

Mechanical, Morphological and Thermal Properties of Dioctylphthalate-Plasticized Polyvinyl Chloride Reinforced Sepiolite/MgO

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Abstract: *The search for nanofillers in polymer industries to improve composite material properties for several purposes has increased significant interest. In this study, dioctyl phthalate-plasticized polyvinyl chloride (PVC) reinforced either with sepiolite or MgO was produced in which the characteristic of composite sepiolite/MgO-filled was compared. Sepiolite and MgO were added into PVC matrices with 5, 10, and 20 phr concentrations. The product was characterized using analytical techniques such as SEM, TGA, DSC, and the mechanical properties regarding ASTM D 638 Type IV. The tensile strength of the composite increased with the presence of sepiolite and MgO. The highest result showed at the concentration of 5 phr. However, the elongation at the break of the composite decreased with the addition of MgO. The morphology analysis showed that PVC-filled sepiolite had a rough surface with a sharp fracture, but no sharp fracture was found in the PVC-filled MgO. At a concentration of 5 phr, both sepiolite and MgO increased the thermal properties of PVC with a residue of PVC control, PVC-Sepiolite, and PVC-MgO at 14.74%, 19.34%, and 26.33% respectively.*

Keywords: *nanofiller, clays, thermoplastics, polymer industries, thermal stabilizer*

1. Introduction

Polyvinylchloride (PVC), one of the highest volume productions of commercial thermoplastics after polyethylene (PE), polypropylene (PP), and polystyrene (PS), has been utilized not only as a commodity but also as engineering materials. The versatility of the thermoplastic resin even enlarges as flexible polymer material due to its good compatibility with various synthetic and natural plasticizers [1]. However, PVC is susceptible to heat and fire environments due to the dehydrochlorination process of the fresh PVC to release HCl gas at moderate temperature (under 100°C) [2]. Therefore, various thermal stabilizers and flame retarders are introduced during the manufacture of PVC. It has been reported that ferrites are incorporated into DOP-plasticized PVC resins to improve thermal stability and fire-resistant ability [3].

Nowadays, various pillared clays, such as montmorillonites and sepiolite, have been utilized intensively as fillers in polymer industries. During their incorporation, the pillared clays intercalate and exfoliate to improve their contact surface area tremendously, which in turn increases the mechanical and thermal properties of the pillared clays-filled polymer composites [4]. Sepiolite, as one of the pillared clays having the chemical structure of hydrous magnesium silicates, has been used as nanofillers in various polymer blends. The effects of sepiolite fillers on characteristics of carbon black-filled natural rubber-styrene butadiene rubber (NR-SBR) blends prepared in a 2-roll mill with a standard vulcanizing system have been studied. The presence of sepiolite in rubber matrices increased the shear in the rubber [5]. Other researchers have also utilized sepiolite as a thermal stabilizer and fire retardant in PP, poly(3-hydroxybutyrate-co-3-polyhydroxy valerate)/polylactic acid (PHBV/PLA), low-density polyethylene (LDPE), and ethylene propylene diene monomer (EPDM) blend [4, 6-8].

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The functions of sepiolite as pillared clay have some advantages such as intercalating during incorporation and distributing finely within the polymer blends. In addition, it forms char residue which exhibits oxygen diffusion during thermal decomposition to improve its efficiency as a thermal stabilizer and fire retardant [9].

Magnesium oxides (MgO), one of the nanofillers classes, have a good impact on the properties of polymer blends such as tensile strength, thermal stabilizer, electrical conductor, and antibacterial agent in the food packaging materials [10]. As electrical conductors, MgO has been incorporated with lithium triflate salt in polymer electrolytes [11]. Furthermore, the antibacterial nanocomposite based on flexible and biodegradable poly-(butylene adipate-co-terephthalate) reinforced MgO has been reported [12]. It was further reported that the thermal stabilizing activity of MgO fillers was related to the ability of the finely distributed nanofillers to scavenge macroradicals formed in the initiate char formation and dissipate thermal energy because of the better thermal conductivity of the fillers [13].

To the best of our knowledge, there is no study yet reported the properties of PVC composite reinforced sepiolite/MgO. This study compared the effects of sepiolite and MgO fillers on the mechanical, morphological, and thermal properties of dioctyl phthalate (DOP)-plasticized PVC.

2. Materials and methods

2.1. Materials

PVC, sepiolite, MgO, DOP, and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. All materials were directly used without further purification.

2.2. Preparation of composite DOP-plasticized PVC reinforced sepiolite/MgO

Fresh PVC resin, DOP, and sepiolite/MgO were mixed in tetrahydrofuran (THF) solvent under reflux and intensive stirring for 30 min based on compositions as summarized in Table 1. The mixture was then cast on a glass plate. It was then dried in a vacuum oven at 40°C for 5 h. The dried blending was cut from laminas on a jig saw machine as per ASTM D 638 Standards. The standard Type IV dumbbell-shaped specimens are used for tensile test specimens with dimensions of 115 and 19 mm, and a thickness of 6 mm.

Table 1. Specimen preparation of DOP-plasticized PVC with various concentrations of sepiolite/MgO

Sample	Parameter		
	DOP (phr)	Sepiolite (phr)	MgO (phr)
PVC control	30	-	-
PVC Sep5	30	5	-
PVC Sep10	30	10	-
PVC Sep20	30	20	-
PVC MgO5	30	-	5
PVC MgO10	30	-	10
PVC MgO20	30	-	20

2.3. Characterization

Dumbbell-shaped specimens were cut from the casted sheets and tested for tensile strengths and elongation breaks, according to ASTM D 638 Type IV, using a universal testing machine (Instron 3366) at a crosshead speed of 500 mm/min with 10 kN load. The morphology of the samples was analyzed using a scanning electron microscopy (SEM) model Zeiss Supra 35-VP, Carl Zeiss NTS GmbH, Oberkochen, Germany. The thermal properties of the specimens were measured using a differential scanning calorimeter (DSC) Shimadzu DSC-60 from 30°C to 200°C with a heating rate of 10°C/min under a nitrogen atmosphere. Thermogravimetric analysis was performed using a (TGA) Shimadzu DTG-60 thermogravimeter from 30°C to 600°C with a heating rate of 10°C/min under a nitrogen atmosphere.

3. Results and discussions

3.1. Mechanical properties of PVC Sep/MgO composites

The mechanical properties of PVC Sep/MgO composites are presented in Figures 1 and 2. As shown in Figure 1, the tensile strengths of PVC (4.49 MPa) increased with the addition of 5 phr sepiolite and MgO (10.19 MPa and 7.04 MPa). It was the highest result compared with the addition of sepiolite and MgO at 10 and 20 phr (9.24 and 8.68 MPa) and (5.82 and 5.51 MPa) respectively. At sufficient concentration, the sepiolite's pillared structure increases the fillers' total contact surface area with PVC matrices and improves the mechanical properties of the blend [5].

In terms of elongation breaks, the presence of sepiolite on the PVC matrix increased from 111.05% to 128.70%, but it decreased with higher content of sepiolite at 10 phr (109.97%) and 20 phr (78.5%). However, the addition of MgO 5, 10, and 20 phr decreased the elongation of the composite to 91.33%, 55.75%, and 52% respectively. It is due to sepiolite being agglomerated at high concentrations, and decreasing the tensile strengths and elongation at the break of the composites [9]. MgO filler at low concentrations also acted as a good reinforcement, but it tends to agglomerate at a high loading level. The modulus of elasticity of PVC Sep/MgO composites (Figure 3) shows a decrease from 1.85 MPa to 0.99 MPa with the loading level of Sep/MgO at 5, 10, and 20 phr.

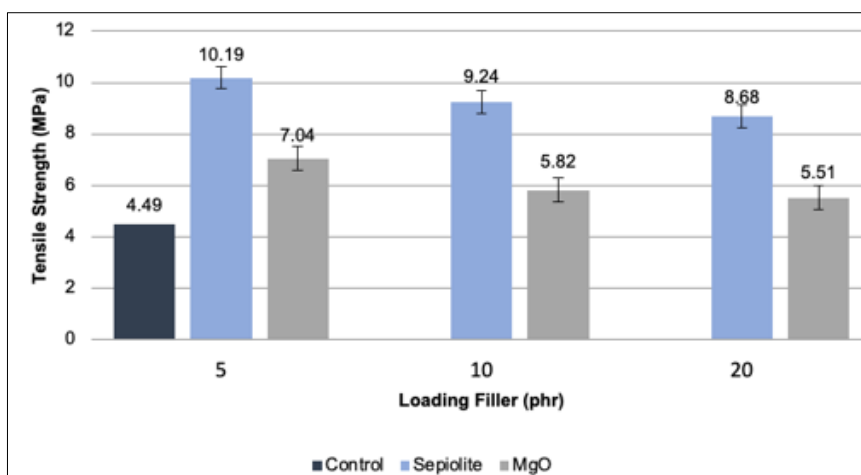


Figure 1. Tensile strength of PVC Sep/MgO composites

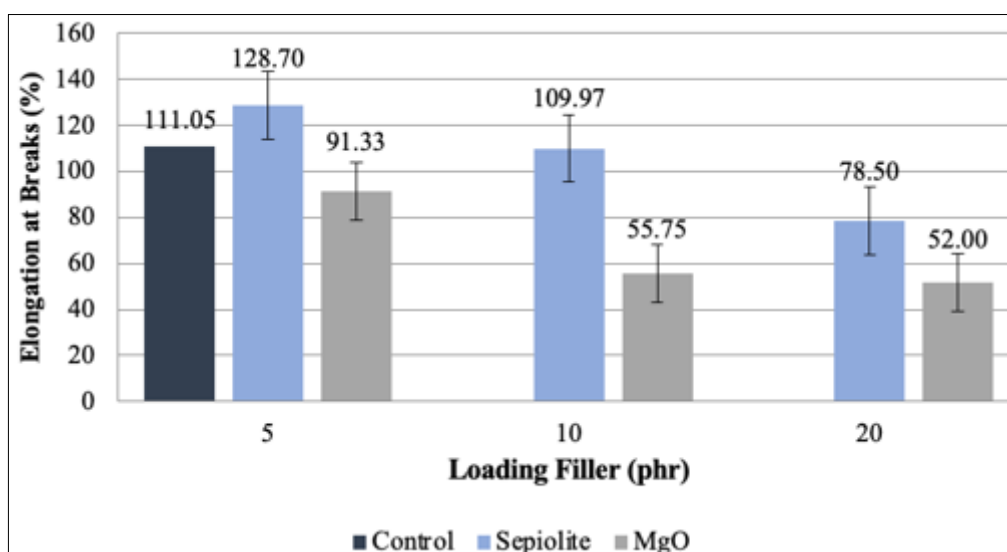


Figure 2. Elongation at breaks of PVC Sep/MgO composites

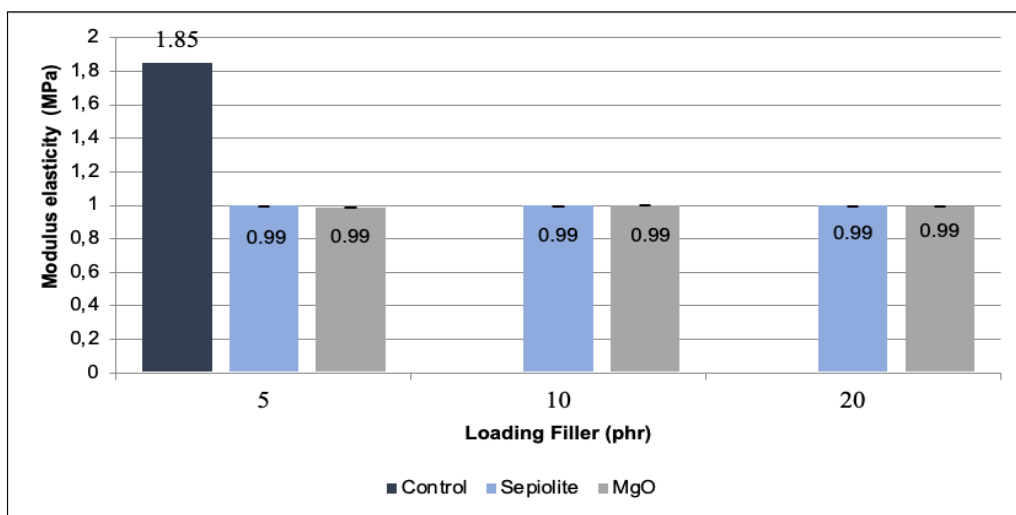


Figure 3. Modulus of elasticity of PVC Sep/MgO composites

3.2. Morphological characterization of PVC Sep/MgO composites

Figure 4 shows the morphology of PVC Sep/MgO composite (filler loading 5 phr). Pure PVC (Figure 4a) shows a smooth fracture due to the presence of a DOP plasticizer [14]. The morphology of PVC-Sep shows a rough and sharp fracture surface, whereas that of PVC-MgO also shows a rough without sharp fracture surfaces. This evidence supports the mechanical properties of the corresponding PVC blends, in which at optimum filler loading the sepiolite exhibits a good reinforcing in the PVC blends due to the formation of higher contact surface area [7].

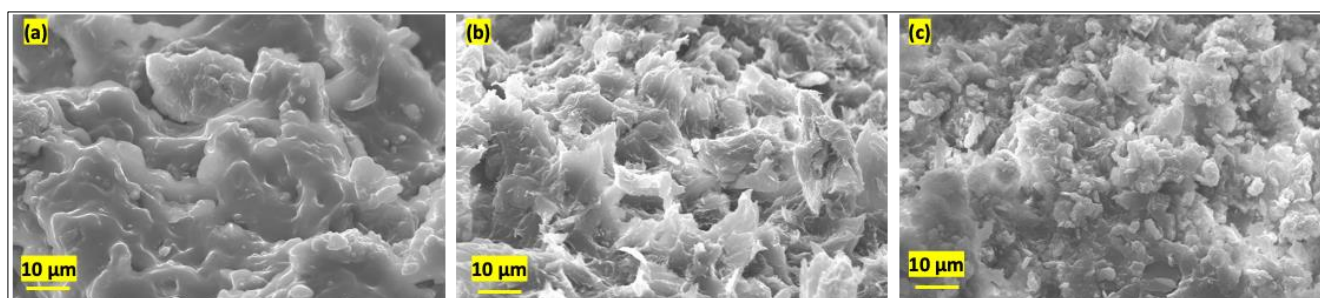


Figure 4. SEM micrographs of PVC Sep/MgO composites (filler loading 5 phr) (a) pure PVC, (b) PVC/Sep, and (c) PVC/MgO at a magnification of 3kx

3.3. Thermal properties of PVC Sep/MgO composites

DSC analysis (Figure 5) is intended to estimate the glass transition (T_g) and melting temperature (T_m) of the PVC blends, and data analysis is summarized in Table 2. PVC control has a T_m of 196.48°C, it slightly increases to 197.75°C and 198.07°C with the presence of sepiolite and MgO filler. T_g of the composites also increases by 30.94% and 7.35% for sepiolite and MgO loading level 5 phr. The endothermic heat flows are also higher with the addition of sepiolite and MgO which are -4.98 J/g and -2.10 J/g respectively. The incorporation of sepiolite/MgO fillers mainly fills the amorphous regions and increases the T_g and mechanical properties of the PVC blends [9].

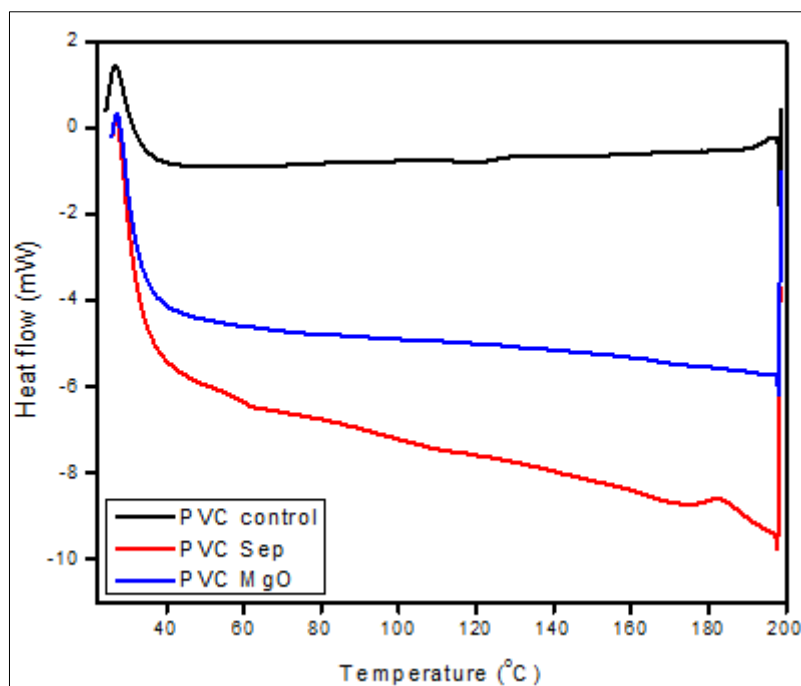


Figure 5. DCS thermograph of PVC-Sep/MgO blends filler loading 5 phr

Table 2. DSC data of PVC-Sep/MgO blend filler loading 5 phr

Sample	Measurement		
	T _g (°C)	T _m (°C)	Heat flow (J/g)
PVC control	87.48	196.48	-1.01
PVC Sep5	94.83	197.75	-4.98
PVC MgO5	118.42	198.07	-2.10

Figure 6 and Table 3 describe the curve and data for TGA analysis of PVC Sep/MgO blends (filler loading 5 phr). From Figure 6, all samples experience two-step of decompositions. The first degradation occurred at 271.92°C, 275.34°C, and 276.99°C for PVC control, PVC-Sep and PVC-MgO respectively. All samples experienced the second degradation at around 312.19°C, with an onset of 234.10°C, 237.71 °C, and 258.86 °C for PVC control, PVC-Sep and PVC-MgO respectively. Total weight loss for the three samples was 85.26%, 80.66%, and 73.67% which shows both fillers increase the thermal stability of PVC composite. Efficiency as a thermal stabilizer of fillers is measured by lower total weight loss and higher char residue formation which covers surfaces and inhibits oxygen diffusion into the PVC blends during the decompositions [6]. Therefore, it is revealed that sepiolite and MgO fillers have good efficiency as thermal stabilizers [12].

Table 3. Data of TGA analysis of PVC-Sep/MgO blends filler loading 5 phr

Sample	Onset (°C)	Decomposition		
		T ₁ (°C)	T ₂ (°C)	Char residue (%)
PVC control	234.10	271.92	312.19	14.74
PVC Sep5	237.71	275.34	312.19	19.34
PVC MgO5	258.86	276.99	312.19	26.33

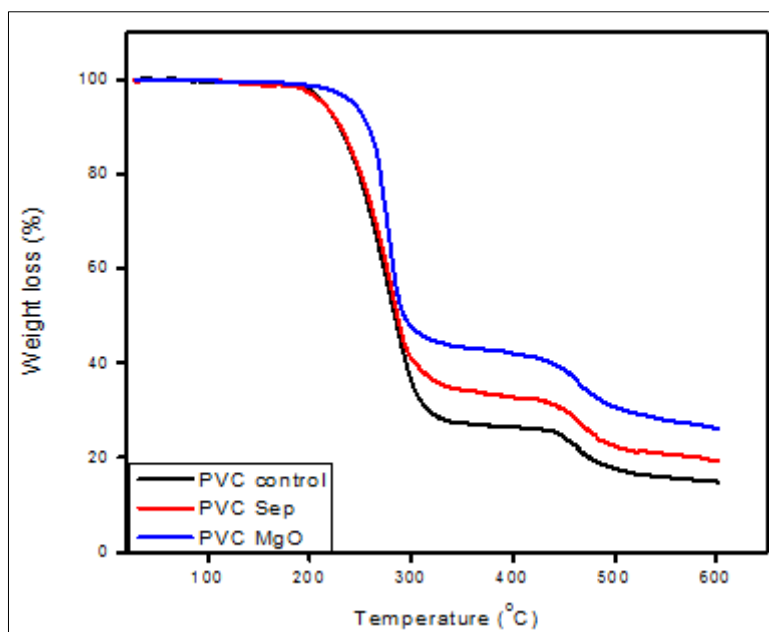


Figure 6. TGA curve of PVC-Sep/MgO blends with filler loading 5 phr

4. Conclusions

The use of sepiolite as a filler at low concentrations exhibits good reinforcement. However, it tends to agglomerate at high concentrations to decrease the tensile strength and elongation at breaks of the PVC-Sep blends. In addition, MgO acts as a good reinforcement at sufficient concentrations and agglomerates at higher concentrations. Therefore, the blend of PVC-Sep/MgO slightly increases the tensile strength at optimum loading filler and decreases the elongation at breaks continuously as the filler concentration increase up to 20%. The surface morphology of PVC-Sep and PVC-MgO looks rough, the former is with a sharp fracture and the latter is without a sharp fracture. Incorporations of sepiolite/MgO fillers mainly fill the amorphous regions and increase the T_g and mechanical properties of the PVC blends. Sepiolite and MgO also exhibit good efficiency as thermal stabilizers (promote lower total weight loss and higher char residue formation).

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