

STUDY ON THE RHEOLOGICAL, PHYSICO-MECHANICAL AND THERMAL PROPERTIES OF POLYVINYLCHLORIDE/WASTE-GYPSUM POLYMER COMPOSITES

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1. INTRODUCTION

Among the commercial polymeric materials, polyvinylchloride (PVC) is a common polymer material that has been widely used for producing industrial goods and household implements as well. Addition to the advantages such as high Young's modulus, high tensile strength, high optical stability, good weathering durability, compatible with plasticizer, fire resistance and so on, PVC also has some drawbacks such as: brittleness, low thermal stability, difficult processing Due to its inherent disadvantages, PVC is subjected to some limitations in certain applications [1, 2]. In fact, the PVC products are usually the combination of PVC resin and some important additives during processing like thermal stabilizers, processing aids, plasticizers, inorganic reinforcement materials ... to improve their properties and enlarge their applications. Generally, in the commercial PVC compounds, the inorganic materials play a role as fillers, take the high contents and strongly affect to the nature and the structure of the products and reduce the costs, the common fillers such as CaCO_3 , talc, carbon black, ZnO ... [3]. This research has mentioned about a potential inorganic materials, waste-gypsum powder that can be used as filler in the PVC matrix.

Table 1. Chemical compositions of waste-gypsum (wt.%)

Components	Average contents	Standard contents	Minimum contents	Maximum contents
Phosphate	1.30	0.79	0.32	3.89
Soluble phosphate	0.93	0.68	0.19	3.01
CaO	33.7	17.37	29.00	36.30
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	23.00	25.76	10.90	36.70
CaSO_4	41.07	55.40	23.60	51.35

Gypsum is a by-product of the production of phosphoric acid. The wet phosphoric acid obtained by dissolving phosphate ore into sulfuric acid in an artificial way, Namhae Chemical Company has been achieved the wet phosphoric acid according to this way to produce phosphatic fertilizers. A lot of obsolete gypsum getting in this process has been buried in the large lands. There for, use of waste-gypsum is not only a partial solution to environmental and ecological

problems; it significantly improves the microstructure, and consequently the durability properties of PVC products, which are difficult to achieve by the use of pure PVC resin. Gypsum consists of a dihydrate sulfate calcite ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrate sulfate calcite ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), calcite oxide (CaO), phosphate, and with particle size less than $50 \mu\text{m}$. The components of waste-gypsum using in this study showed in Table 1 [4].

Waste-gypsum is quite soft, it ranked at the second position in the Mohs hardness [3,5]. Among the inorganic materials, this is a remarkable property of waste-gypsum since the abrasion of polymeric composites depends on the hardness of inorganic dispersive fillers, the lower hardness of inorganic filler is, the higher abrasive strength of composite reaches [6]. In recent years, there have been some researches those investigated the applications of waste-gypsum to the field of fabrication of polymeric composite materials [7-11]. However, the study of the effect of waste-gypsum contents on the properties and structure of thermoplastic composites has been not much interested in Vietnam so far. Waste-gypsum particles are strong hydrophilic materials, therefore, the aggregates of particles usually occurs in the polymeric structure due to their high surface energy and the interaction between particles. Hence, to improve the dispersive ability and the adhesion of waste-gypsum in PVC matrix, waste-gypsum particles were modified by using sodium dodecyl sulfate (SDS) as surfactant. The S=O groups of SDS can be interact with the S=O of CaSO_4 and bonding with CaO particle to form an organic layer on the surface of particle. Owing to that organic layer of SDS on the surface, MWG particles are hydrophobic and more compatible than original waste-gypsum particles in the polymeric matrix [12]. In this research, we mainly present the effect of modified waste-gypsum (MWG) contents on the rheological, physico-mechanical and thermal properties of the PVC/MWG polymeric composite materials. Four kinds of rigid PVC/MWG composite with different MWG contents were prepared by melt blending method. The morphological development of the PVC/MWG polymeric composite samples is also discussed in this paper.

2. EXPERIMENTAL

2.1. Materials

PVC pellets (suspension polymerization PVC, LS-100, DP = 1000) was provided by LG Chemical Co., South Korea. Waste-gypsum samples were kindly supported by Namhae Chemical Co, Yeosu City, South Korea with particle size less than $50 \mu\text{m}$. Prior to use, waste-gypsum particles were washed by water for eliminating the contaminants and dried to stable weight. Owing to the low hardness of waste-gypsum particles, so they were ground and sieved to the smaller particle size (about $1-3 \mu\text{m}$) for the better interaction with surfactant. The modification of waste-gypsum was carried out at laboratory by using an internal mixer Banbury (Farrel Co., USA). Dried waste-gypsum and sodium dodecyl sulfate (a ratio of sodium dodecyl sulfate of 3 wt.% used) were mixed at $80 \text{ }^\circ\text{C}$ for 3 hours and rotor speed at 100 rpm. After mixing, modified waste-gypsum (MWG) material was carefully washed by water-alcohol (1:1) for removing the odd surfactant. Lubricant (Wax polyethylene powder) and thermal stabilizer (liquid barium-zinc-phosphite and calcium-zinc-phosphite complexes, ratio as 1:1) were purchased from Lucky Co., Sunchon City, South Korea. The component ratios of PVC/MWG and additives were shown in Table 2.

Table 2. Sample codes and compositions of PVC/MWG composites

Samples	PVC (g)	Lubricant (g)	Stabilizer (g)	MWG (g/wt.%)
PVC0	100	0.5	3.0	-
PVC1	100	0.5	3.0	20.0/16.26
PVC2	100	0.5	3.0	30.0/22.56
PVC3	100	0.5	3.0	40.0/27.97
PVC4	100	0.5	3.0	50.0/32.67

2.2. Preparation of PVC/MWG composites

First of all, for each sample, PVC, MWG and processing additives were mixed by an internal mixer Banbury (Farrel Co., USA) at 80°C, rotos speed of 70 rpm for 7 minutes. And then, the compounds were roll-milled by an instrument model KR-250 (Nishimura Co., Japan) at 175°C for 5 minutes. After that, the melt compounds were quickly molded into sheets of 3 mm in thickness by hot pressing machine (Wabash, G302-BCLX, USA) at 175°C and 20 MPa for 3 minutes, followed by cooling to room temperature at 5 MPa. The sheets were prepared for the structure characterization and the measurements.

2.3. Measurements

Determination of torques of melt-mixing of composites (expression of relative melt viscosity) versus time was carried out in Haake PolyLab System 600 with the chamber capacity of 69 cm³, a couple of Roller rotors at 60 rpm, start temperature at 180°C for 10 minutes. The tensile strength and the elongation at break were performed using a Universal Tensile Tester (Instron, series IX automated materials testing system, USA) according to ASTM D638 standard. The tensile test was conducted and obtained the average value by measuring each sample piece five times at a crosshead speed of 10 mm/min. To measure the impact strength of the sample pieces, the impact strength test (Izod impact, Grove Co., USA) was conducted according to ASTM D256-97 standard. For impact strength, the results also obtained the average value by measuring each sample piece five times with a hammer speed of 3.5 meter/second and pendulum weight of 0.818 kg at room temperature. Differential scanning calorimeter (DSC) analysis was conducted on a DSC2, Dupont 2000 (TA Instrument Co., USA) at a heating rate of 10°C/min under a flowing nitrogen atmosphere. The temperature scan ranged from room temperature to 300°C. Thermogravimetric analysis (TGA) was conducted on a TGA, Dupont 2000 (TA Instrument Co, USA) at a heating rate of 10°C/min under a flowing nitrogen atmosphere. The temperature scan ranged from room temperature to 600°C. The polymer composites for scanning electron microscopy (SEM) observation were coated with gold-palladium prior to examination. The SEM micrographs were obtained by using Jeol JSM-T330 system (Japan).

3. RESULTS AND DISCUSSION

3.1. Rheological study and processing characteristics of PVC/MWG composites

The torque measurement has been successfully used to obtain qualitative information concerning the relative melt viscosity and mixing process of the polymeric composites. Figure 1 presented the relationship between the torque and the mixing time of PVC0-PVC4 composites.

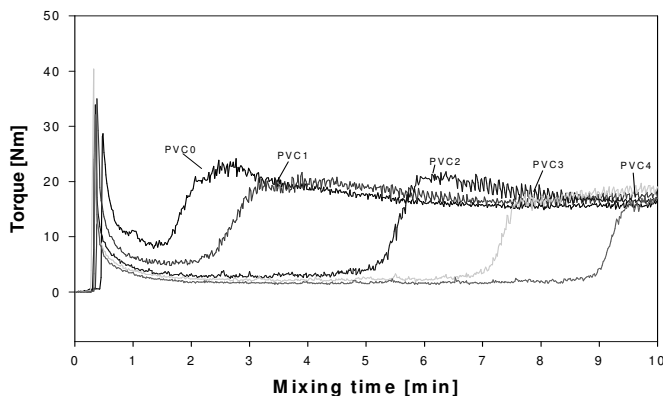


Figure 1. Torque curves of PVC/MWG composites with the different MWG contents

From Figure 1, the plots of torque of mixing for different ratios of PVC/MWG composites (or relative melt viscosity of composites) distinctly expressed thermo-mechanical mixings and cross-linking processes of PVC in those composites. During first minute, the peaks depicted the loaded materials into the mixing chamber, and then, the torques gradually decreased until ground values. If MWG contents of composites increased, the ground values decreased and the mixing time of the compounds was longer. When cross-linking reactions of PVC matrix took place, the fusion peaks occurred. As shown in Figure 1, the fusion peaks of PVC0, PVC1, PVC2, PVC3, and PVC4 reached at around 1.7 min., 2.5 min., 5.1 min., 7.1 min., and 9.1 min., respectively. Also, the intensities of torque at the fusion peaks are not the same for those composites, and they decreased with the increase of MWG contents. These can be thought that the increase of MWG contents in compositions which led to the temperature transmissive process from hot walls of chamber to PVC matrix phase was longer than those of the smaller MWG content in the compositions. On the other hand, the higher MWG ratios were loaded; the mixing processes became more difficult. Actually, these results is important information for controlling and setting up the processing parameters such as processing temperature, processing time, stabilizers to obtain the good composite products.

3.2. Physico-Mechanical Properties

The results of the physico-mechanical properties are presented in terms of the tensile strength, elongation at break, Young's modulus, and impact strength by comparing MWG contents to the PVC/MWG composite compositions those are given in Figure 2. From Figure 2(a), upon adding the MWG to the PVC compound with the content of 16.26 wt%. (PVC1), the tensile strength of composite was increased from 43.8 MPa (PVC0) up to 49.6 MPa. The highest tensile strength among five samples was measured on PVC2 with the MWG content of 22.56

wt%, reached 51.3 MPa (increase of 17 % compared with PVC0), then gradually decreased to 48.5 MPa and 40.9 MPa at PVC3 and PVC4 composites, respectively. Obviously, the modified surface of MWG particle improved significantly the tensile strength of the composites. From the results, these may be expected that the content of MWG dispersive phase had a critical value on which the MWG particles were regularly distributed in the bulk polymer and the good compatibility with PVC matrix made a peak of tensile strength value as shown in Figure 2(a). If the content of MWG phase is added over this value, the compound system may be taken the consequence of the coalescence effect and this may cause the decrease of the tensile strength of composites.

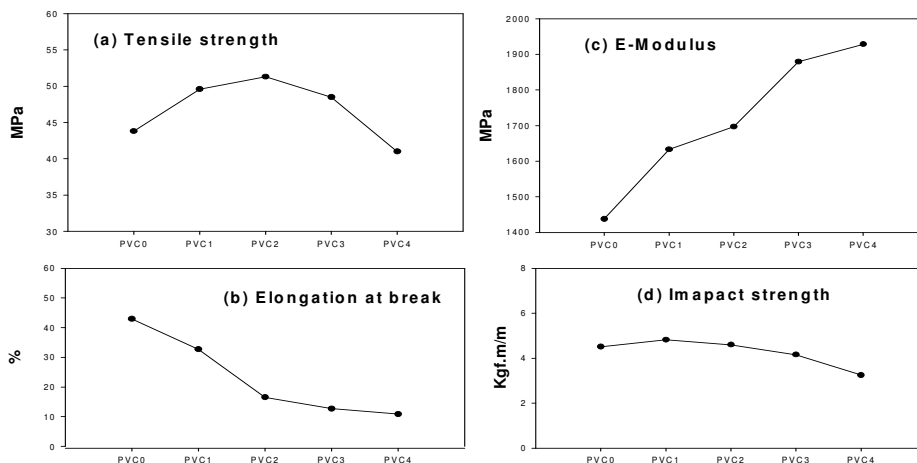


Figure 2. The physico-mechanical properties of PVC/MWG composites

On observation of the elongation at break of PVC/MWG composites in Figure 2(b), the elongation at break decreased slightly from 42.9% of PVC0 to 32.7% of PVC1, and then 16.5%, 12.7%, 10.85% of PVC2, PVC3 and PVC4, respectively. It was revealed that the MWG phase played a role as an inorganic dispersive phase, which caused a decrease of the flexibility of PVC matrix phase, therefore, reduced the elongation at break of composites. Figure 2(c) presented the Young's modulus (E-modulus) (which depicts the stiffness of composite). Generally, upon the increase of filling MWG contents led to the improvement of E-modulus of the composites. However, the level of those increases was disproportional to the amount of fillers.

From the observation in Figure 2(d), the impact strength of composites increased with the addition of MWG from 4.51 kgf.m/m (of PVC0) to 4.85 kgf.m/m. (of PVC1). Thus, it was clear that the dispersion of MWG particles in PVC matrix has actively affected to the impact strength of composite. This indicated the good adhesion of inorganic-organic interface owing to the organic part of surfactant of MWG particles was easily compatible with polymeric matrix. And then, the impact strength of PVC2, PVC3, PVC4 composites gradually decreased with increasing of MWG contents due to the high loaded inorganic component, the aggregates of MWG occurred and the defects of structure caused the reduction of impact strength of composites. The impact strength of PVC4 reduced 29% (3.22 kgf.m/m) in comparison with PVC0. Thus, although the high MWG contents were added to the composites, the impact strength of composites reduced slightly,

3.3. Thermal Properties

Figure 3(a) showed the DSC curves of the PVC/MWG composites (PVC0, PVC1 and PVC2). On the observation of the glass transition temperature (T_g) of three samples, it was realized that the shifts of glass transition temperature occurred through the PVC0, PVC1 and PVC2 at 78.2, 79.5 and 81.4 °C, respectively. This implied that the distribution of MWG particles into PVC matrix had a significant effect on the structure of composites with a tendency of increase of stiffness of composites, hence, an increase of the glass transition temperature found. This result proved the good compatibility at the interface between MWG particles and PVC matrix.

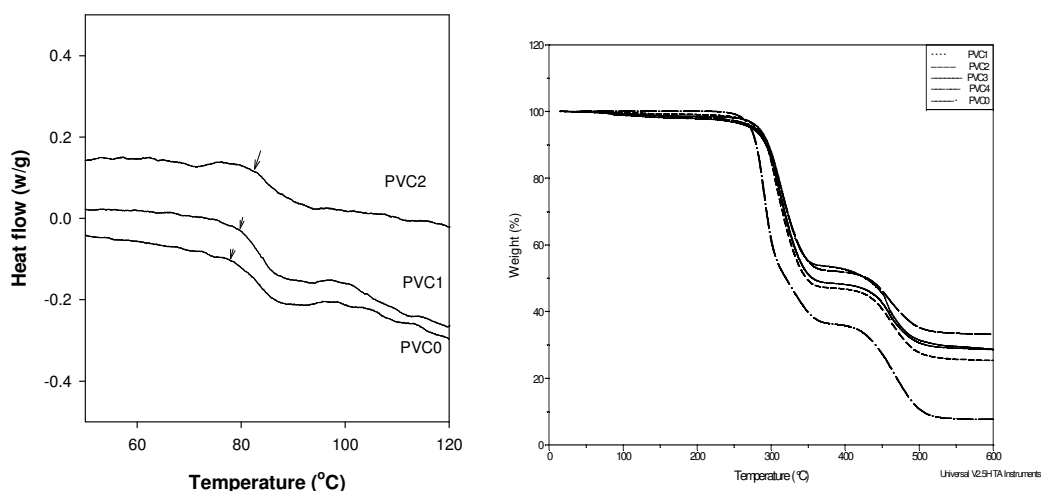
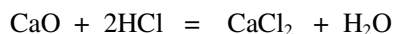


Figure 3. Thermal analysis of PVC/MWG composites: (a) DSC curves showed the shift of the glass transition temperature; (b) TG analysis indicated the thermal stability of composites

Figure 3(b) exhibited the TGA curves of the PVC/MWG composites. It was interesting that in the case of non-present MWG in PVC, the decomposed temperature of polymer was about 278 °C, however, for PVC/MWG composites, the decomposed temperature was the same at 285 °C. Thus, the presence of MWG in the polymeric composites can expand the range of the processing temperature of the composite materials. This might be expected that calcium oxide (CaO) presented in waste-gypsum composition which played a role as a fire resistance, effectively scavenge HCl gas liberated from burning halogenated polymer (PVC):



Thereby reducing the corrosiveness of the generated smoke and improving the thermal stability of PVC/MWG polymeric composites obtained [3,13].

3.4. Morphological observation

Figure 4 showed the SEM micrographs of the PVC2 and PVC4 composites, in which, the white dots exhibited the dispersion of MWG particles into PVC matrix. It is clearly realized that

in the case PVC2 picture (Figure 4(a)), the MWG particles dispersed finely into polymeric matrix and the particle size was quite small (about 200-300 nm). Thus, during the processing, the MWG particles seemed to be divided into smaller sizes by the effects of the pressing, friction forces and high temperature from the mill rotors, therefore, the MWG particles could easily intercalated into the PVC amorphous molecules. This is a significant point of waste-gypsum in comparison with other inorganic fillers. However, if the amount of MWG continuously increased up, the appearance of the coalescence of the MWG particles resulted in the structure of polymeric composites as showed in Figure 4(b). The aggregates of particles usually possess the bubbles as defects in the structure and caused the reduction of the physico-mechanical properties of composites as mentioned above.

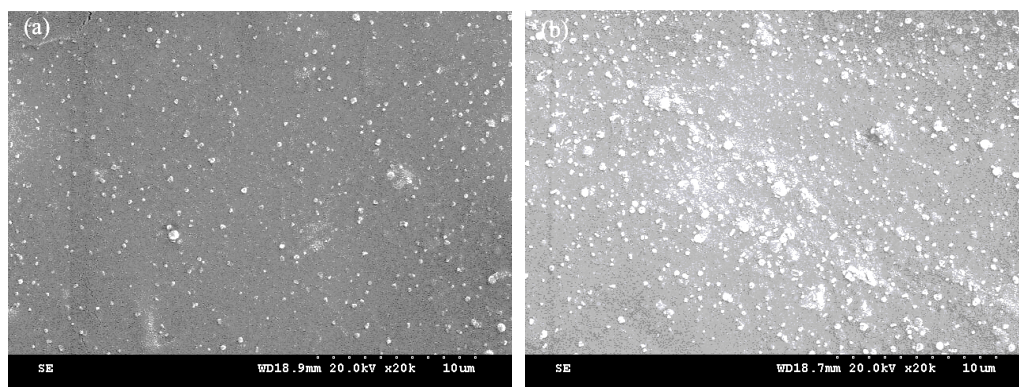


Figure 4. SEM micrographs of PVC/MWG composite: (a) PVC2, (b) PVC4

4. CONCLUSION

The PVC/MWG polymeric composites were prepared by a melt blending process. The rheological study proved that by the increase of MWG contents, the appearance of fusion peaks was slower than that of the smaller MWG content used. Young's modulus of composites was enhanced with the increase of MWG content in all composites. The highest tensile strength of composites was measured at PVC2 with the content of MWG of 22.56 wt.%. The impact strength of composites improved with 16.26 wt.% (PVC1) of MWG loaded and then gradually decreased with increasing the MWG contents. Research on the glass transition temperatures of composites, it was clear that the significant shift occurred from PVC compound without MWG to the PVC1 and PVC2 composites, this indicated that the gypsum phase was finely intercalated into PVC matrix and a good interaction between two initial phases. TGA curves also exhibited the presence of MWG contents increased the thermal stability and expended the processing temperature range of the polymeric composites. The fine dispersion of MWG particles on SEM micrograph of PVC2 composite (22.56 wt% of MWG content) proved to the good physico-mechanical properties in comparison with other composites.

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TÓM TẮT

NGHIÊN CỨU TÍNH CHẤT LƯU BIẾN, CƠ LÝ VÀ NHIỆT CỦA VẬT LIỆU POLYME
COMPOZIT POLYVINYLCLORIT/GYPSUM PHẾ THẢI

Vật liệu polyme compozit trên cơ sở nhựa polyvinylclorit (PVC) và gypsum phế thải được chế tạo bằng phương pháp nóng chảy trên máy cán trộn và máy ép nhiệt. Để tăng khả năng phân tán và kết dính với nền nhựa PVC, gypsum phế thải được rửa sạch và biến tính bề mặt bởi natri dodecyl sulphat. Ảnh hưởng của hàm lượng gypsum biến tính (MWG) lên tính chất lưu biến trạng thái nóng chảy, cơ lí và nhiệt của vật liệu polyme compozit PVC/MWG được thảo luận. Sự có mặt của MWG trong thành phần kéo dài hơn thời gian phối trộn trong quá trình gia công compozit. MWG làm tăng độ cứng, độ bền kéo đứt ở tỉ lệ 22,56% khối lượng (kl.) cho giá trị lớn nhất (tăng 17% so với mẫu không sử dụng MWG), độ bền va đập giảm 29% khi tăng hàm lượng MWG lên đến 32,67% kl. Nghiên cứu nhiệt độ chuyển thủy tinh (T_g) của vật liệu compozit PVC/MWG xuất hiện hiện tượng trượt của chúng khi tăng hàm lượng MWG trong thành phần. Khoảng gia công của vật liệu compozit cũng được mở rộng nhờ việc tăng nhiệt độ phân hủy của chúng. Phân tích hình thái cấu trúc qua ảnh hiển vi điện tử quét (SEM) cho thấy hạt MWG kích thước từ 200 - 300 nm phân tán đều trong nền PVC ở tỉ lệ 22,56% kl., do đó cải thiện đáng kể độ bền kéo đứt của vật liệu.

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