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Degradation Effect of Different Environments on Characteristics of Calcium Carbonate Reinforced Polyethylene

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Abstract

High-density polyethylene (HDPE) is a thermoplastic made from petroleum. Deterioration of HDPE materials takes long time due to high molecular mass. In this study, neat HDPE and 5-50% calcium carbonate ($CaCO_3$) reinforced HDPE materials were exposed to different environments for aging. Aging was done in pure water, mineral oil, conventional unleaded gasoline, ammonium hydroxide (NH_4OH) and marine conditions. Exposing time of the samples under different liquid medium has been planned for 2, 4 and 6 month periods.

After realization of the exposing periods, TMA (thermomechanical analysis), MFI (melt flow index), SEM (scanning electron microscope) analysis were performed. Degradation effect of different aging conditions on characteristics of different weight rate calcium carbonate reinforced polyethylene was investigated. The MFI test results showed that MFI increases with higher calcium carbonate rates. Beside this, TMA test results showed that the glass transition temperature (Tg) decreases with higher calcium carbonate rates. Morphological investigation was done by scanning electron microscope (SEM).

1. INTRODUCTION

Polymers are increasingly used in the manufacture of different kinds of objects, such as car accessories, mechanical parts, pipes, etc., in substitution for metals and woods, which become increasingly expensive [1]. Polyolefins have become the most used thermoplastic within the industry [2]. Polyethylene is the polyolefin produced by polymerizing the olefin ethylene. Polyethylene is a semicrystalline material, whose structure is comprised by three major structured regions: the ordered crystalline region, the disordered (isotropic, interlamellar) amorphous region and the interfacial one [3]. Thermoplastic polymers are produced and consumed today in vast quantities. However, these materials are seldom used as neat polymers; they are usually compounded with mineral fillers [4-6]. The main purpose of incorporating fillers, such as calcium carbonate, into blends of polyolefins is to decrease costs [7,8]. It is known that this mineral filler can profoundly change the characteristics of a polymer system [4,9 and 10]. Nevertheless, the use of fillers provides us with a means of adjusting the properties of the resins to each specific application [2]. Mineral supplementation generally improves the hardness of polymers, but reduces the ductility and toughness values [8]. The microstructure and the interfacial interactions between nanoparticles and the surrounding polymer matrix play an important role to improve the mechanical properties of materials [11]. If a large amount of reinforcement is used, the mechanical and thermal properties are affected negatively. Fillers are used together with binding agents in order to eliminate these disadvantages [2,5,12]. One of the main limitations in application of polymers, particularly thermoplastic polymers such as high density polyethylene (HDPE) and polypropylene (PP), is their poor thermal properties compared to metals. The properties of HDPE and HDPE/$CaCO_3$ composite were investigated through thermo mechanical analyzer (TMA) tests by Sahebiana et al. [13]. They were found that calcium

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carbonate-reinforced polyethylene samples showed dimensional stability. Many investigations have been reported on irradiation of polymers and its effects on chemical structure and physical properties [14-17]. Effects of the main degradation products (gas, petrol and diesel) on polymers were investigated by Miskolczi et al. [18]. In fact, many investigations of waste polymer degradation of polyolefins with or without catalysts are published in the literature [18-27]. Although there are lots of experiments performed on polyolefine degradations, there is some lack of investigations about HDPE/$CaCO_3$. To compensate some lack of investigations about degradation effect of different aging conditions on characteristics of different weight rate HDPE/$CaCO_3$ were planned. Due to the fact that, the effect of different aging conditions on the mechanical and thermal properties of different weight rate HDPE/$CaCO_3$ was examined under TMA and MFI tests. Beside this, morphological properties of different weight rate HDPE/$CaCO_3$ were determined by SEM analysis.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

Type of polyethylene used in this study is manufactured by Solvay SA. This product is called ELTEXTUB172 commercially. ELTEXTUB172 which is a type of high-density polyethylene has been developed for use in the production of natural gas pipe by Solvay S.A. Calcium carbonate minerals used in this study are manufactured by Omya A.G. This mineral is called Omyalane 10 2M-OG commercially. Omyalane 10 2M-OG is used as reinforcement. Its grain size is 2 µm. This reinforcement can be used directly with polyolefins. HS-5430 sensitive balance manufactured by Hana Electronics Systems was used for preparing mixture ratios. Before injection molding of samples, calcium carbonate and HDPE granules were mixed properly. Neat HDPE and 5-50wt% $CaCO_3$ reinforced HDPE materials were produced. Samples containing different weight proportions of calcium carbonate were studied. Flow chart of the study can be seen in Fig 1.

2.1. Thermomechanical Analysis (TMA)

Thermal analysis (TA) is used to examine the differences caused by temperature changes of the material. There are various methods of thermal analysis. These methods include the measurement of the time dependence of the sample temperature [28]. Thermomechanical analyzer (TMA) measures the dimensional changes of a material as a function of temperature and time. The tests were carried out using a Shimadzu TMA-50 tester, following the ASTM E831 procedure.

Table 1. *Experimental settings of TMA-50 tester*

Metering mode	Expansion
Temperature range	From room Temperature to 135 ^oC
Measuring range	The amount of the probe movement: 2500 mm

Dimension of TMA sample is 6x6x3.2 mm. The samples were heated from room temperature to 135 ^oC by heating rate of 5 ^oC/min. Each experiment was repeated for at least three times. Experimental settings of TMA-50 tester can be seen in Table 1.

2.2. Melt Flow Index (MFI)

Melt Flow Index (MFI) is flow in grams that occurs in 10 minutes through a standard die of 2.09 mm diameter and 8 mm in length. The pressure is applied to the melt via a piston at a temperature of 190°C, using a 2.16 kg weight–piston pair, after a 6 min pre-heating treatment [29]. MFI investigations are performed by using a capillary canal melt viscometer Zwick 4105 according to ASTM D1238.

2.3. Scanning Electron Microscope (SEM)

SEM studies were carried out using a Jeol JSM-6060LV device. SEM micrographs of the samples unexposed to any environment and exposed to mineral oil, conventional unleaded gasoline, ammonium hydroxide (NH_4OH) and marine conditions were taken. Surface and inner section images of samples were taken at 1000x magnification.

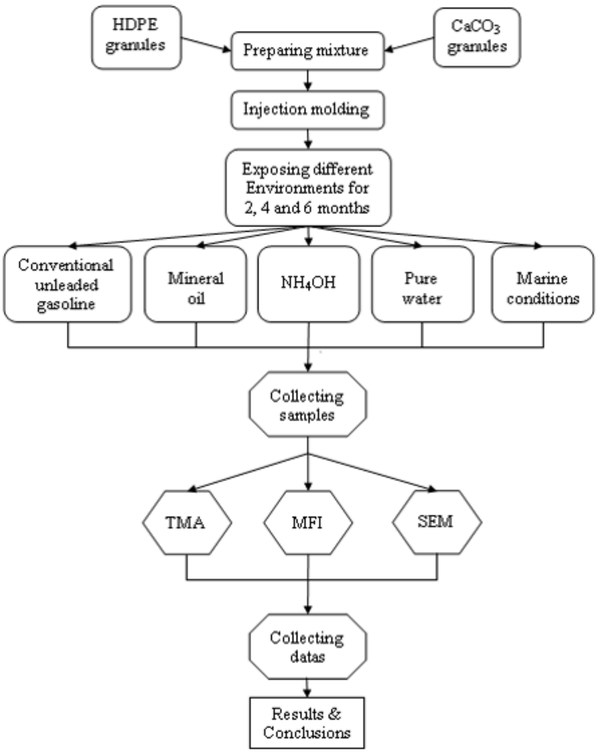

Figure 1. *Flow chart of the study*

3. RESULTS AND DISCUSSION

3.1. Thermomechanical Analysis (TMA) Results

The results of the TMA give very good tips about degradation mechanisms of polymers. In fact, unique degradation characteristics of each polymer can be revealed by TMA test analysis. Information about degradation characteristics of a polymer is useful in determining working conditions [30]. Therefore, the properties of neat HDPE and HDPE/$CaCO_3$ composites were analyzed through TMA tests. TMA graphs related to a sample which is unexposed to any corrosive environment are indicated in Fig. 2. According to the TMA curves given in Fig. 2, neat HDPE reinforced with 5 wt% $CaCO_3$ shows very good mechanical properties. The base material mixed with more than 5 wt% $CaCO_3$ shows adversely effects on mechanical properties of the HDPE composites.

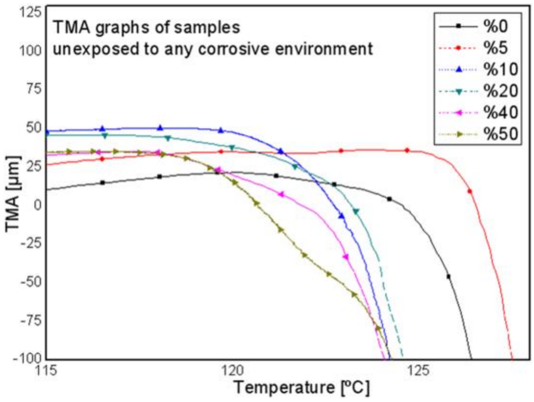

Figure 2. *TMA graphs of samples unexposed to any corrosive environment*

TMA graphs of the samples taken from the environment which is prepared by exposing to unleaded gasoline are presented in Figs. 3-a, b by considering their exposing time as 2 and 6 months, respectively.

After have completed the comparison process of Figs. 2 and 3, it has been detected that the best results on improving of mechanical properties has been got from the samples which are prepared by 5 wt% $CaCO_3$.

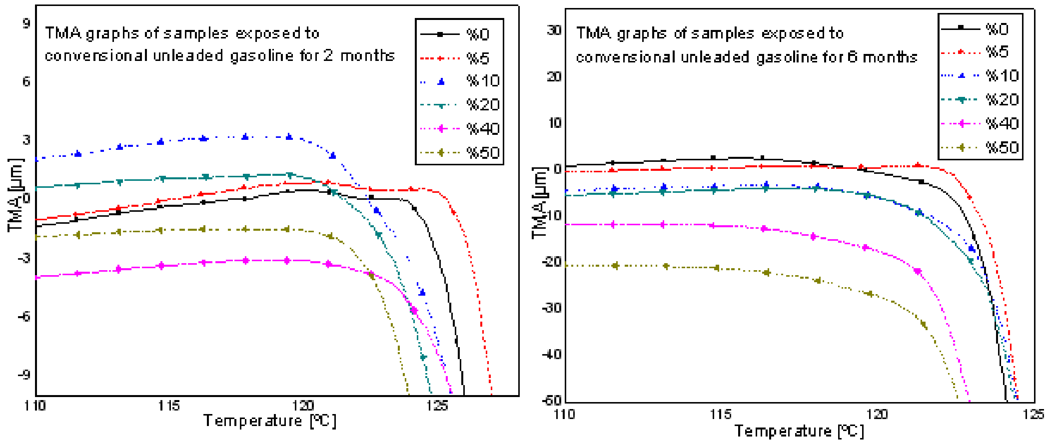

Figure 3. *TMA graphs of samples exposed to conventional unleaded gasoline*

On contrast that, the poor mechanical parameters were measured from the samples which are reinforced 50 wt% $CaCO_3$. The other curves keeping between upper and lower limits of the addition $CaCO_3$ such as 5 and 50 wt% shows some fluctuations but these can be accepted as generally no radical change on mechanical properties. The other interpretation has been performed by taking results of the samples unexposed and exposed to unleaded gasoline environment indicated in Figs. 2 and 3. Comparing of the curves shows that unleaded gasoline does not degraded mechanical properties of the samples.

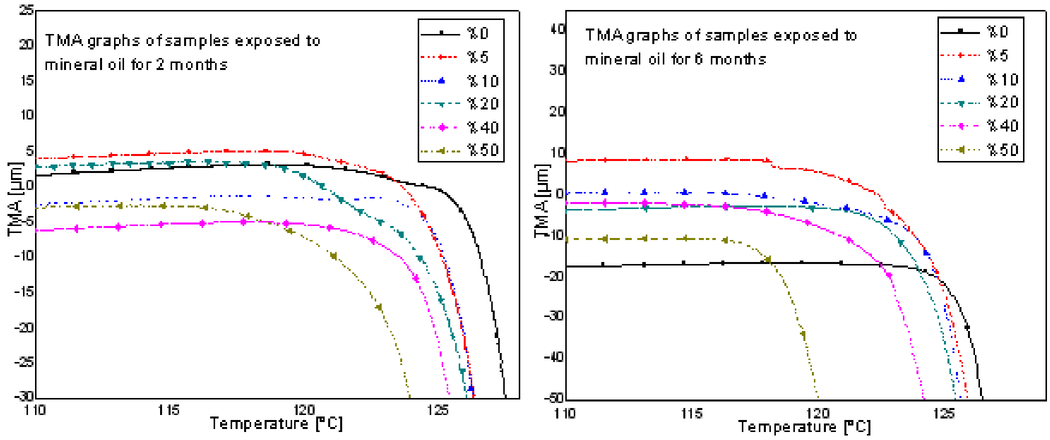

Figure 4. *TMA graphs of samples exposed to mineral oil*

The TMA graphs of the samples exposed to mineral oil, ammonium hydroxide, marine conditions and pure water environments are shown in Figs. 4, 5, 6 and 7, respectively. These graphs have been compared with TMA graphs of samples not exposed to any environment in Fig. 2. As a result of the comparison, addition of 5 wt% $CaCO_3$ has no positive effect on mechanical properties except unleaded gasoline environment. Moreover, additions of $CaCO_3$ in higher rates into HDPE have negative effects on the Tg values of the samples taken from the planned exposing environments.

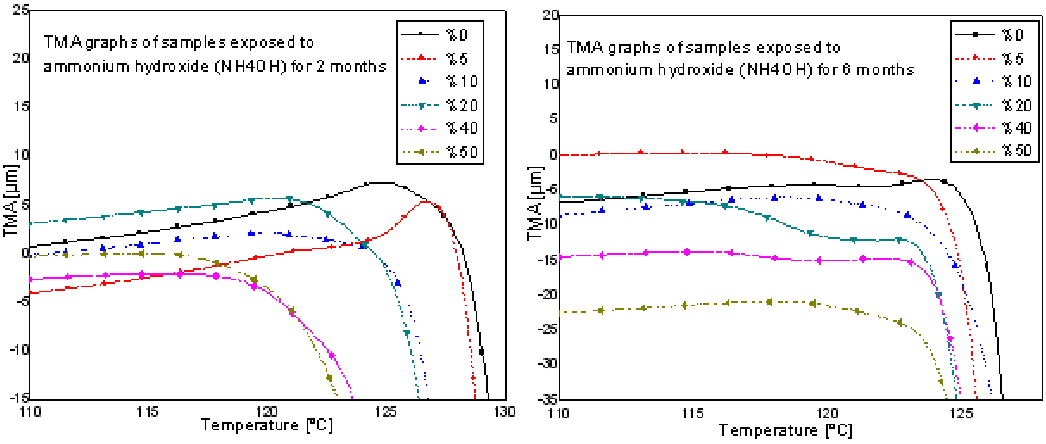

Figure 5. *TMA graphs of samples exposed to* NH_4OH

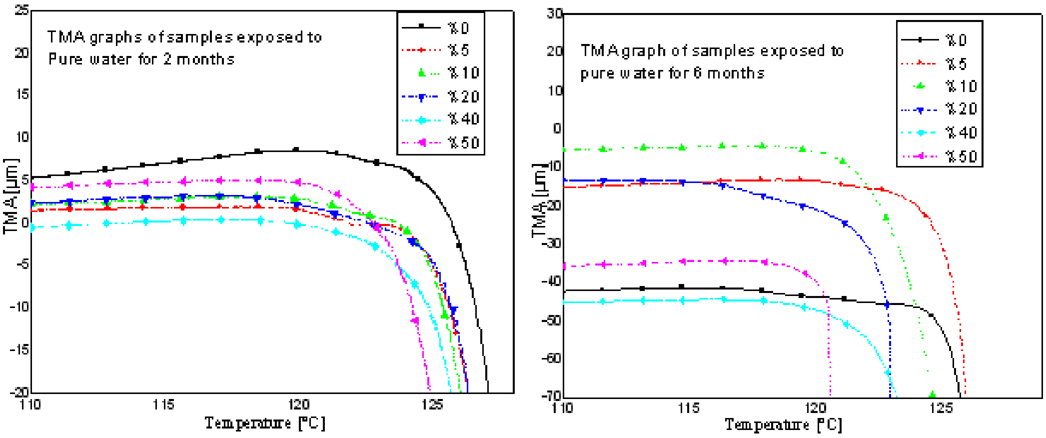

Figure 6. *TMA graphs of samples exposed to pure water*

Measured Tg values from the samples exposed to different planned test environments are shown in Table 2. According to these data, conventional unleaded gasoline has reasoned in reduction effect on Tg values of the test samples.

Table 2. *Tg values of the samples exposed to corrosive environments*

		Conventional Unleaded Gasoline		Mineral Oil		Ammonium Hydroxide (NH_4OH)		Pure Water		Marine Conditions	
	0 month	2 months	6 months	2 months	6 months	2 months	6 months	2 months	6 months	2 months	6 months
0%	125.2	124.3	123.7	127.3	126.1	126.4	126.8	125.3	125.2	127.7	127.3
5%	126.4	125.1	124.3	126.1	124.7	127.1	125.7	125.4	125.1	127.4	125.7
10%	124.1	121.4	123.5	125.2	123.6	124.9	124.8	125.3	123.7	126.2	125.6
20%	123.7	119.3	123.2	124.3	123.5	124.2	124.4	125.4	123.3	124.2	124.2
40%	120.2	118.3	122.1	124.1	122.1	123.1	123.2	122.1	123.2	122.2	124.2
50%	118.1	120.1	121.2	117.6	117.1	122.3	122.2	123.2	122.1	119.3	120.1

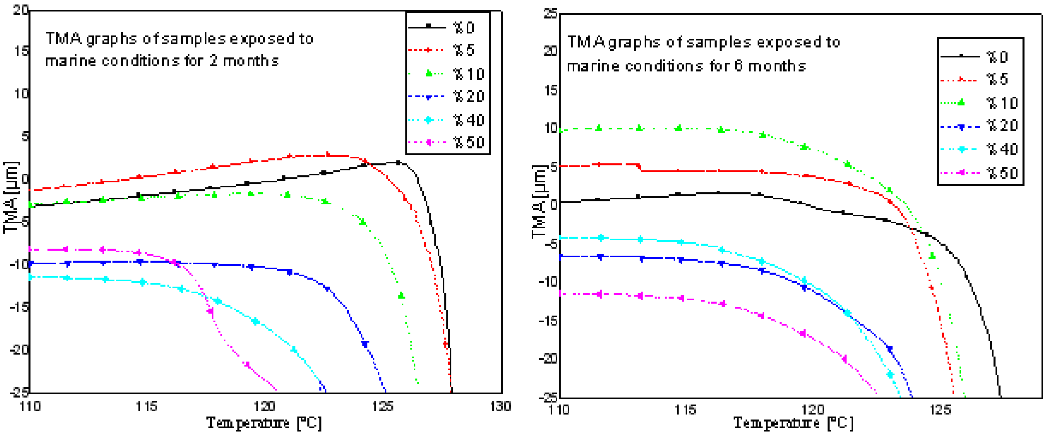

Figure 7. *TMA graphs of samples exposed to marine conditions*

The data collected from the samples exposed to mineral-oil and pure water given in Table 2, shows no significant increase or decrease of Tg values. Moreover, ammonium hydroxide and sea water environment have caused a significant increase in Tg values as also shown in Fig. 5 and Fig. 7. This increasing is around 3% of Tg values. The results of TMA test indicate dimensional stability of the all samples prepared from HDPE/$CaCO_3$ material. As a conclusion of TMA research, the findings indicate very good conformity with the earlier results presented in ref 13. On the other hand, the parameter of thermal expansion coefficient shows increasing regularly up to the glass transition temperature as seen in TMA Figs. 2–7.

Coupling agent and additive size are the two main factors on glass transition temperature of polymers. Different results have been reported in the literature on this phenomenon. Mojtaba et al. [31] studied on HDPE/maleic anhydride grafted polyethylene (PE-g-MA) nanocomposites containing 1, 3, 5 wt% of $CaCO_3$ nanoparticles. They reported that attendance of nanoparticles in PE matrix and addition of PE-g-MA led to enhancement of thermal stability. Zebarjad et al. [32] investigated on thermal behaviour of high density polyethylene and its nanocomposites reinforced with both uncoated and coated calcium carbonate. Their results showed that crystallization temperature of HDPE with addition of 10 vol% calcium carbonate increases, while addition of stearic acid causes to decrease it. Sirin et al. [33] investigated on the influence of filler component on mechanical properties and thermal analysis of PP-LDPE and PP-LDPE/DAP ternary composites. Their results showed that thermal stabilities of the composites increased usually with increasing $CaCO_3$ content. HDPE/$CaCO_3$ blends with and without an impact modifier (POEg) were investigated by Yang et al. [34]. They reported that the glass-transition peak of HDPE decreases at the same time as the POEg peak increases. The addition of an agent and nano-particles enhance activation energy and degree of conversion. Thus, Tg value of modified blends with an agent increases. Otherwise the Tg value of neat blends tends to decrease.

3.2. Melt Flow Index (MFI) Results

MFI Melt flow index is an assessment of average molecular mass. It is also an inverse measure of the melt viscosity. Knowing of MFI value of a polymer is vital to control its processing. MFI is an effective method for characterizing the type of polymer degradation (Chain breaking, chain scissions, crosslinking etc.). And it is known that the presence of very few high molecular weight tails or long-chain branching strongly affect to rheological and final properties [35].

In our study, determination of the MFI parameters has been determined Zwick type 4105 test equipment. Depending on the data collecting from MFI tests related on the HDPE, the observed structural modifications did not influence on the MFI parameter. Although literature mentions that many factors affect to flow properties of the HDPE. These factors are molecular weight distribution, co-monomers, chain branching and crystallinity. The MFI values are increased by decreasing flow resistance. This mechanism has been also approved by the research given in ref. 36, which also explains that different degradation phenomena mainly like “chain scissions” and “chain branching” took place on HDPE materials. These two facts are usually responsible for the increase and the reduction of the MFI parameter, respectively [36].

The MFI results were examined according to the different environments and additive quantity of $CaCO_3$. The MFI results of samples exposed to NH_4OH and marine conditions are shown in Fig. 8. These figures indicate that the MFI values of samples containing 0—5 and 10 wt% $CaCO_3$ show smooth horizontal trend for different exposing times 2, 4 and 6 months up to 20 wt%. After examination of curves it can be seen easily that addition rate of $CaCO_3$ up to 20 wt% has no affectivity on MFI parameter. Nevertheless, after passing wt% 20 the radical increasing of the parameter MFI has been observed.

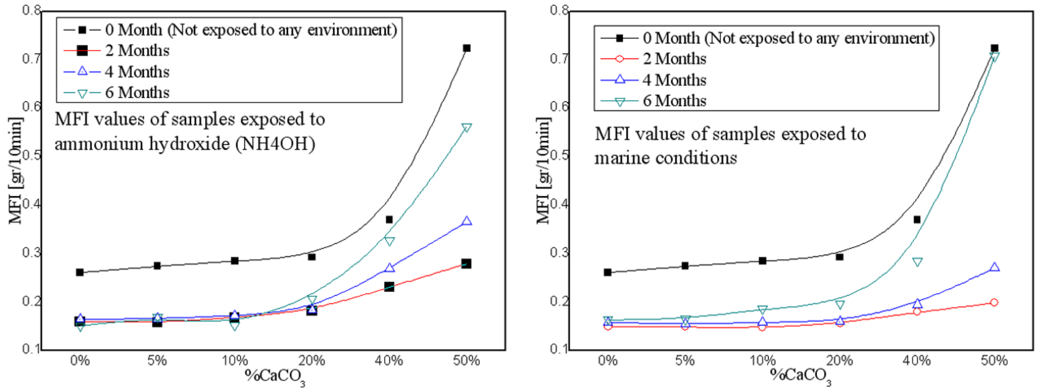

Figure 8. *MFI values of samples exposed to ammonium hydroxide (NH_4OH) and marine conditions*

After having completed the analysis of Fig. 9 and then comparing with Fig. 8, a similar trend has been detected easily. However, the data for Figs. 8 and 9 were collected from the samples exposed to different environments.

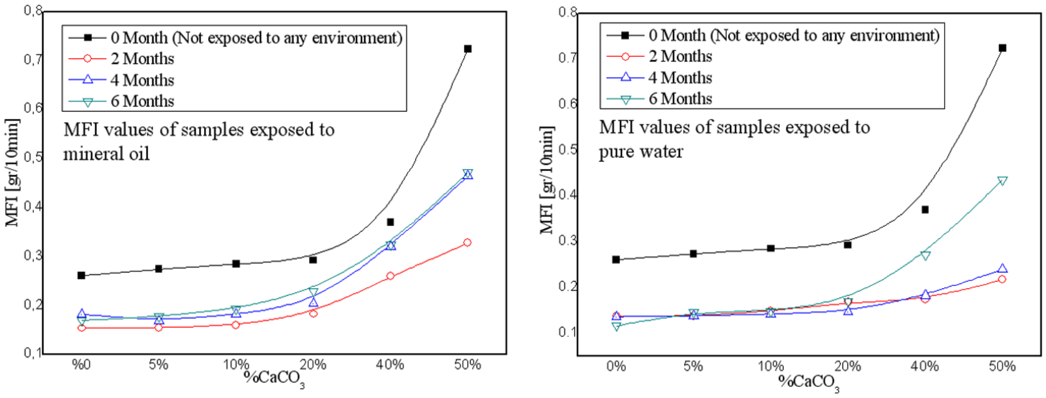

Figure 9. *MFI values of samples exposed to mineral oil and pure water*

Smooth regular increasing of MFI parameters for the samples exposed to NH_4OH, pure water, marine conditions and mineral oil environments show time-depended trend. According to the values presented in Fig. 10, MFI values of samples exposed to unleaded gasoline have little effects on the parameters with exposing time. Changes are independent of the amount of $CaCO_3$. Content of 40 and 50 wt% $CaCO_3$ additives have been exposed to unleaded gasoline, which haven't shown a radical increase on the MFI parameters unlike the other environments. According to MFI results, addition of $CaCO_3$ in HDPE composites should be used up to 10 wt% for using different environments other than unleaded gasoline.

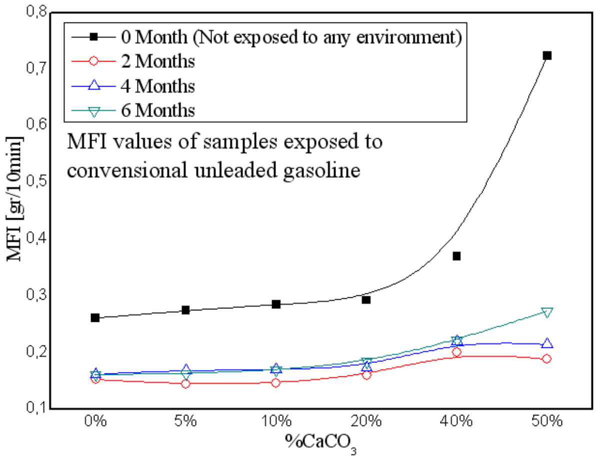

Figure 10. *MFI values of samples exposed to conventional unleaded gasoline*

Finally, MFI parameters have increased independent on both environment conditions and the exposure time as shown in Figs. 8, 9 and 10. The reason of MFI increases are the chain scissions that have taken place because of degradation effects of environments. In conclusion, flow resistance decreases with higher $CaCO_3$ weight rates. For this reason, MFI parameters of higher $CaCO_3$ rates have the highest values compared to other rates.

3.3. SEM Micrographs Analysis

Morphology of each sample was observed with scanning electron microscope. Analysis of Inner and outer surfaces of the samples taken from the neat HDPE and HDPE/$CaCO_3$ composites were carried out to detect changes due to planned environmental conditions. Outer regions of the samples are in direct contact with the test medium. Surface quality of the samples before exposing to environmental conditions has been detected as a very good in the aspect of roughness criteria. On the other hand, the sample examined after exposing to test mediums shows some defects appeared on its surface as well as some chain degradation. Chain system deteriorations on the surface of the samples are indicated in Figs. 11-13.

After having completed the analysis of the figures taken from the samples, it has been pointed out that increasing of the quantity of the $CaCO_3$ can accelerate the degradation. The reason is due to the increasing the interfacial distance of the HDPE-$CaCO_3$. In the exposing time, the samples and medium interactions was triggered by environmental conditions so that the distance increases. This phenomenon has been confirmed by the result of TMA and MFI tests.

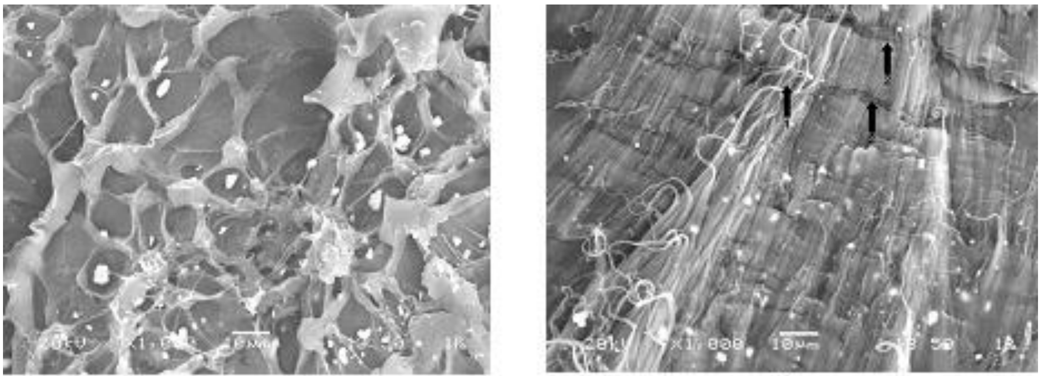
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Figure 11. *Inner (a) and surface (b) section images of 5 wt% content of $CaCO_3$ in HDPE/$CaCO_3$ samples exposed to mineral oil at 1000x magnification*

Moreover, chain branching and micro-cracks were observed in Figs. 11-13. Chain scissions are precursor to formation of micro cracks. These micro-cracks detected in the samples shows time dependency related to the exposing time. Degradation types defined above are shown in the micrographs with the help of the black arrows. Chain branching and micro-cracks were indicated with number 1 and 2, respectively.

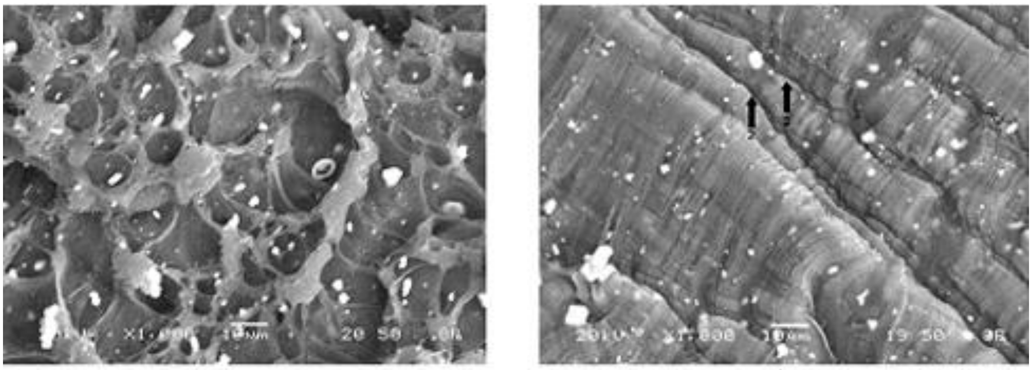
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Figure 12. *Inner (a) and surface (b) section images of 10 wt% content of $CaCO_3$ in HDPE/$CaCO_3$ samples exposed to ammonium hydroxide (NH_4OH) at 1000x magnification*

Images taken from the inner (a) and outer section of the samples (b) which have content of $CaCO_3$ with 5 wt% in HDPE/$CaCO_3$ exposed to mineral oil are shown in Fig. 11. This image clearly explains that deterioration of the material has occurred on the outer surface of the samples due to direct contact with the exposing medium.

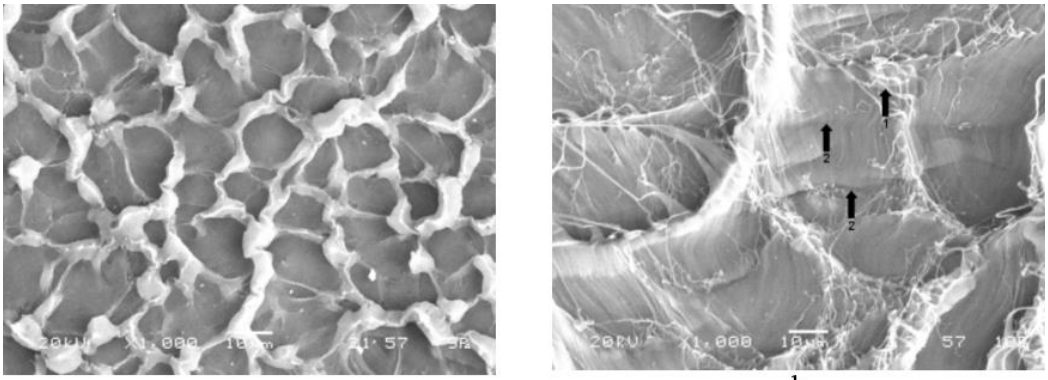
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Figure 13. *Inner (a) and surface (b) section images of 0 wt% content of $CaCO_3$ in HDPE/$CaCO_3$ samples exposed to conventional unleaded gasoline at 1000x magnification*

On contrast that the analysis for detecting deterioration level in the inner part of the samples do not show any radical indicative evidence such as chain branching and micro-cracks. Images taken from the inner (a) and outer surfaces (b) of the samples which have content of $CaCO_3$ with 10 wt% in HDPE/$CaCO_3$ exposed to NH_4OH are shown in Fig. 12. In this figure the coding of micro-cracks and chain branching are performed as 1 and 2, respectively.

4. CONCLUSION

After interpretation of the study datum, the results can be summarized as below:

I- Thermal and mechanical properties of the samples were affected by all the planned test environments. The MFI values of samples containing 0, 5 and 10 wt% $CaCO_3$ have showed radical decreases. The time periods and $CaCO_3$ rates are detected to be ineffective parameters on these radical decreases. Nevertheless, the effects of time periods are observed to be effective parameters for 20 wt% content of $CaCO_3$. Moreover, MFI values of 40 and 50 wt% content of $CaCO_3$ samples have shown a radical increase.

II- The MFI results of samples exposed to ammonium hydroxide (NH_4OH), pure water, marine conditions and mineral oil environments have shown time-dependent increase. They also have increased with higher $CaCO_3$ contents. It is also detected that addition quantity of the $CaCO_3$ into the HDPE composites should be used up to 10 wt% under the effects of planned test environments.

III- Tg values and coefficient of thermal expansion show generally increasing at all the mediums until the glass transition temperature.

IV- SEM analysis on the inner and outer surfaces of neat HDPE and HDPE/$CaCO_3$ composites were carried out to observe the changes caused by environmental degradations. After performing of the analysis, occurring of chain branching and micro-cracks were observed. Chain scissions are precursor to formation of micro cracks. These micro-cracks grow with increasing exposure time. It is clear that the increase of $CaCO_3$ can accelerate the degradation because of the HDPE-$CaCO_3$ interfacial distance increasing due to environmental interactions of the material. This phenomenon has been confirmed by the result of TMA and MFI tests.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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