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Study on UV resistance of high density polyethylene composite using waste gypsum

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ABSTRACT

Every year, a large amount of waste gypsum, a by-product of fertilizer production, was produced and landfilled that increasing the harm to the environment. In this study, for the purpose of utilizing waste gypsum, it was studied as the filler in blend of high density polyethylene (HDPE) and ethylene vinyl acetated (EVA) with anti UV additives in order to improve the mechanical strength and lifespan of this composite. After using ethylene bis stearamide (EBS) to modify waste gypsum, modified waste gypsum (mGyp) and anti-UV additives at various contents were dispersed into HDPE/EVA blend by melt-mixing method to obtain HDPE/EVA/mGyp composites. As the results, the color difference and tensile strength of composite using additives did not changed much after 20 cycles of accelerated weathering test. In the presence of anti-UV additives, the photodegradation process was inhibited by showing the low carbonyl index of composite compared with samples without additives. Beside, the structure of composite using anti-UV additives is smooth and without cracks after accelerated weathering test as observed in SEM images. That led to the tensile strength of sample did not change much.

Introduction

For many years, the difficulty in dealing with waste gypsum as solid waste is not only the problem in Vietnam's fertilizer industry, also in many countries in the world[1,2]. This problem requires the scientific and technological solutions to minimize the impact of waste gypsum on the environment. Recently, waste gypsum has been successfully applied in the manufaction of sanitary ceramics, building materials, fertilizer, or fillers for rubber and polymer-composite materials[3,4,5]. For thermoplastic processing, the traditional filler materials such as $CaCO_3$, talic powder, black coal powder, clay particles, bentonite,… are very popular. Unfortunately, their sources come from nature that causing climate change during exploitation. Besides, the price of the fillers become higher day-by-day, so using waste gypsum as filler for polymer composite materials does not only contributes to solving the problem of environmental pollution but also has scientific significance, improves the durability of composite materials and increases economic efficiency[6,7]. The use of gypsum in combination with anti-UV additives can expand the applicability of composite products, especially in environment with high UV enery such as Vietnam. However, gypsum and polymer do not mixed well in its composite due to the difference in hydrophobicity. Then, using organic

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compounds to modificate the surface of waste gypsum, the compatibility between gypsum and polymer improved. This could enhance the mechanical, weather resistance and reduce the production cost of composite.

Experimental

Materials and sample preparation

High density polyethylene (HDPE) and ethylene vinyl acetate (EVA) copolymer resin were supplied by Honam Petrochemical Corporation (Korea) with density of 0.935 and 0.930 g/cm3, respectively. Ethylene bis stearamide (EBS) was purchased from Merk Company with purity of 99.8%. Hindered Amines Light Stabilizers (HALS 791) and ultraviolet light absorber (UVA 531) were products of Shanghai Deborn Co.ltd (China) with purity higher than 99.5 %. Waste gypsum is a by-product of DAP-Vinachem Limited Company (Vietnam) with the particle size range in 20 – 30 µm.

Modification of gypsum by EBS preparation: Original waste gypsum (Ogyp) was mixed with 4 % EBS (compared to the mass of gypsum) at 170 0C for 15 minutes, then the mixture was washed in Soxlet device using a mixture of ethanol and water (50: 50) to remove residual EBS. The obtained modified waste gypsum (Mgyp) was dried at 80 0C in a vacuum oven before melt mixing with resin.

Composite preparation: First, HDPE, EVA and gypsum are weighed in proportion 85: 5: 10 to ensure a filling factor of 0.8 in mixing chamber. This mixture is then pre-mixed to ensure dispersion before introduced into the HAAKE Rheomix melting mixer with the following processing conditions:

Table 1: Additives ratio in composite samples HDPE/EVA/gypsum

Number	Sample	HALS content (wt.%)	UVA content (wt.%)
1	HDEV	0	0
2	HDEV33	0,3	0,3
3	mGyp0	0	0
4	mGyp06	0	0,6
5	mGyp60	0,6	0
6	mGyp33	0,3	0,3
7	OGyp33	0,3	0,3

Characterization

Melting rheology data was collected by using Polylab simulating software connected to Haake Rheomix 610 equipment (Germany). The tensile strength was obtained as average values by measuring each sample piece with five times at a crosshead speed of 50 $mm.min^{-1}$ in Zwick Tensiler 2.5 (Germany) according to ASTM D 638 standard. Fourier transform infared spectrum was carried on Fourier NEXUS 670 (USA) in range of 4000-400 cm^{-1} at 4 cm^{-1} resolution and 32 scan signal averaging. The UVCON Model UC-327-2 Weatherproof accelerator was used to evaluate the weathering resistance of samples according to ASTM G 154. Color change of sample was recorded by Cielab color metter 6650.

Results and discussion

Color difference of composite samples after accelerated weathering test of composite samples

Table 2: Color difference of HDPE/EVA/gypsum composite at various gypsum contents.

Sample	Order	Color difference		
		ΔL	Δa	Δb
HDEV	1	2,376	0,126	0,714
HDEV33	2	0,708	-0,224	0,728
mGyp0	3	1,064	-0,556	-0,068
mGyp06	4	0,742	-0,204	-0,342
mGyp60	5	0,404	-0,11	-0,244
mGyp33	6	0,368	-0,364	-0,062
oGyp33	7	0,648	0,058	0,026

Color fastness is very important for plastic products in the natural environment with high UV energy and moisture. In accelerated weathering test, under UV irradiation cycle, the polymer chains were decomposed into polar groups containing C=O and C=O radicals and the degradation productions were removed away during the condensation cycle. The cycles repeated causing the discoloration of samples. From Table 2, it is shown that the HDEV sample has the strongest discoloration, which is shown by the increase in and values. Although, by adding waste gypsum, the color fastness of the sample is still relatively high.

In the presence of the HALS 791 and UVA 531 additives, the color difference was significantly reduced. It shows that samples containing additives have good anti-discoloration ability, which is most evident in the HAL: UVA ratio of 6:0 and 3:3. In addition, color fastness was also improved in composite using Mgyp. In this case, HALS 791 reduced the free radicals generation during UV test while UVA 531 converted UV energy to thermal energy that harmless to materials[8,9].

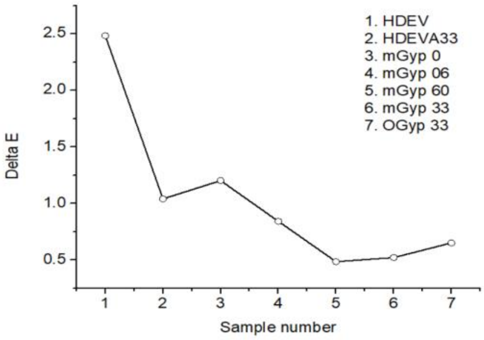


Figure 1: Color change during accelerated weathering test of composite samples

Tensile strength of composite samples after accelerated weathering tes

Figue 2 below presents the tensile strength of composite samples using Ogyp, Mgyp and anti-UV additives at various contents after 0, 10 and 20 cycles of accelerated weather testing. Before weathering test, the tensile strength of HDEV was highest. This property decreased by addition of waste gypsum and anti UV additives. But after 10 and 20 cycles, tensile strength of HDEV rapidly decreased from 26.04 to 13.8 MPa. In presence of gypsum in the composites, the tensile strength of mGyp0 decreased to 10 MPa. It is difference in composite using HALS 791 and UVA 531, these tensile strengths remained quite high for mGyp06 and mGyp33.

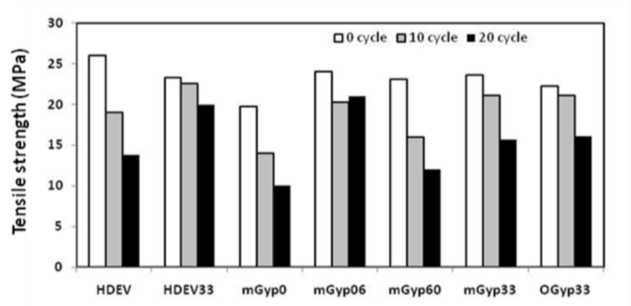


Figure 2: Tensile strength of composites after 0, 10 and 20 cycles of accelerated weathering test

During accelerated weathering test, the tensile strength of composite decreased due to the degradation of polymer by ultraviolet light, high tempearature and moisture. This can be explained by the NH group in HALS791 could interact with the C=O group in EVA and EBS on the surface of the gypsum, improving the dispersion of the gypsum in the resin matrix that made the material more homogeneous.

FTIR analysis of the composite before and after accelerated weathering test.

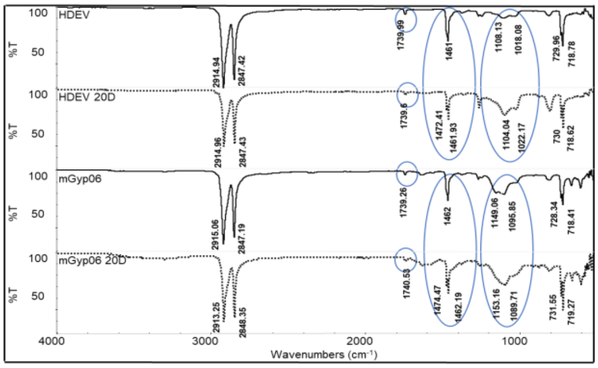


Figure 3: FT-IR spectra of samples before and after weather acceleration

Figure 3 shows the FT-IR spectrum of the HDEV and mGyp06 before and after UV test. Samples represent the functional groups present in HDPE. EVA and gypsum. The peak region 2915 cm^{-1} is characteristiced of asymmetric oscillations of CH_2 and CH_3 groups. CH_2 deformation is located at 1462 cm^{-1}. While the wavenumber at 1133-1157 cm-1 is typical for valence oscillations of SO_4^{2-}.

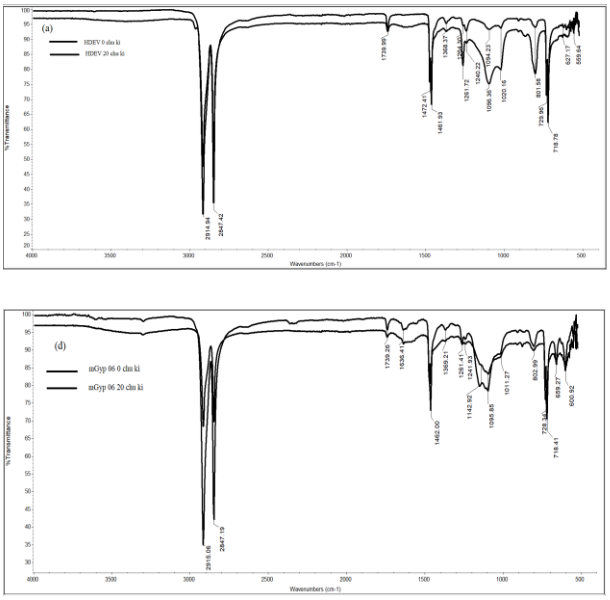


Figure 4: FTIR peaks comparision of HDEV and Mgyp06 before and after 20 cycles of accelerated weathering test

After testing, the infrared spectrum of HDEV has a significant change as seen in Figure 4. In which the peak intensity at 1739 cm^{-1} of the C=O group increases. which shows that the photodegradation occurs strongly with HDPE/EVA. While the peak intensity of SO_4^{2-} group at about 1153 cm^{-1} had a significant de crease. This can be explained by gypsum leaching during the water condensation cycle in UV test. EVA. and HDPE materials are protected by the presence of anti-UV additives. That proved the effective protection of the structure of the material against the effects of weather which improves the lifespan of the material.

To evaluate the photodegradability of sample in accelerated weathering test, the carbonyl index (CI) was used to compare the change before and after the test. Carbonyl index is calculated as the ratio of peaks' height at particular wavenumbers or areas of particular peaks. [10]

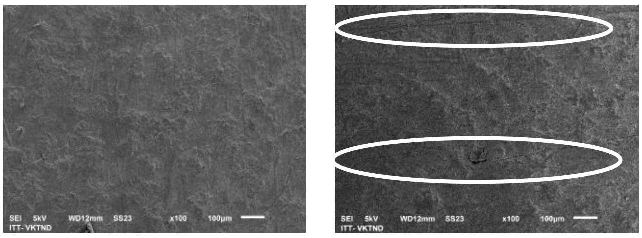
Table 3: The carbonyl index of composite before and after accelerated weathering test

Sample	ST	CI before UV test	CI after UV test	%
HDEV	1	34.399	53.005	154
HDEV33	2	70.577	49.991	71
mGyp0	3	58.948	75.503	128
mGyp06	4	37.883	66.851	176
mGyp60	5	54	17	31
mGyp33	6	54.730	37.633	69
OGyp33	7	31	28	90

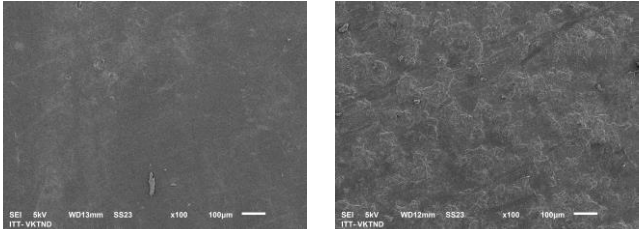
As seen in Table 3, the carbonyl index of the sample is inversely proportional with the content of anti-UV additives. In which. the samples without anti-UV additives had a large change in CI like HDEV (154 %). which showed that the photodegradation strongly occurred. In contrast. the samples with the additive had a much lower change in the carbonyl index. especially in the HDEV33, mGyp33 or mGyp60 samples which decreased to 71, 69 or 31 %, respectively. This proved that HALS 791 and UVA 531 has enhanced to UV resistance of the materials.

Scanning electron microscopy (SEM) images of the samples during the accelerated weathering test

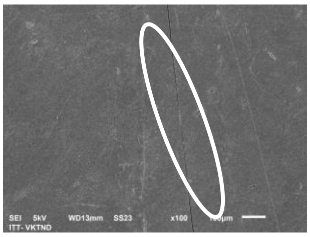
The Figure 5 shows the surface of the samples during the weather acceleration. At 0 cycle, there is no crack on the surface of the mGyp0 sample (Image a). After 20 cycles of weathering test, some cracks appeared on the surface of mGyp0. Naturally, under the effect of UV light in accelerated weathering chamber, the resin in composite was decomposed which led to the decrease of mechanical properties. By using anti UV additives, UV resistance of samples were improved as seen in Images C, D, E. Especially, when combine UVA-531 and HALS-791 at contents of 0.3 % each in the composites, the surface of composite became smooth and no crack (Image C).



A. mGyp0 0 cycle
B. mGyp0 20 cycles



C. mGyp33 20 cycles
D. mGyp60 20 cycles



E. mGyp06 20 cycles

Figure 5: SEM images of samples surface after 20 cycles of accelerated weathering test

Conclusion

UV resistant HDPE/waste gypsum composite was prepared using melt-mixing method. In presence of anti UV additives such as UVA-531 and HALS-791, the tensile strength composite were remained. Carbonyl index showed the effect of anti UV additives in decomposition process that prolong the lifespan of materials.

Acknowledgments

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