

# Thermo-mechanical chain branching of commercial high density polyethylene during extrusion

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## To cite this article:

Yadollah Teymouri, Saeed Houshmandmoayed, Mohammad Adibfar, Reza Rashedi. Thermo-Mechanical Chain Branching of Commercial High Density Polyethylene during Extrusion. *International Journal of Materials Science and Applications*.

Vol. 3, No. 5, 2014, pp. 168-176. doi: 10.11648/j.ijmsa.20140305.17

**Abstract:** Two different phenomena may affect average molecular weight (Mw) of molten polyethylene during extrusion process. The first is crosslinking, which can be divided to two categories of chain branching and network formation, leading to an increase in Mw. The second is chain scission which leads to a decrease in the average Mw. In this work, chain branching of molten stabilized pipe grade high density polyethylene (HDPE) and unstabilized one, extruded in industrial twin screw extruder, has been studied. Therefore a series of analytical techniques including melt flow rate (MFR), capillary rheometer, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and Fourier transform infrared spectroscopy (FTIR) were employed. The unstabilized samples' MFR were lower than stabilized ones' which showed a higher melt viscosity of unstabilized samples due to their higher Mw. By applying rheometry test in different modes, the unstabilized PE samples showed a higher shear viscosity in comparison with stabilized ones agreeing with MFR results. DSC results showed a difference in degree of crystallinity between samples. This difference was verified by DMA result of solid state which showed a higher shear storage modulus for stabilized samples. Also, DMA results confirmed the obtained results from rheometry test in melt state. Additionally, FTIR results of stabilized and unstabilized samples demonstrated the difference between their chemical structures. Although it seems that the level of chain branching in this grade of HDPE is low however, all techniques' results are in a good agreement which makes the provided results and data reliable. Moreover, a combination of the applied methods in this work can be helpful to determine the validity and efficiency of antioxidants.

**Keywords:** Thermo-Mechanical Chain Branching, High Density Polyethylene, Extrusion, Antioxidant

## 1. Introduction

Although Polyethylene (PE) is one of the fastest growing commercial thermoplastic polyolefin materials due to its low cost and desirable properties such as high strength, good barrier properties, light weight, water resistance and higher stability [1], its weakness is tendency toward degradation which may occur as an undesirable phenomenon at any stage, from manufacture to end use. However, for most applications, the melt-processing stage is characterized by the most rapid degradation. Mechanical shear and temperatures between 180 °C and 280 °C are experienced during melt processing [2-4].

The conditions for melt processing of polymers, namely high temperature, the presence of oxygen, and substantial mechanical stresses, can cause chemical reactions to occur.

Even a small extent of reaction can have an enormous effect on the physical properties of the polymer [5]. It is known that thermal degradation occurs by a radical mechanism, and it offers many oligomers by hydrogen transfer from the tertiary carbon atom along the polymer chain to the radical site [6, 7].

Although chain scission and crosslinking occur simultaneously, one may predominate, depending on such factors as molar mass, shape of molar-mass distribution, chain branching level, oxygen concentration, polymerization catalyst system (and associated residues) [3, 4, 8]. For example, it has been confirmed that the polyethylene with lower molecular weight (Mw) shows low sensitivity to degradation during reprocessing [9]. Shorter chains are more mobile, not suffering scission but instead are used for grafting the macroradicals, increasing the Mw. Increase in the oxygen concentration, temperature, and vinyl

end groups' content facilitates the thermo-mechanical degradation reducing the amount of both, longer chains via chain scission and shorter chains via chain branching, leads to narrowing the polydispersity [2].

The degradation of high-density polyethylene (HDPE) during processing is a subject of great interest not only for its scientific importance but also for industrial reasons. The methods of HDPE polymerization give rise to differences in the structure of polymer chains, like differences in concentration and type of unsaturations, mainly vinyl, transvinylene, and vinylidene groups. This is an important aspect to be considered since the thermo-mechanical degradation mechanisms are affected by these unsaturations [2]. Depending on Polymerization catalyst system (ZN or Phillips), HDPE may undergo many radical reactions; chain scission and chain branching leading to crosslinking are generally favored [5, 10].

Different evidences have been obtained based on the applied catalyst system. S. V. Canevarolo *et al.* reported that Phillips HDPE produces a higher level of chain branching than the Ziegler Natta's type at the same processing condition [2]. A study of reprocessing via multiple extrusions indicated that the main cause of properties loss in unstabilized Phillips HDPE (Cr-catalysts) was crosslinking, whereas that of unstabilized Ziegler HDPE (Ti-catalysts) was chain scission [9]. I. A. Hussein *et al.* reported that the HDPE produced by Phillips process, which uses a Cr-based catalyst, undergoes chain scission while that made by Ziegler-Natta catalyst goes through crosslinking [11].

The effect of chain branching on the property of polyethylene has been studied. The chain branching leads to a change in polymer melt viscosity which can be observed in variation of melt flow rate (MFR) as a simple method and data from cone and plate rheometry. Using these methods, an increase in molecular weight for reprocessed non-stabilized HDPE has been reported [9, 12 -17].

Using rheometry as a technique to investigate the effect of any change in the chemical structure of polymer chains, i.e. chain branching, has been reported by researches [5, 11 and 16]. Chain branching leads to a change in Mw and consequently has an effect on polymer rheology. Any change in Mw can be detected by comparison of samples' viscosity vs. shear rate curves. Jiří Dostal *et al.* employed capillary rheometry to study the influence of the repeated extrusion on the degradation of polyethylene [10].

The changes in the material structure and properties were analyzed using DSC of which, based on research results reported in the literature, chain scission or crosslinking are the causes. In the case of Ziegler-Natta HDPEs crosslinking prevails. The effect of crosslinking, i.e. chain branching, is a decrease in crystallinity [5, 9, 12, 17-25].

Although many researchers have reported that FTIR method is ineffective at detecting small structural changes, some employed FTIR as a reliable technique to detect any changes in the structure and generated functionalities on the polyethylene chain after degradation process. Degradation of polyethylene usually has been investigated by

FTIR-spectroscopy in order to quantify vinyl, *trans*-vinylene, and vinylidene functionalities. Existence of each functional group can help one to guess the mechanism of crosslinking including network formation and chain branching [1, 12, 19-29].

This work is conducted to study chain branching occurring during HDPE powder processing in an industrial twin-screw extruder. Hence, for investigation of chain branching occurrence, a series of techniques consists of MFR, capillary rheometry, DSC, dynamic mechanical analysis (DMA) and FTIR were employed. For the first time in the case of HDPE grades, DMA technique was applied to investigate the chain branching effect on the HDPE's storage modulus ( $G'$ ). Moreover, by using the capillary rheometer, thermal stability and activation energy of samples were determined and investigated. Considering the obtained results in this work, for other research centers depending on their facilities and instruments, this study can be regarded as an instruction to determine applied antioxidants efficiency and validity.

## 2. Experimental

### 2.1. Material

Polyethylene granules used in this study were pipe grade HDPE (HM 5010 T2N, EX3) supplied by Jam Petrochemical Company (JPC). This grade is designated with sample code of "EX3" and produced by using Ziegler-Natta catalyst and 1-Butene as comonomer. Samples of "AOEX3" contained antioxidant (AO) and "NEX3" were neat HDPE. The mixture of antioxidants used in this study was a 50/100 blend of the primary AO, Irganox 1010 {Phenol B, tetrakis[methylene 3-(30,50-di-*t*-butylphenol) propionate]methane, Mw=1178 gr/mol}, and a secondary AO, Irgafos 168 {P-1, tris[2,4-di-*t*-butylphenol] phosphite, Mw= 646 gr/mol}. The primary and secondary antioxidants are made by Song won of Korea and GCH of China, respectively. Normally, 0.1% (1000 ppm) of primary and 0.2% (2000 ppm) of secondary antioxidants are used for polyethylene pipe grade.

### 2.2. Methods

#### 2.2.1. Preparation of Granules

The processing and granulating of polyethylene melt in HDPE plant was carried out in a commercial counter-rotating, non-intermeshing twin-screw extruder (model JSW, Japan Steel Work, Ltd.). Screw rotation speed and its L/D were 360 rpm and 11, respectively.

#### 2.2.2. Melt Flow Rate (MFR)

MFR technique was performed, according to ASTM D1238, as the first and simplest method to investigate the effect of AO absence and consequently degradation occurrence, either chain branching or chain scission. In this work, MI4 melt flow indexer from GÖTTFERT Co. in two different loads of 5 and 21.6 Kg was employed.

### 2.2.3. Rheometry Tests

The steady state capillary flow properties were measured using a GÖTTFERT capillary rheometer, Rheograph 25. Two dies with diameters,  $D$ , of 1 mm and lengths of 20 mm and 0 mm were used. The Bagley and the standard Rabinowitsch corrections were implied to calculate real data of shear stress ( $\tau$ ), shear viscosity ( $\eta$ ) and shear rate ( $\dot{\gamma}$ ).

In order to study the effect of chain branching phenomenon on rheological properties of EX3 samples, the capillary rheometer was employed in different modes including apparent viscosity ( $\eta_{ap}$ ) vs. apparent shear rate ( $\dot{\gamma}_{ap}$ ), thermal stability test and temperature shift test. EX3 granules were preheated and melted for 6 min in the barrel at 190 °C. Afterward,  $\eta_{ap}$  vs.  $\dot{\gamma}_{ap}$  graphs were plotted for 10 different shear rate points. In thermal stability test firstly, EX3 samples were preheated at 190 °C for 6 min and then, a constant shear rate of 112.9 s<sup>-1</sup> and the temperature of 190 °C were applied to measure pressure variation during 45 min. Similar to the first modes procedure were done at the temperature of 180 °C and 200 °C to obtain temperature shift factors and activation energy by WLF and Arrhenius equations, respectively.

### 2.2.4. Differential Scanning Calorimetry (DSC)

Samples of 5-10 mg were sliced from the granules and then were placed into aluminum sample pans for testing in a TA Instruments DSC-823 from Mettler-Toledo Co. equipped with a nitrogen gas flow established from a nitrogen cylinder; this further protected the samples from oxidation. A scan rate of 5 °C/min was applied to heat up the samples from 25 °C to 200 °C in nonhermetic pans.

### 2.2.5. Dynamic Mechanical Analysis (DMA) Test

In order to investigate samples storage modulus ( $G'$ ) as a function of temperature, shear mode of dynamic mechanical analysis (DMA) was performed. The samples were hot-pressed at 200 °C during 60 seconds by using spacers in order to produce films with a fixed thickness of 400  $\mu$ m. The prepared films were split up into smaller pieces with areas of 4×5 mm<sup>2</sup> to satisfy the dimensional requirements of the shear clamp test fixture. After mounting a prepared rectangular sample in the DMA shear clamp, the furnace was sealed. Subsequently, using a flow of liquid nitrogen the rectangular sample was cooled down to 0 °C. Afterward, it was heated with the ramp of 5 °C/min from 0 °C to 200 °C. Using a dynamic force with a frequency oscillation of 1 and amplitude of 0.7  $\mu$ m, DMA test was down on the sample. The storage modulus for each run was calculated as a function of temperature. Finally,  $G'$  vs. temperature curves were plotted for single frequency oscillation.

### 2.2.6. FTIR Test

The characterization of the EX3 granules was conducted by infrared spectroscopy; using IR-Tensor 27 from Bruker Co. In order to produce films with a fixed thickness of 200  $\mu$ m, the samples were hot-pressed at 200 °C during 60 seconds using spacers. All spectra were measured in the range of 4000-400 cm<sup>-1</sup> at a resolution of 2 cm<sup>-1</sup> after 32

scans. The major picks were considered as an indication of change in samples structures.

## 3. Results and Discussion

### 3.1. Practical Evidences in an Industrial Extruder

An industrial twin screw extruder in HDPE plant of JPC was employed to granulate polyethylene powder. Regarding to the high molecular weight of polyethylene chains in the pipe grade, it is very critical to have a continuous infusion and an effective mixing of additives in the polymer powder in the mixer.

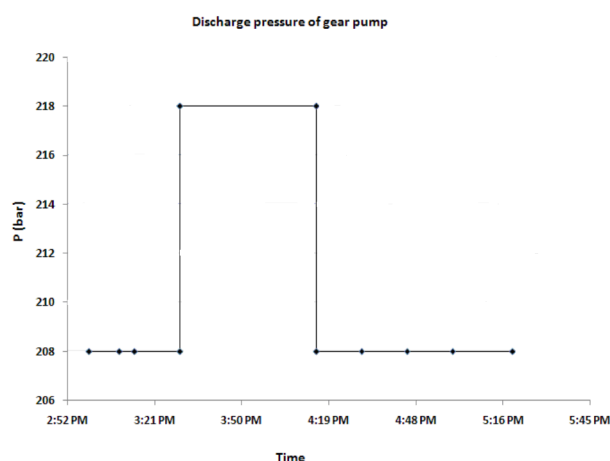


Fig. 1. Discharge pressure of gear pump vs. time in the commercial twin screw extruder in HDPE plant.

If additives infusion does not take place appropriately during the processing, pressure of polyethylene melt will be increased, leading to an enhancement in discharge pressure of gear pump of extruder, and power consumption of mixer. Regarding to Fig. 1, discharge pressure increased from, normal pressure of 208 bars, to 218 bars in absence of additives and again descended to a plateau at 208 bars after injecting the additives.

Considering mentioned problem, motivated us to investigate the reason of this problem by using analytical techniques which has been mentioned before in section 2.2. The results of these techniques and related discussion have been followed in the next sections.

### 3.2. Melt Flow Rate (MFR)

MFR is a simple technical quantity determined by a standard method. It is extensively used for the characterization of various polymers, but it can be used excellently for the monitoring of the melt stability of polyolefins [13].

Table 1. Results of MFR tests for NEX3 and AOEX3 samples.

Sample Name	Polymer Grade	MFR 190/5 (gr/10 min)	MFR 190/21.6 (gr/10 min)
AOEX3	HDPE	0.43	10.31
NEX3	HDPE	0.32	9.53

Based on the Table 1, NEX3 showed a lower MFR in comparison with AOEX3 which means that NEX3 samples had higher viscosities and Mws, comparatively. Since the temperature was set on 190 °C and loads of 5 Kg and 21.6 Kg were applied, the obtained difference shows thermo-mechanical degradation with crosslinking mechanism predominance in the case of NEX3 samples which were vulnerable in such a condition [9].

What has been observed in NEX3 MFR results can be a consequence of continuously decrease of number of vinyl groups that has a relation with polymer's Mw and MFR. Addition of alkyl radicals to the vinyl group results in a decrease of this functionality and in the decrease of MFR. Moreover, according to the hypothesis chain branches form during processing decreases MFR [12, 13]. Analysis of the data indicates that a few chain branches form during processing. A clear proof for the modification in the structure of the polymer chains, i.e. chain branching, has been supplied by the FTIR measurements which have been expressed in section 3.6.

### 3.3. Rheometry Tests

#### 3.3.1. Melt Viscosity Behavior

Rheometry diagrams, i.e.  $\eta_{ap}$  vs.  $\dot{\gamma}_{ap}$  diagrams, can be used to compare samples molecular microstructures. A sample with a higher viscosity has a higher Mw. Moreover, the slope of the curve at the melt's non-Newtonian rheological behavior region is a reliable criterion to compare samples molecular weight distribution (MWD). The steeper curve is the broader MWD and/or more chain branching is [5, 16].

At low shear rates, the Newtonian viscosity simply represents the resistance to the shear flow due to coil volume (which is lower for branched polymers in contrary to linear polymers) and number of active entanglements between polymer chains (which is higher for branched polymers in contrary to linear polymers). Therefore it could happen that branched polymers, here NEX3, may have higher Newtonian viscosity at low deformation rates than more linear polymers, here AOEX3, due to higher number of active entanglements; whereas, at high shear rates, the number of active entanglements is significantly reduced.

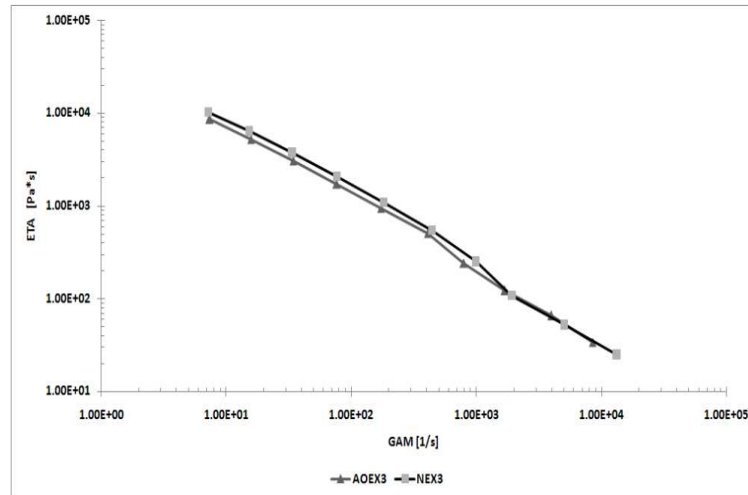


Fig. 2. Viscosity ( $\eta$ ) vs. shear rate ( $\dot{\gamma}$ ) diagrams for NEX3 and AOEX3 samples at 190 °C.

Fig. 2 depicts  $\eta_{ap}$  vs.  $\dot{\gamma}_{ap}$  diagram of which was performed at 190 °C and  $\dot{\gamma}_{ap}$  of  $1-10^4 \text{ s}^{-1}$ . Regarding to this figure, at  $\dot{\gamma}_{ap} > 1000 \text{ s}^{-1}$ , NEX3 and AOEX3 samples  $\eta_{ap}$ s are equal which can be caused by higher mechanical stress, which orientates the polymer chains in the same direction. In this range of shear rate, generated chain branching during the process does not have any significant effect on the viscosity since the number of active entanglements reduces due to higher shear forces. On the other hand, at  $\dot{\gamma}_{ap} = 200 \text{ s}^{-1}$ , absence of AO leads to a significant increase of  $\eta_{ap}$  which is considered as a function of samples Mw and chain branching [5, 10, 16]. Therefore, for more detailed assessment, Carreau-Winter equation, Eq. 1, which was defined by the instrument's software, was fitted on the experimental data to calculate the equation's coefficients:

$$\eta = \eta_0 / (1 + \lambda \times \dot{\gamma})^{m_c} \quad (1)$$

which  $\eta_0$ ,  $\lambda$ ,  $\dot{\gamma}$  and  $m_c$  are zero viscosity, relaxation time,

shear rate and 1-n, n is the power law index, respectively. These data are reported in Table 2.

Table 2. Rheological parameters for NEX3 and AOEX3 samples calculated by capillary rheometer.

Parameter	AOEX3	NEX3
$\eta_0$ (Pa.s)	$1.62 \times 10^4$	$1.71 \times 10^4$
$\lambda$ (s)	$1.64 \times 10^{-1}$	$1.22 \times 10^{-1}$
$m_c$	$8.53 \times 10^{-1}$	$8.93 \times 10^{-1}$
N	0.147	0.107
$r^2$	0.999	0.999

Considering Table 2,  $\eta_0$  rose from  $1.62 \times 10^4 \text{ Pa.s}$  (for AOEX3) to  $1.71 \times 10^4 \text{ Pa.s}$  (for NEX3) which was attributed to possible differences in susceptibility toward chain branching due to absence of AO in NEX3. Higher number of active entanglements of molten NEX3 samples, caused by higher content of chain branching, lead to higher  $\eta_0$  at lower shear rate. On the other hand, power law index decreased from

0.147 to 0.107 in the absence of AO. This observation shows a higher shear thinning due to NEX3 samples more chain branching during the process and less coil volume [9, 10].

According to above, chain scission mechanism cannot be the predominant mechanism of our samples degradation. Hence, chain branching which leads to an increase in molecular weight and finally enhancement in viscosity, is assumed to be the main mechanism of degradation. Higher  $\eta_0$  of NEX3 and lower power law index support this claim.

To probe our claim more deeply, thermal stability test was applied on NEX3 and AOEX3. Acquired result has been discussed in the next section.

### 3.3.2. Thermal Stability Test

Thermal stability test provides a valuable characterization

parameter associated with long-term stabilities of polymers. In order to ensure that HDPE samples will exhibit acceptable long term stability, simple test by capillary Rheometry needs to be preformed which will provide a reliable indication of the stability of polyethylene. The technique measures the pressure difference of the molten sample during 45min while temperature and shear rate have been remain constant. As a result, depends on the slope of pressure against time (p-t) curve, three various observations might be feasible: 1) pressure may increase which means the chain branching on polymer chains has occurred, 2) pressure can drop rooting from chain scission of polymer and 3) pressure may stay unchanged, revealing no degradation has happened and polymer is stable.

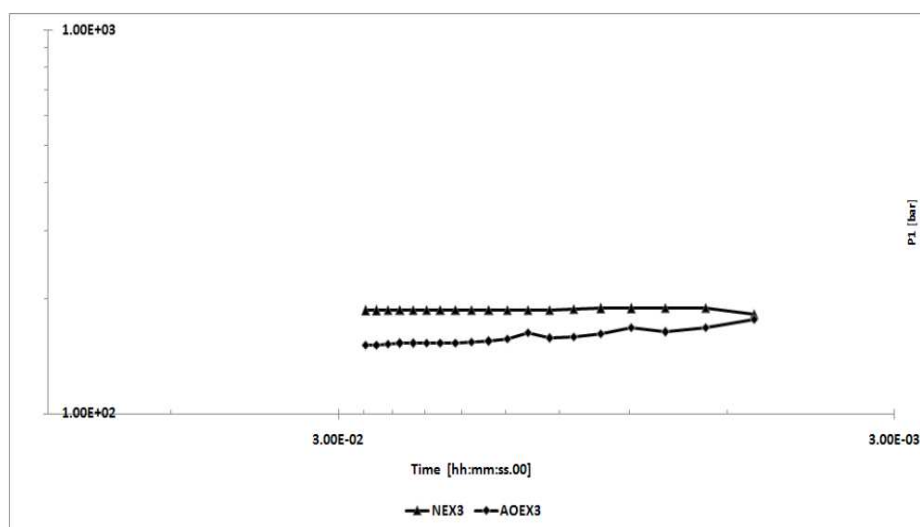


Fig. 3. Changes in melt pressure for NEX3 and AOEX3 samples at 190 °C and constant shear rate.

EX3 samples were conditioned at 190°C and constant shear rate of  $100 \text{ s}^{-1}$ , for 45 minutes to measure pressure changes, Fig. 3. NEX3 sample, reached a maximum melt pressure of 200 bar in the end of test while AOEX3 melt pressure remained unchanged at about 160 bar. This difference shows that in the case of NEX3, due to the composed macro radicals and propagated active radicals, crosslinking or chain branching has occurred.

### 3.3.3. Temperature Shift Test

Samples were preheated in the barrels at 190 °C for 6 minutes. Then, the molten samples underwent 10 different ascending shear rates to calculate the related rheological parameters. Similar procedures were carried out at 180 °C and 200 °C. Using Arrhenius (Eq. 2) and WLF (Eq. 3) equations, related shifting factors and master curves were obtained.

$$K = A \times \exp(-\Delta E_a / RT) \quad (2)$$

$$\text{Log}(\eta_T / \eta_{T_g}) = -((1.744(T - T_g) / (51.6 + (T - T_g))) \quad (3)$$

Fig. 4 shows master curve of EX3 samples. Temperature of 180 °C has been selected as reference temperature to obtain parameters and diagrams. Shifting factor ( $\alpha_T$ ) and

activation energy  $E_a$  were determined for both EX3 samples (Table 3)

Table 3. Results of temperature shift test for NEX3 and AOEX3 samples.

Parameter	AOEX3	NEX3
$T_0$ (°C)	180	180
$E_a$ (KJ/mol)	20.7	50.9
$1 = \alpha_{180}$		$1 = \alpha_{180}$
$\alpha_T$	$0.92 = \alpha_{190}$	$0.81 = \alpha_{190}$
	$0.79 = \alpha_{200}$	$0.56 = \alpha_{200}$
$r^2$	0.984	0.986

When test temperature increases, shifting factor ( $\alpha_T$ ) decreases; indicating that the viscosity of samples in all regions of shear rates will decrease by increasing the temperature. AOEX3 sample showed a decreased  $\alpha_T$  from 1 at 180 °C to around 0.79 at 200 °C. In contrast, NEX3 samples showed a significant drop from 1 at the reference temperature to about 0.56 at 200 °C. These results reveal the instability of NEX3 samples in comparison with AOEX3 samples. According to Fig. 4,  $\eta-\gamma'$  master curve of NEX3 jumps obviously to a higher value in low shear rates in comparison with AOEX3 samples. This observation can be regarded as an indication of chain branching between polymer chains in absence of AO. In addition of shifting

factor, activation energy ( $E_a$ ) as a measure of sensitivity of viscosity to temperature was determined by Temperature-Shift test in capillary Rheometer [30]. AOEX3's  $E_a$  was about 21 KJ/mol while it went up to about

51 KJ/mol for NEX3. This difference shows comparatively harder movement of NEX3 chains attributed to increase in their Mw caused by chain branching.

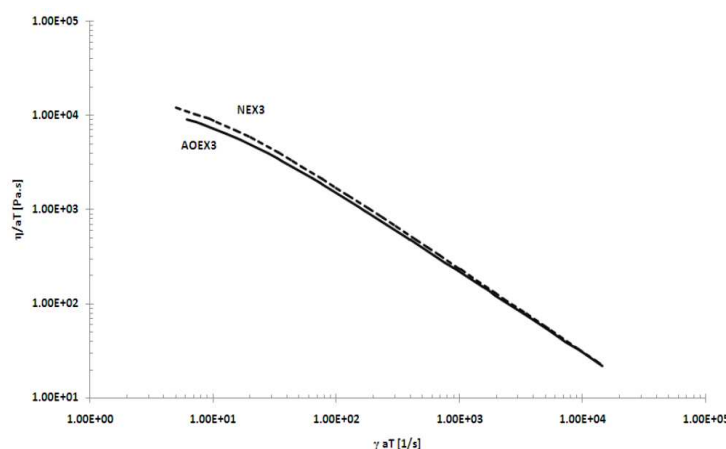


Fig. 4. Viscosity ( $\eta$ ) vs. shear rate ( $\dot{\gamma}$ ) master curves of NEX3 and AOEX3 samples.

### 3.4. Differential Scanning Calorimetry (DSC)

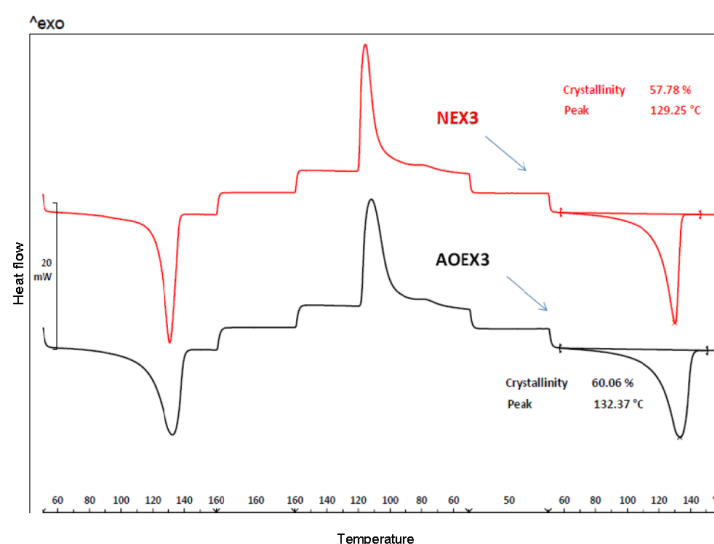


Fig. 5. DSC diagram of NEX3 and AOEX3 samples.

The DSC analysis was carried out after conditioning the samples. All Samples were heated in the DSC under Nitrogen ( $N_2$ ) from 25 °C to 200 °C at a scan rate of 5 °C/min. DSC data were analyzed to probe any differences in the samples melting peak ( $T_m$ ) and degree of crystallinity ( $X_c$ ).  $X_c$  was determined from  $X_c = \Delta H_m / \Delta H_{m100}$ , where  $\Delta H_m$  and  $\Delta H_{m100}$  represent the melting enthalpy of the polymers tested and that of a 100% crystalline polyethylene, respectively [9]. In current work, the latter value was taken as 293.6 J/gr.

A comparison between DSC diagrams of NEX3 and AOEX3 is illustrated in Fig. 5. The results of  $T_m$  and  $X_c$  for both samples is given in Table 4.

The melting peak of NEX3 sample was 129 °C while it

rose to 132 °C for AOEX3. Similar trend was observed in  $X_c$ . These differences, clearly suggest that structural changes have taken place in the case of NEX3 sample caused by chain branching and Mw enhancement.

Table 4. DSC results for NEX3 and AOEX3 samples.

Sample	$T_m$	$X_c$ (%)
AOEX3	132	60
NEX3	129	57.8

Chain branching and enhancement of Mw lead to a decrease of the macromolecules mobility and thus induce a reduction in the possibility of the material to organize itself in large crystalline domains. Therefore, crystallinity and  $T_m$  turns lower due to difficulty of movement for chains to

contribute in crystalline formation [5, 9]. These observations support the rheology test results and suggest that chain branching has occurred in NEX3 sample.

### 3.5. Dynamic Mechanical Analysis (DMA) Test

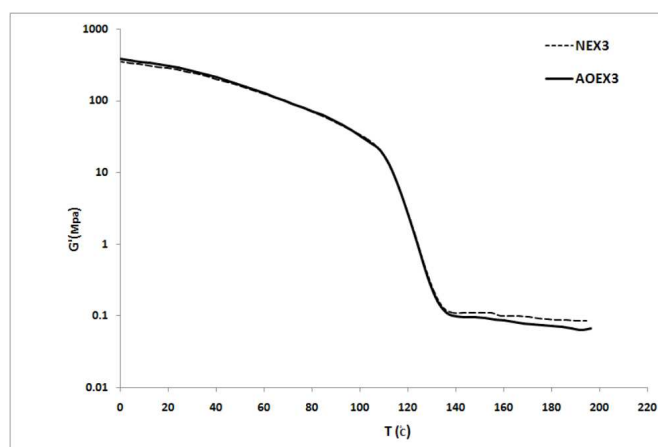


Fig. 6. Storage shear modulus ( $G'$ ) vs. temperature for NEX3 and AOEX3 samples in single frequency of 1 Hz.

Fig. 6 shows DMA graphs of  $G'$  vs. temperature for the different tested EX3 samples.

The sudden drop in the storage modulus toward the middle of the test for both samples was due to the onset of the melting point around 117 °C.

Below the melting temperature there was no significant difference between the  $G'$  of NEX3 and AOEX3 samples except some small differences in their  $G'$  of room temperature ( $G'$  of AOEX3 is slightly higher). This observation is due to higher crystallinity of AOEX3 sample in comparison with NEX3 sample. In contrast, above the melting point,  $G'$  of NEX3 is higher than AOEX3 that means in the absence of AO, some parts of macroradicals, which has been generated under the heat and shear stress, propagated and formed chain branching, leading to increase the  $G'$  from 70.2 KPa in AOEX3 sample to 88.5 KPa in NEX3 sample at about 185 °C. This observation confirms the results which have been discussed in the previous sections.

Shear mode of DMA test with the condition of single frequency of 1 Hz and amplitude of 0.7 mm was performed on EX3 samples to determine storage modulus ( $G'$ ) changes as a function of temperature.

### 3.6. FTIR Test

When polyethylene is exposed to high temperatures, alkyl macroradicals are formed. The alkyl radicals' abstract hydrogen from the backbone of the polymer, and alkyl macroradicals are formed [25]. The degree of functionalization or chain branching degree can be determined by FTIR [12, 19].

Fig. 7 illustrates FTIR spectra of NEX3 and AOEX3 samples. All samples display IR characteristic peaks at 720, 1377 and 1465  $\text{cm}^{-1}$  which assign to the  $\text{CH}_2$  rocking and  $\text{CH}$  bending vibrations of methyl and methylene groups, respectively [22, 31].

Monosubstituted double bonds, vinyl, give rise to two strong bands, one near 990  $\text{cm}^{-1}$  and the other near 910  $\text{cm}^{-1}$  for alkyl-substituted alkenes. An overtone of the 910  $\text{cm}^{-1}$  band usually appears at 1820  $\text{cm}^{-1}$  and helps confirm the presence of vinyl group. Trans double bond absorbs near 970  $\text{cm}^{-1}$ .

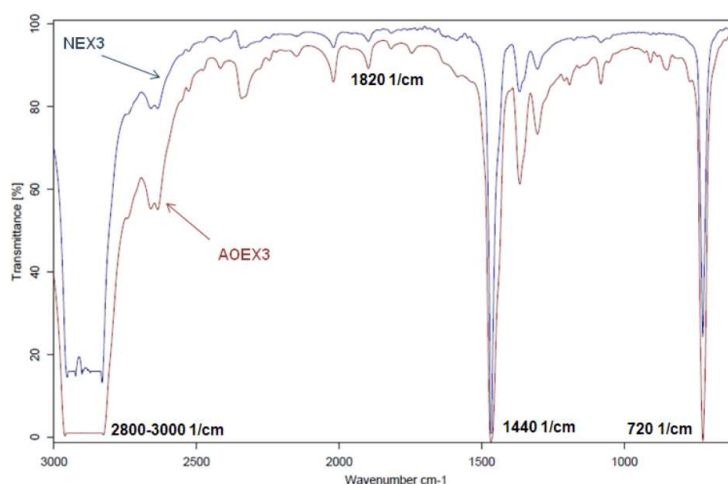
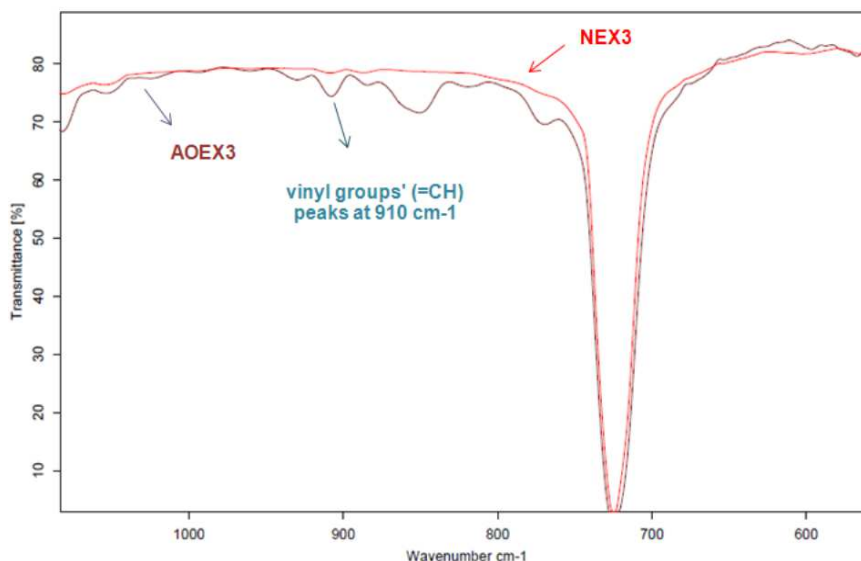


Fig. 7. FTIR spectra of NEX3 and AOEX3 samples.



**Fig. 8.** Intensity of vinyl group peaks for NEX3 and AOEX3 samples.

In AOEX3 sample, peaks of  $910\text{ cm}^{-1}$ ,  $970\text{ cm}^{-1}$ , comparatively small, and  $1820\text{ cm}^{-1}$  were distinguished [12, 19 and 31]. These peaks have disappeared for NEX3 as is shown in Fig. 8. This difference reveals the double bonds consumption of alkenes group during the chain branching reactions in the absence of AOs.

#### 4. Conclusion

Inspired by the evidences of increase in discharge pressure of gear pump when shortage of AOs happened, investigation of thermo-mechanical crosslinking of a pipe grade HDPE, in the lack of AOs, was conducted. A lower MFR was observed for NEX3 in comparison with AOEX3 due to higher number of side branches and lower content of double bonds. According to rheometry results, NEX3 sample showed higher  $\eta_0$ , melt pressure and  $E_a$  in comparison with AOEX3 which support MFR results. Combination of DSC and DMA results illustrated that NEX3 sample had a lower degree of crystallinity in comparison with AOEX3 sample. In opposition, NEX3 Mw is higher than AOEX3 Mw which relatively higher  $G'$  of molten NEX3 confirms it. Finally, FTIR test of samples proved higher double bonds consumption in the chain branching reactions in the absence of AOs whereas the intensity of vinyl group for NEX3 was considerably lower than the intensity of AOEX3. FTIR result has a good compatibility with what was observed in MFR results of employed two types of samples. The results of employed analytical techniques had a good agreement with of each others. They showed that, for this grade of HDPE process, chain branching was the predominant mechanism of degradation. Considering what has been reported, this work can be regarded as a practical instruction to determine the used antioxidants efficiency and validity.

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