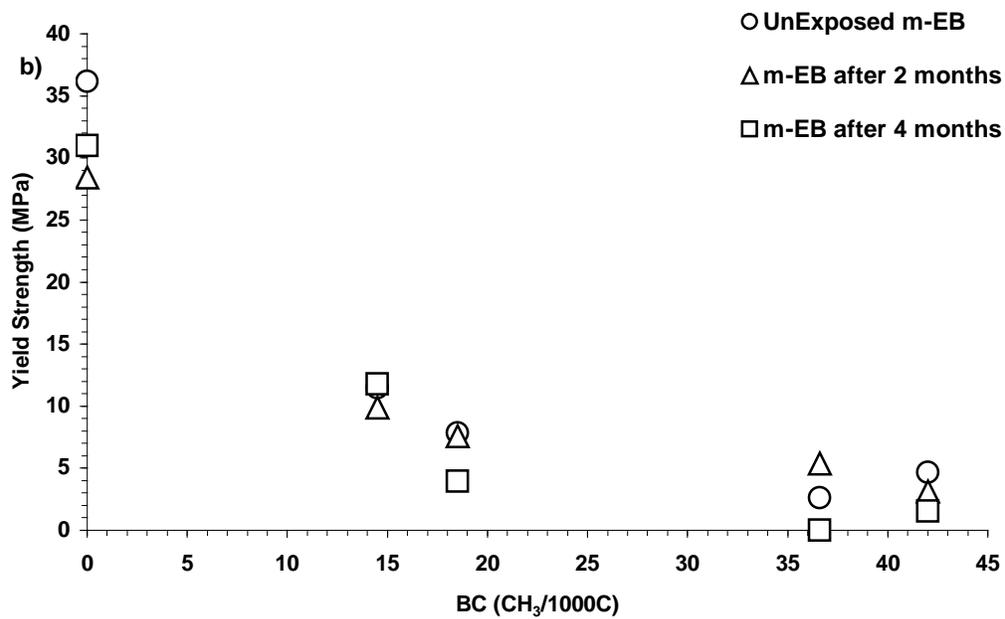
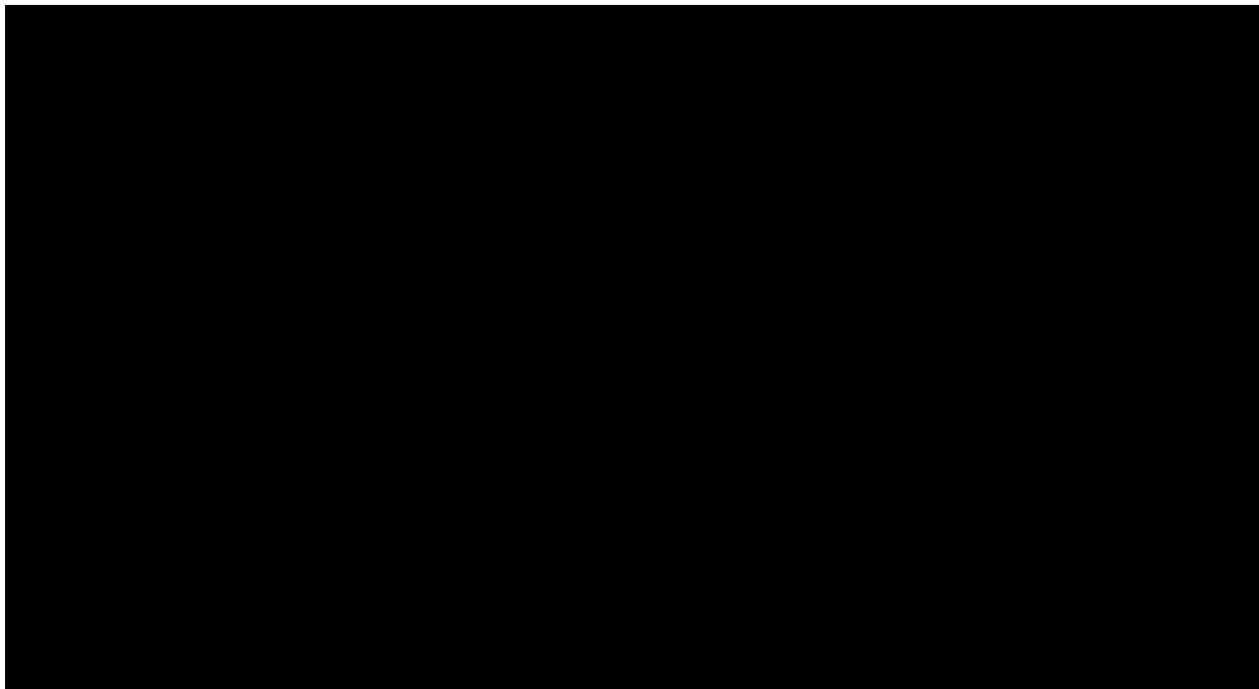


Figure 3: Low strain properties of m-EBs as a function of BC (a) Modulus (b) Yield Strength

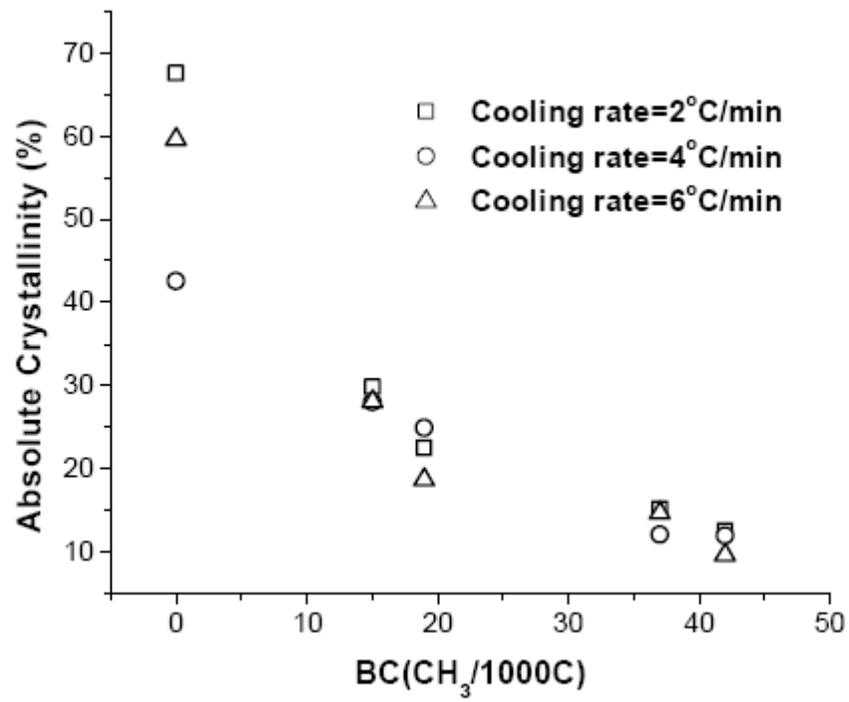


Figure 4: Absolute Crystallinity as a function of BC

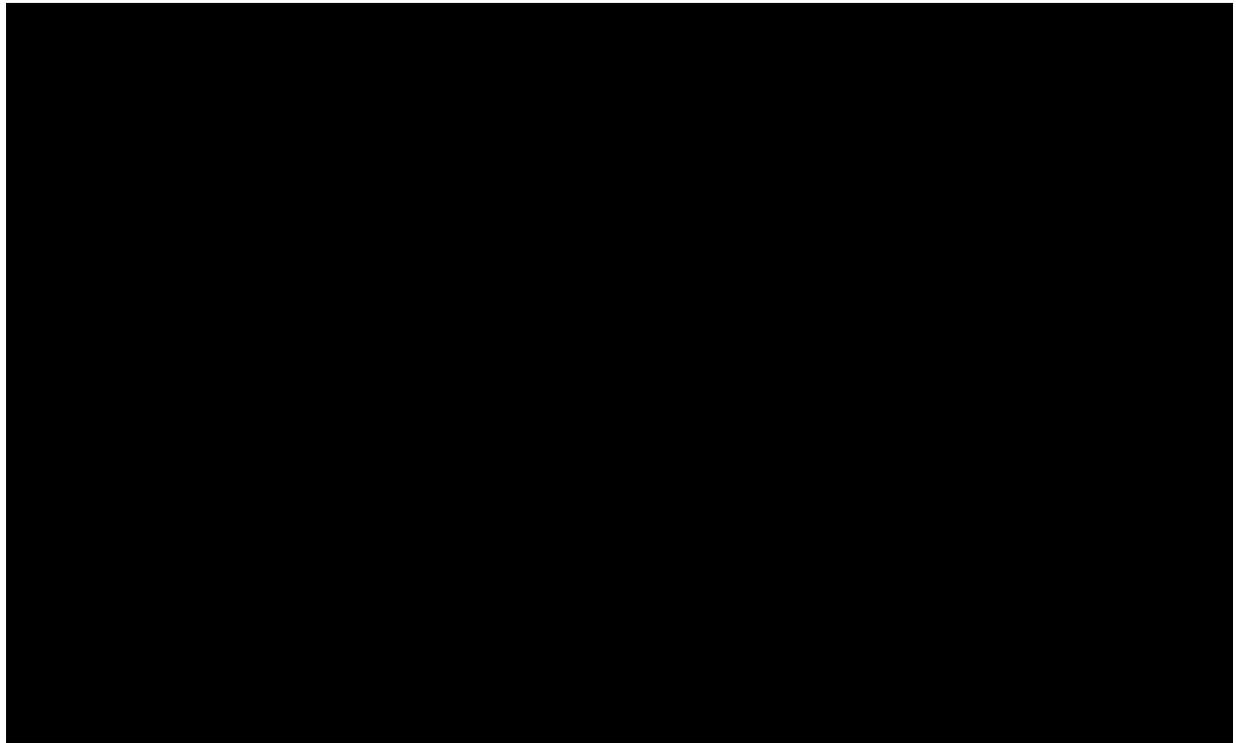
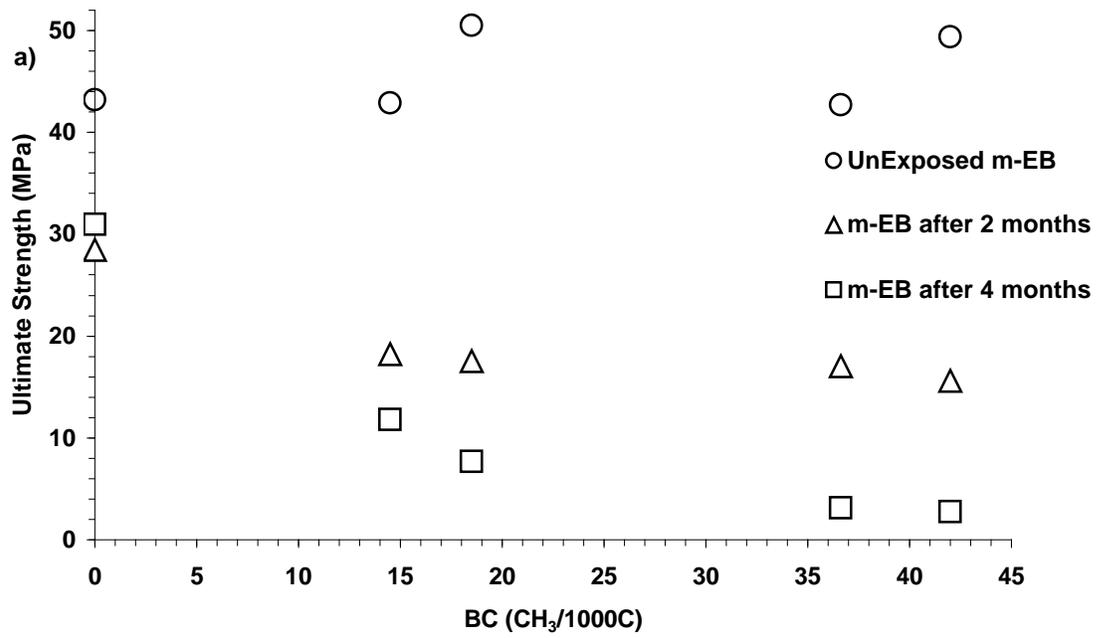


Figure 5: High strain properties of m-EBs as a function of BC (a) Ultimate Strength (b) Strain at Break

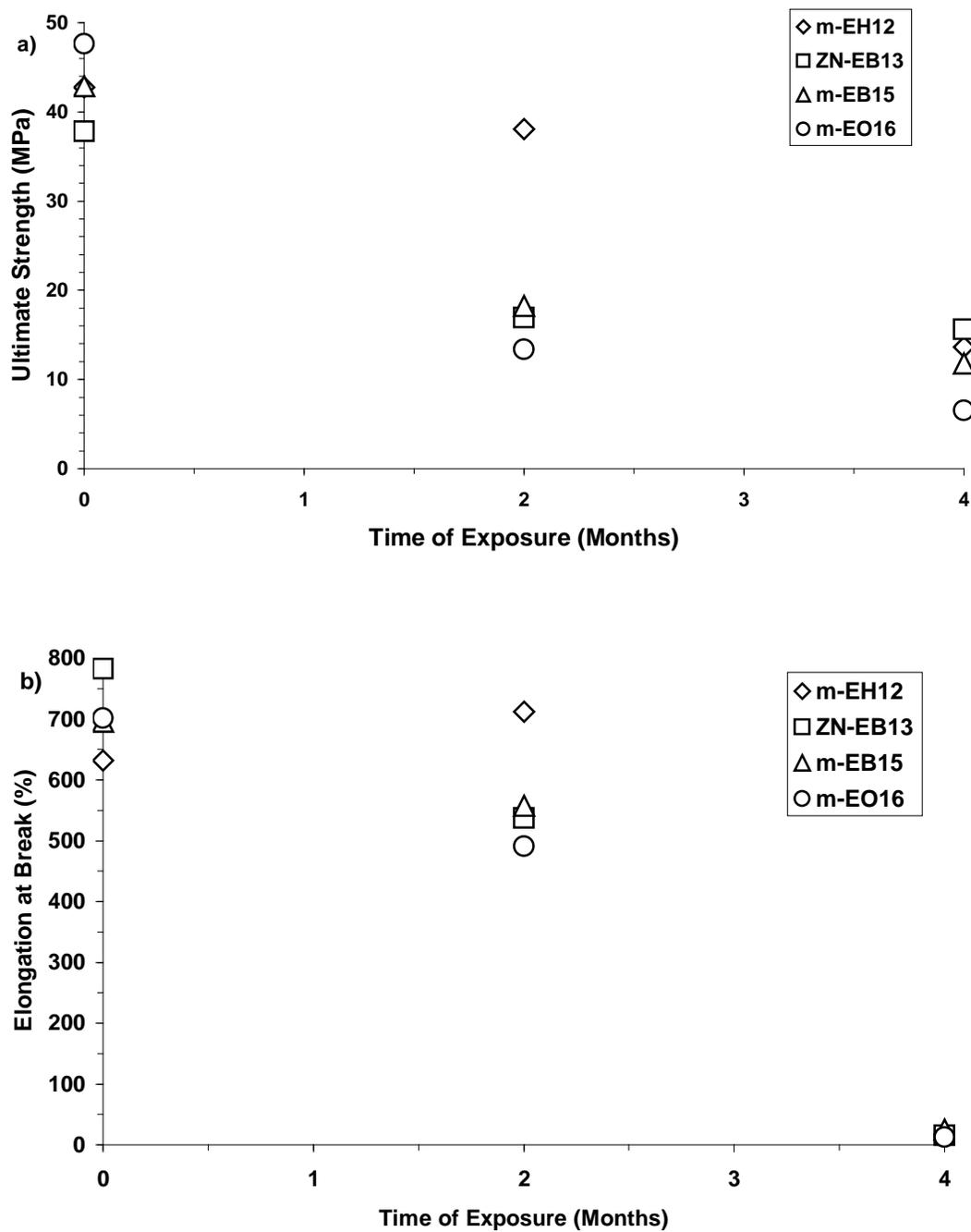


Figure 6: High strain properties of LLDPEs (average BC ~ 14 branches/1000C) as a function of exposure time (a) Ultimate Strength (b) Strain at Break

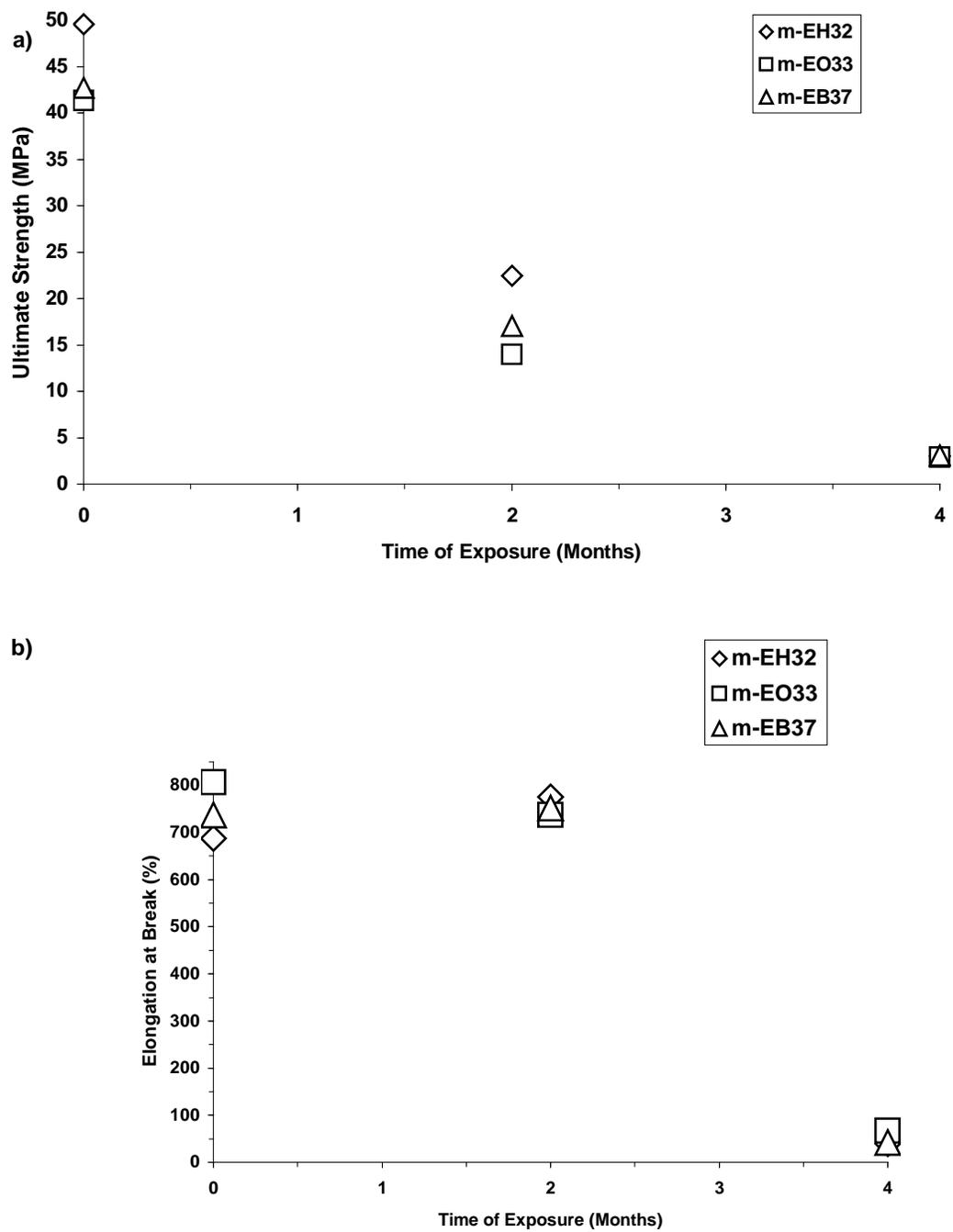


Figure 7: High strain properties of LLDPEs (average BC ~ 34 branches/1000C) as a function of exposure time. (a) Ultimate Strength (b) Strain at Break