

STUDY ON CHANGE OF SOME CHARACTERS AND MORPHOLOGY OF POLYETHYLENE COMPOUND EXPOSED NATURALLY IN DONG HOI-QUANG BINH

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Abstract

The degradation and stability of high density polyethylene (HDPE) compound depend strongly on geographic, weather and climatic factors (solar radiation, temperature, humidity, etc.). From June 2014 to June 2015, the samples of HDPE compound were tested naturally on outdoor shelves in Dong Hoi sea atmosphere region (Quang Binh province) for evaluation of change of their morphology and properties. The tensile property results show that tensile strength and elongation at break of HDPE compound reduced significantly while their Young modulus rose as increasing natural testing time. After 12 months of exposure, the tensile strength and elongation at break of HDPE compound decreased 47.63% and 1.39% in comparison with unexposed HDPE compound, respectively. Scanning Electron Microscopy (SEM) analysis on the surface of HDPE compound shows the number of cracks and size of cracks of the samples increase and the cracks become bigger and deeper when increasing natural exposure time. The thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) indicate that the thermal stability of HDPE compound steadily declines versus natural exposure time.

Keywords. HDPE, photo-degradation, natural exposure, tensile property, thermal property, morphology.

1. INTRODUCTION

HDPE is one of the most popular thermal plastics. Owing to its reasonable cost and low energy demand for processing, HDPE is ideal for many applications as packaging, bottles, films, pipes manufacture etc. HDPE has high crystalline structure and tensile strength. Besides, HDPE offers a good barrier for humidity and resistance to abrasion and corrosion. Furthermore, HDPE is inertness the most of chemicals, and has high weather stability.

HDPE is a potential material for application in outdoor exposure, so its life time is determined by various environmental factors as solar radiation, temperature, thermal cycling, humidity, pollutants, ultra-violet (UV) radiation. In the recent years, many studies have been conducted to investigate various aspects of the weather stability of HDPE. Torikai et al.[1] have studied the photodegradation of four commercial polyethylene types by using a laboratory tester (samples were photo-irradiated with a Toshiba

H-400P medium pressure mercury lamp ($\lambda \geq 250$ nm) in vacuum and in air at 30°C, and they were frequently turned over to give the same irradiation dose on both sides). They concluded that density, crystallinity and crystal size of polyethylene play important roles in its photostability. The study on the change in structure and mechanical properties of HDPE, which was natural tested during a Canadian winter were reported by Carrasco et al. [2]. The authors considered that the loss in crystallinity and thermal fatigue caused the drastic decrease in impact energy of HDPE. Hoekstra et al. [3] have published the fracture behavior, mechanical and morphological properties of photo-oxidized HDPE in a Xenotest. For Charpy specimen which is a an HDPE granulate supplied by DSM and about 350 ppm 'phenolic antioxidant' was added to the material for thermal stabilization, the authors observed a gradual increase in density of HDPE with exposure time and the concentration of carbonyl groups in the amorphous phase were decayed with the depth of the HDPE sample.

Up to now, the study on weather stability of HDPE compound in typical sea atmosphere condition for North Middle Region of Vietnam has not been presented. Therefore, this work focuses on the degradation of HDPE compound samples according to natural exposure time in Dong Hoi sea atmosphere region (Quang Binh, Vietnam). The change of morphology, mechanical, thermal properties was determined and discussed.

2. EXPERIMENTAL

2.1. Materials

The materials used in this work were a HDPE (Daelim, Korea), density = 0.937 g.cm^{-3} ; melting flow index, $\text{MFI}_{190^\circ\text{C}/2.16\text{kg}} = 1.20 \text{ g.min}^{-1}$, CaCO_3 powder (supplied by Minh Duc Chemical Stockshare Co.), density = 2.7 g.cm^{-3} .

2.2. Preparation of HDPE compound samples

The HDPE/ CaCO_3 (wt./wt.) compounds were prepared by melt mixing in a Haake internal mixer at 160°C for 5 minutes. Immediately after melt mixing, the HDPE compounds were pressed by hydraulic heat press machine at a temperature of 160°C , the pressure of 5 MPa to form sheets with thickness from 1 to 1.2 mm.

2.3. Natural exposure HDPE compound samples

The samples of HDPE compound were exposed starting from June 20th on outdoor testing shelves at the Natural Weathering Station of the Institute for Tropical Technology in Dong Hoi sea atmosphere region (Quang Binh, Vietnam). Inclining angle of shelf in comparison with the ground is 45° as typically shown in Fig. 1 and total exposure time of the samples was 12 months.



Figure 1: View of outdoor exposure testing shelves

After every three months, the samples were withdrawn and stored under standard conditions

before determining properties and morphology. The signed samples were M0, M3, M6, M9, M12 corresponding to the samples were exposed for 0, 3, 6, 9, 12 months, respectively.

2.4. Characterizations

The HDPE compound samples before and after natural exposure were characterized by Fourier Transform Infrared (FTIR) spectra (using a Nicolet/Nexus 670 spectrometer, USA) at Institute for Tropical Technology (ITT), Vietnam Academy of Science and Technology (VAST). The tensile properties of samples were conducted on Zwick Tensile 2.5 Machine (Germany) according to ASTM D638 standard at ITT, VAST. Field Emission Scanning Electron Microscopy (FESEM) analysis was carried out by using a S-4500 SEM (Hitachi, Japan) at Institute of Material Science, VAST. Thermal property studies were performed on a DTG-60H and DSC-60 thermo-gravimetric analyzer (Shimadzu. Co, Japan) under argon gas from room temperature to 600°C with a heating rate of 10°C/min at Hanoi national University of Education.

3. RESULTS AND DISCUSSION

3.1. FTIR spectra

The effect of natural exposure conditions on the M0, M3, M6, M9, M12 samples was evaluated by FTIR spectra as presented in Fig. 2.

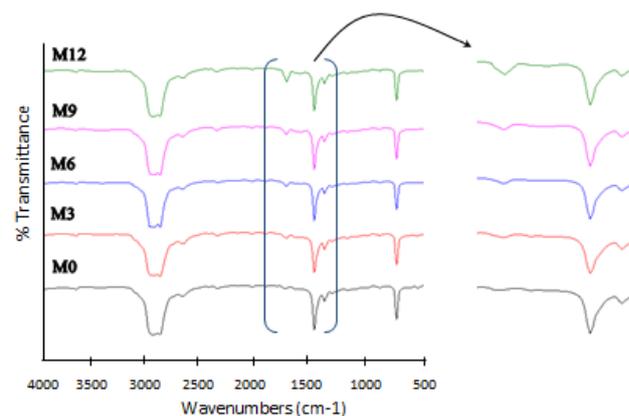
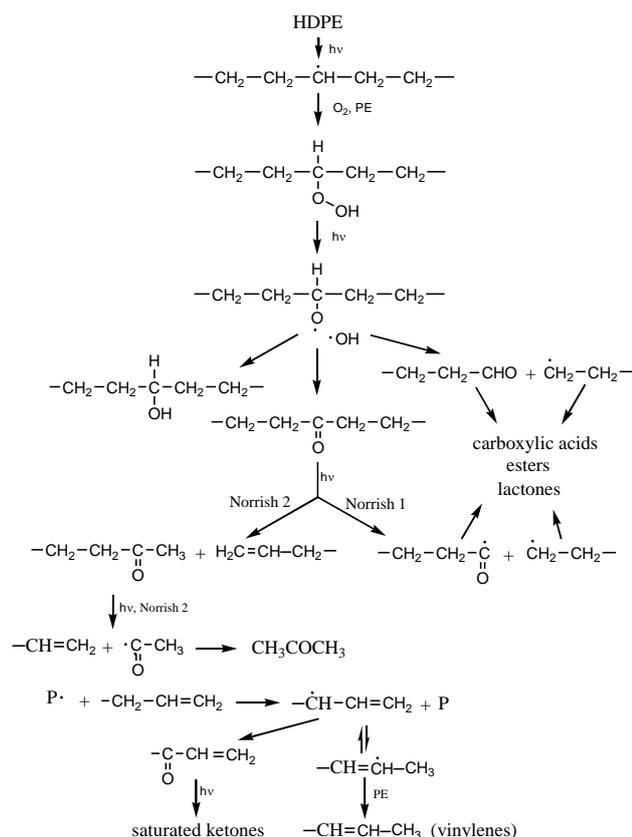


Figure 2: FTIR spectra of HDPE compounds versus natural exposure time

In the FTIR spectrum of M0 sample, some peaks characterize for stretching and bending vibrations of CH groups in HDPE were found at 2921 , 2854 , 1465 and 1380 cm^{-1} . Beside, a peak corresponding to out-of-plane bending vibration of CH group appears at 725 cm^{-1} . For the exposed samples, the FTIR spectra

also indicate the peaks characterized for stretching and bending vibrations of CH groups in HDPE. Interestingly, the absorption peak around 1735 cm^{-1} characterizes for the stretching vibrations of carbonyl groups was seen clearly in FTIR spectra of the exposed samples. This is caused by the formation of the carbonyl groups such as ketone, lactone carbonyl and aliphatic ester occurring in photodegradation process of HDPE according to the Norrish 1 and Norrish 2 reaction and mechanism has been well described in the scheme 1 of literatures [4].



Scheme 1: Simplified photo-degradation mechanism of polyethylene.

To quantify relatively the carbonyl group content existed in the exposed samples, carbonyl index (CI) was calculated using the following equation:

$$\text{CI} = \frac{I_{1725}}{I_{1465}}$$

Where, I_{1725} and I_{1465} are absorption peak intensity at 1725 cm^{-1} and 1465 cm^{-1} .

Figure 3 displays that the CI of the samples

increases as a function of natural exposure time. The significant increase of the CI was observed for the samples exposed from 0 to 6 months while from 6 to 12 months, the CI varies more slowly. The irregular varieties can be explained by the change of weather in Dong Hoi during natural exposure time. The climate in Dong Hoi exhibits clearly two seasons: the hot season from March to November and the cold season from December to February (see table 1). In the cold season, the average temperature/month in Dong Hoi and the average sunny hours/month are low, reach to $19.6\text{ }^\circ\text{C}$ and 76.3 hours, respectively. Therefore, the solar radiation is low, resulting in that the photodegradation of HDPE occurs slowly, leading to that the CI increases slightly. In the hot season, the average temperature/month and average sunny hours/month are higher, thus the samples have been affected by solar radiation more strongly. This caused the faster photodegradation of HDPE, so the CI value increases significantly [5].

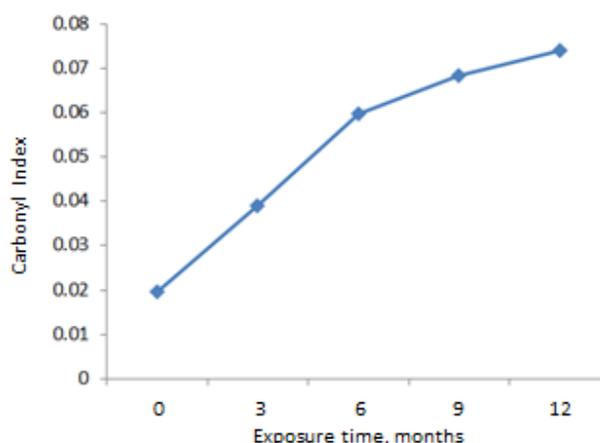


Figure 3: CI value of HDPE compound versus natural exposure time

3.2. Tensile property

The change in tensile properties of HDPE compounds is described through remained percent of tensile strength ($\Delta\sigma$), elongation at break ($\Delta\varepsilon$) of the samples versus natural exposure time is performed in figure 4. The tensile strength and elongation at break of HDPE compounds have a decrease trend as increasing the natural exposure time. They decrease significantly during the first 3 months of natural exposure and then reduce more slowly. The above tendency in the first period of natural exposure may be due to the effect of weather factors such as solar radiation, humidity, temperature on the amorphous region of HDPE as above mentioned.

Table 1: Climate database in Dong Hoi – Quang Binh from June 2014 to June 2015

2014	Ttb (°C)	Tx (°C)	R (mm)	Rx (mm)	Utb (%)	E (mm)	S (h)	St (d)	CC (d)
June	30.9	39	78	41	67	163	191	22	0
July	30.1	37.5	85	31	71	137	220	12	0
August	29.6	38.5	132	60	72	134	176	11	0
September	29.6	38.5	132	60	72	134	176	11	0
October	25.6	32.0	605	189	87	57	129	0	0
November	24.2	30.0	344	160	88	48	106	0	0
December	19.2	25.8	160	48	82	70	35	0	0
2015									
January	18.8	25.0	84	42	84	55	130	0	0
February	20.7	27.2	40	9	91	28	64	0	0
March	24.2	36.7	32	24	90	39	100	0	0
April	25.6	41.0	206	133	85	72	173	8	0
May	31.0	40.5	9	6	70	176	298	18	0
June	30.9	39.5	73	36	69	153	290	22	0

T_{tb}, T_x: Average and highest temperature; R, R_x: Rainy total and highest rainy quantity in day; U_{tb}: Average humidity; e: Steam quantity; S: Sunny hours; St: Storm; CC: Day numbers have drizzle.

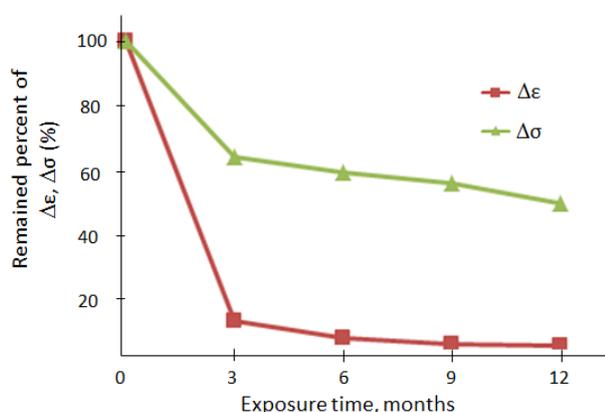


Figure 4: The remained percent of tensile strength, elongation at break of HDPE compound versus natural exposure time

From data in table 1, it is clearly seen that, in the first 3 months of natural exposure, the average temperature is from 29.6 to 30.9 °C, total sunlight hours are quite high, 587 hours, respectively. The high intensity of solar radiation could make a significant contribution to the photodegradation in amorphous part of HDPE. This can lead to the

formation of carbonyl, carboxyl, hydroperoxide groups and free reactive radicals in polymer chains, causing the occurrence of chain scission, thus deteriorating mechanical properties of HDPE compounds. After first 3 months of natural exposure, the photodegradation mainly happens in crystalline part of HDPE and more difficultly compared to the amorphous part of HDPE. Therefore, the tensile strength and elongation at break of HDPE compounds decrease slower.

The Young modulus of HDPE compounds has an increase tendency with increasing natural exposure time. After 3, 6, 9, 12 months of natural exposure, the Young modulus of HDPE compounds increase 6, 17, 36, and 56% compared to the unexposed HDPE compound, respectively. These results demonstrate that when increasing natural exposure time, the samples lose their ductility and become stiffer but brittle and weaker in terms of tensile strength. In addition, crosslinking of HDPE molecules is happened due to the high rate of radical termination in the bulk of the polymer where oxygen cannot gain access. Thus, there is an observed increase in the Young modulus.

3.3. Morphology

As mentioned in [6], the photodegradation of a polymer material usually begins from the surface and then develops along the depth gradually. Hence the surface photo-degradation of the material has a direct influence on the bulk oxidation of the material. Figure 5 demonstrates the surface images of the samples before and after natural exposure. Before natural exposure testing, the sample surface is relatively smooth, only has some small cracks (M0 sample). After 3 to 12 natural exposure months, there are more cracks found on the surface of the exposed samples. When increasing natural exposure time, the number and size of cracks increases, the

cracks become bigger and deeper. As shown in the SEM image of M3 sample, the surface damages are somehow slighter. Only few small cracks were found on the surface of the sample. There can be observed some holes on the surface of the samples after 6 to 12 natural exposure months. The photodegradation of the samples can occur in the amorphous region before crystalline region because the higher density and regular structure in the crystalline region prevent permeability of oxygen into structure of the samples [4]. Therefore, the photodegradation of amorphous region in the samples to be main reason to form the holes on the surface of these exposed samples.

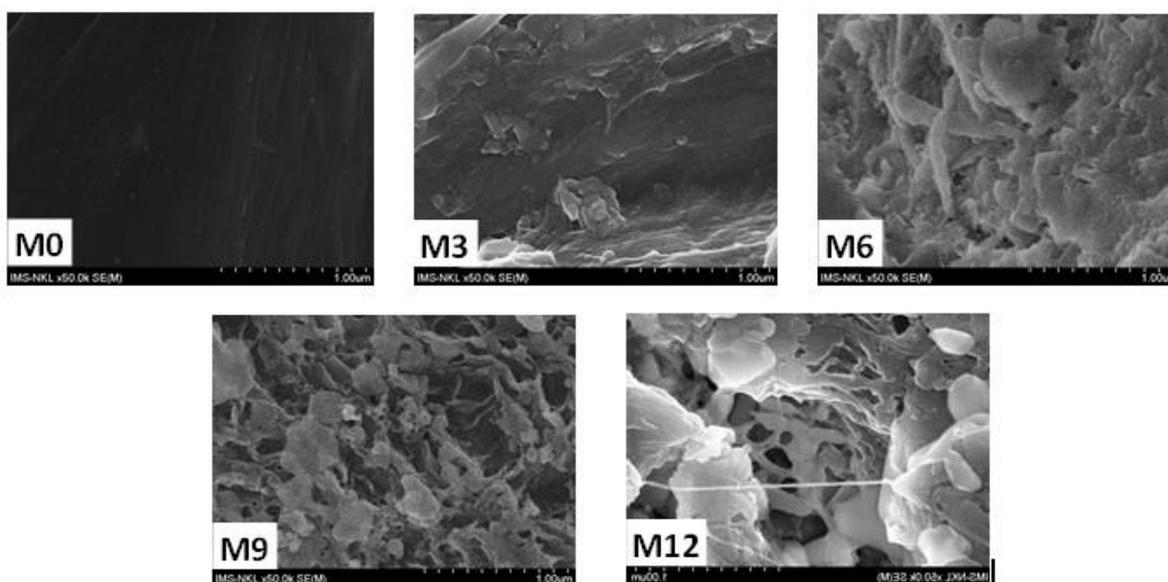


Figure 5: SEM images of HDPE compound versus natural exposure time

3.4. Thermal property

Figure 6 performs DSC curves of HDPE compound versus natural exposure time. The melting temperature (T_m) of exposed and unexposed samples is almost constant, around 144 °C. Table 2 exhibits a slight increase of melting enthalpy and relative degree crystalline during the first 9 months of natural exposure. It may be attributed to the slight increase in the crystallinity of HDPE compound, which is caused by the rearrangement in structure crystalline of HDPE, the appearance of spherulite particles and the increase of carbonyl group content in the amorphous region after chain scission by photo-degradation of HDPE macromolecules. However, after 12 natural exposure months, the relative crystalline degree of M12 sample is reduced. This can be explained by the photodegradation of

HDPE macromolecules continues in crystalline regions of HDPE.

Table 2: Melting temperature (T_m), melting enthalpy (ΔH_m) and relative degree crystalline (χ_c) of HDPE compound versus natural exposure time

Samples	T_m, PE (°C)	$\Delta H_{m, PE}$ (J)	χ_c (%)
M0	144	168.5	57.4
M3	143	169.3	57.7
M6	144	169.3	57.7
M9	143	179.7	61.2
M12	145	159.1	54.2

Thermo gravimetric (TG) diagrams of the samples versus natural exposure are in Figure 7 and the TG data are listed in table 3. The TG curves demonstrate first weight loss stage of the samples

observed at 300-465 °C. Then, the highest weight loss stage of the samples is at 465-500 °C, and finally, small weight loss stage is at 500-600 °C. The results in figure 7 and table 3 show the initial thermo-degradation temperature, maximum thermo-degradation temperature, as well as remained weight of the samples to have a decrease trend versus natural exposure time and aging temperature. This confirms the influence of natural exposure time on decrease of average molecular weight and chemical durability of HDPE macromolecules [7].

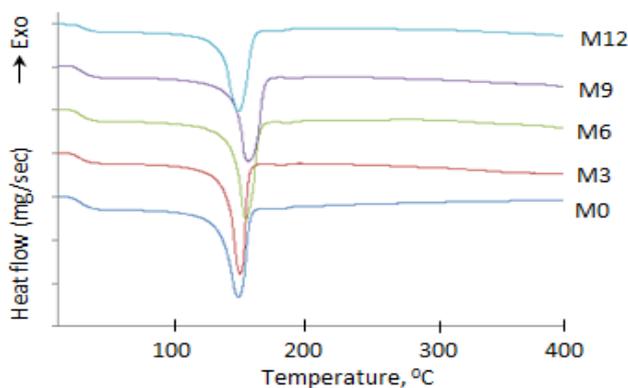


Figure 6: DSC curves of HDPE compound versus natural exposure time

Table 3: TG data of HDPE compound versus natural exposure time

Samples	T_{ini} , °C	T_{max} , °C	Remained weight (%) at		
			400 (°C)	450 (°C)	500 (°C)
M0	463	467	89.55	56.75	3.45
M3	462	465	88.55	55.92	2.72
M6	455	459	87.46	54.82	1.22
M9	453	461	87.44	53.60	1.40
M12	451	460	86.77	52.27	1.07

Where, T_{ini} : initial degradation temperature,
 T_{max} : maximum degradation temperature

4. CONCLUSIONS

Some remarks related to the change of IR character, morphology, mechanical, thermal properties of HDPE compound samples exposed naturally in Dong Hoi-Quang Binh as follows.

1. Carbonyl index of HDPE compound is increased versus natural exposure time.

2. From 6 months to 12 months of natural exposure, the size of voids, cracks and holes on the surface and inside the structure of HDPE compound are bigger, larger and deeper in comparison with the original HDPE compound and the sample after 3

months of natural exposure.

3. Tensile strength and elongation at break of HDPE compound are decreased quickly while its Young modulus is increased in the first 3 months of natural exposure.

4. Melting temperature of HDPE compounds is decreased, and their melting enthalpy, relative crystalline degree is slightly increased during the first 9 months of natural exposure. Initial thermodegradation temperature, maximum thermodegradation temperature, remained weight of HDPE compound are decreased versus natural exposure time and aging temperature.

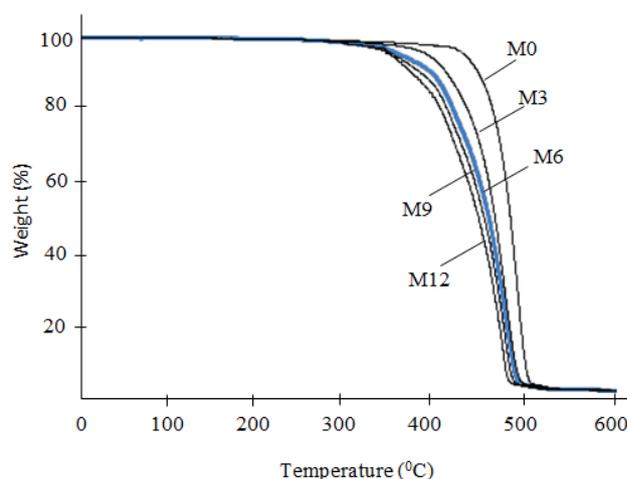


Figure 7: TG curves of HDPE compound versus natural exposure

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