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Chemical And Mechanical Properties Analysis Of Extruded Polyvinyl Choloride (Pvc)/Sepiolite Composite

Hasan Candan Öteyaka[1], Mustafa Özgür Öteyaka*[2]

Abstract

In this study, poly vinyl chloride (PVC)/ sepiolite composites were produced using an extruder. Two different sepiolite powders: white and gray were added to the PVC in order; 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.%. The morphology alteration, chemical behavior and mechanical properties of the powders and the composites were examined by X-ray fluorescence (XRF), tensile test, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and ultimate tensile strength (UTS). The results showed that the sepiolite white powder had 20.72 wt.% CaO and approximately half of the 20.81 wt.% SiO2 as compared to the sepiolite gray powder. The XRD analysis confirmed that the structure of calcined white sepiolite contained dolomite, while gray calcined-sepiolite contained zeolite. The composites with 5 wt.% sepiolite white or gray powders exhibited higher tensile strength. Increasing the quantity of both sepiolite powders in the composites deteriorated the surface with cracks and shifted the thermal degradation of the sepiolite gray toward higher temperatures.

Keywords: Sepiolite, Poly vinyl chloride (PVC), Composite, Planetary micro mill.

1. INTRODUCTION

The poly vinyl chloride (PVC), which is manufactured worldwide, is used extensively for windows, door frames, transportation and construction [1-3]. The benefits of this material are low cost, chemical resistance, fire retardant and good mechanical properties. However, brittleness and poor thermal stability features are the major weakness of PVC. To enhance these properties, different filler materials, such as elastomers, rubbers, and inorganic clay are added [4-6].

The mineral filler plays a major role in the plastic composite industry, because it extends and improves the mechanical properties and cost of composites [7-12]. For example, the processing, dimensional stability, mechanical strength and thermal resistance of composites can be improved by the addition of clay mineral filler (montmorillonite, saponite, sepiolite, etc.). The characteristics of composite are dependent on the shape, particle and aggregate size, quantity and dispersion of the filler [13-17]. Various studies attempted to improve the strength and toughness of PVC by addition of $CaCO_3$ powders [18-20], but the mechanical properties were in fact lower than

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desired. The industry is in need of new fillers that can increase mechanical properties.

Sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$) is a complex magnesium silicate clay mineral. The structure of sepiolite was explained in [12, 21]. It can be found naturally in fibrous, fine-particulate, and solid forms [22]. The advantage of sepiolite is that it can absorb water because of its high surface area, as determined by Brunauer–Emmett–Teller (BET) analysis. This mineral appears in cat and pet litters, absorbents, waste treatment, roof panels, polymers, elastomers, etc. [2, 23, 24]. Recent studies [12, 25, 26] were presented for a fabric composite fortified with plastic and sepiolite.

In this study, PVC/ sepiolite composite was extruded for use in the manufacturing industry; specifically, door and window frame applications. Milled and calcined sepiolite powders, both white (SW) and gray (SG), with different chemical composition were added into PVC granules by 5, 10, 15 and 20 wt. %. The sepiolite powders and extruded PVC/Sepiolite composites were investigated by X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and ultimate tensile strength testing.

2. MATERIALS AND METHODS

2.1 Preparation of PVC/Sepiolite composites

The sepiolites of the white (SW) and grey (SG) clay minerals were obtained from a deposit located near Eskişehir, Turkey, while the poly vinyl chloride PVC (mol wt ~48 000) was purchased from Sigma-Aldrich as powder form. Before manufacturing the composite by extrusion, the sepiolites were crushed and dry-milled by planetary micro mill (Planetary Pulverisette 7) for five minutes. The powders were then calcined at 350°C for eight hours and cooled at room temperature for one day. The powders were added with mass fractions of 5, 10, 15 and 20 wt.% into the PVC and mixed homogeneously before extrusion. The extruder contained three chambers with temperatures of 120°C, 140°C and 160°C. After feeding the extruder with the mixed powder, the screw was adjusted to 500 rpm and the solid composite with a diameter of 6 cm was extruded to a length of 60 cm. The composite was then cut to alternate sizes for analysis.

2.3 Characterization of powders and composites

The average particle size of the sepiolite powders was measured by a Mastersizer 2000 (Malvern Instruments Ltd., Worcestershire, UK) particle size analyzer. The chemical compositions of the powders were determined by X-ray fluorescence (XRF). A PE-EL press (Breitländer GmbH, Wesel, Germany) was used to round tablet samples by mixing 4 g of powder and 0.9 g of binding material. An analytical X-ray diffractometer (XRD, MiniFlex; Rigaku Corp., Tokyo, Japan) used Cu K(α) radiation with a Ni filter between 10° and 70°, with a scanning speed of 2°/minute in steps of 0.01° to determine phase information. The results obtained by XRD were compared to the Joint Committee on Powder Diffraction Standards (JCPDS) pattern. Scanning electron microscopy (SEM) was performed to analyze defects on the surface of the composites and to determine the distribution of powders. Prior to the analyses, the samples were coated with gold to obtain conductivity. The images were taken at a magnification of 500X and 1000X. The chemical bonding of powders was investigated by an FTIR–attenuated total reflectance (ATR) (Perkin-Elmer Spectrum) spectrophotometer in the range of 4000–600 cm^{-1}. The tensile tests were executed according to ASTM D3039 at a rate of 2 mm/min. Three samples of each composite were tested and the average values of ultimate tensile strength were reported.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of Sepiolite Powders

The chemical composition of sepiolite is composed mainly of magnesium (Mg) and silicon (Si) oxides [27]. In this study two types of sepiolite were used, as presented in table 1. Both sepiolite minerals were composed predominantly of SiO_2 and MgO, with minor concentrations of CaO, Al_2O_3, Fe_2O_3, and K_2O oxides. For both powders, there was 19 wt.% MgO. The main differentiation between SW and SG was observed in the quantity of SiO_2 and CaO. SW contained half the SiO_2 of SG, which can lead to diminished network bonding and mechanical properties [28, 29]. The 20.72 wt.% of CaO in SW may improve the mechanical properties as described in [9, 30].

The minerals milled by planetary micro mill were analyzed by SEM to confirm the shape and the dimension of the powders (Fig. 1). SW had a particle size of ~33.72 µm, while SG was ~43.78 µm. To better understand the particle size distribution of SW and SG powder, laser diffraction was used. The mechanical mixing of SW resulted in an average particle size distribution of d_{50}= 0.22 µm, with d_{10}= 0.03 µm and d_{90}=26.3 µm. For SG, an average particle size distribution of d_{50}= 14.4 µm, with d_{10}= 4.8 µm and d_{90}= 41.3 µm was found. The mean particles size of SG was six times larger than SW. The shape of the particles was irregular for both powders. Decreasing the particle size of SW to 1 µm was adequate when compared to the SG milling process.

A deeper analysis was needed to identify the type of mineral and the phase in the SW and SG powders. For this reason, XRD analysis was performed on SW and SG to confirm the chemical differences between the two powders (Fig. 2). XRD exposed the presence of sepiolite peaks for SW and SG between 5°and 30°. Dolomite was found in SW and zeolite was observed in SG. The main peaks of zeolite and dolomite were located between 30°and 70°. This is consistent with [31] and [32].

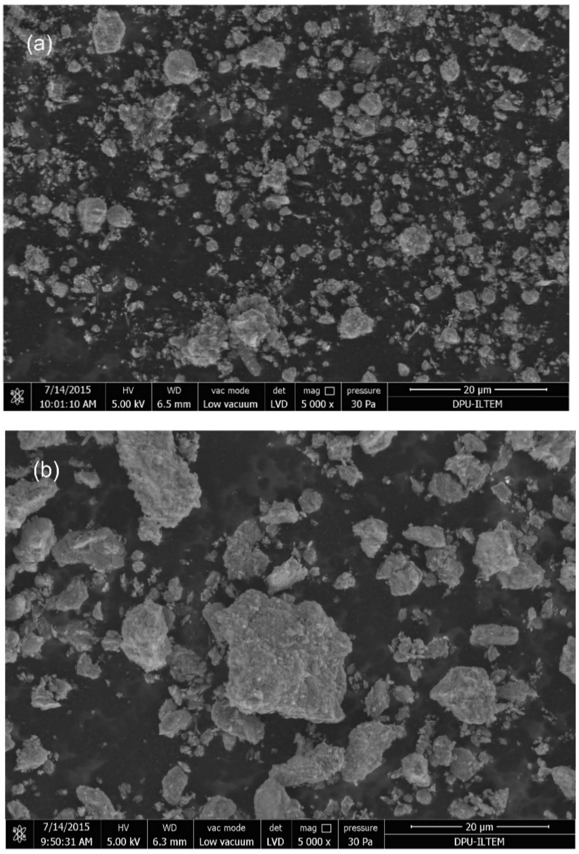

Figure 1. SEM images at 5000X of SW and SG powders after milling process a) white sepiolite (SW) and b) gray sepiolite (SG).

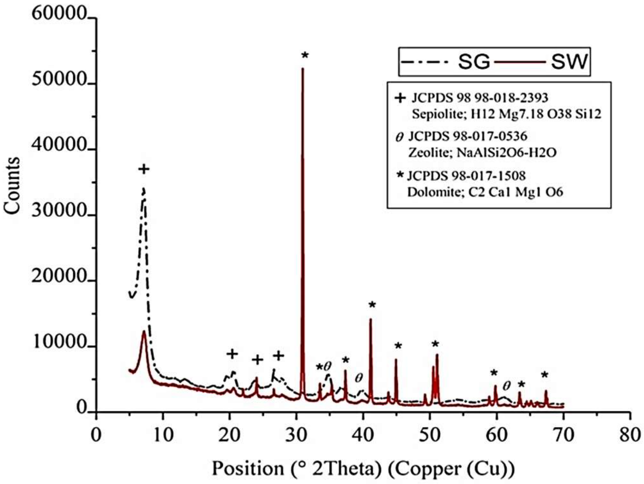

Figure 2. XRD spectra of SW and SG powder.

Table 1. The chemical composition of SW and SG powders.

Chemical Composition of sepiolite powders (wt. %)

	SiO2	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	SrO	TiO_2	Na_2O	F
SW	20,81	20,72	19,15	0,72	0,44	0,15	0,26	0,06	---	0,62
SG	46,75	0,27	19,78	1,29	0,75	0,28	---	0,12	0,05	1,34

3.2 Characterization of PVC/sepiolite Composites

The phase transformations of extruded PVC/SW and PVC/SG composites of 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.% were analyzed by XRD and presented in Fig. 3. The spectra of 10 wt.% and 15 wt.% of PVC/SW and PVC/SG composites were similar to the 5 wt.% samples. For this reason, that data were not presented in Fig. 3. In general, PVC containing crystallinity will display main peaks at 12° and 25° [33].

These peaks were observed only in the XRD chart of the PVC/SG composite at 20 wt.%. Sepiolite had clear peaks at 2θ =7.2°, 20°, 25° and 28° as shown in Fig. 2. Lower concentrations of powder in PVC/SG composites decreased the intensity of sepiolite peaks at 7.2° and PVC peaks at 12°. These peaks, however, were not more intense for PVC/SW when compared to PVC/SG composites. Thus, the zeolite peaks located between 35° and 37° and the dolomite between 32° and 42° were visible at lower concentrations for both composites.

The surface analyses of each composite are given in Fig. 4. In general, the surface of PVC/SG and PVC/SW composites consisted of congregated powders in the matrix. For the 5 wt.% PVC/SW composite, small bundles (black colour) were found uniformly dispersed on the surface (Fig. 4a).

In addition, the SW powders were well dispersed into the PVC matrix. The 20 wt.% SW deformed the surface, such that the matrix surface area decreased (Fig. 4b). The 5 wt.% PVC/SG had increased agglomeration because of the size of the powders as seen in Fig. 4c. Adding more SG to the matrix deteriorated the surface, and bonding with the matrix became difficult (Fig. 4d). In brief, using white or gray sepiolite powders at 5 wt.% will produce a composite without surface defects.

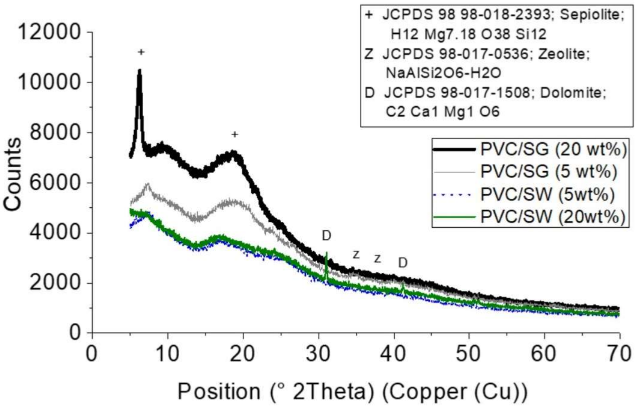

Figure 3. XRD spectra of PVC/SW and PVC/SG composites.

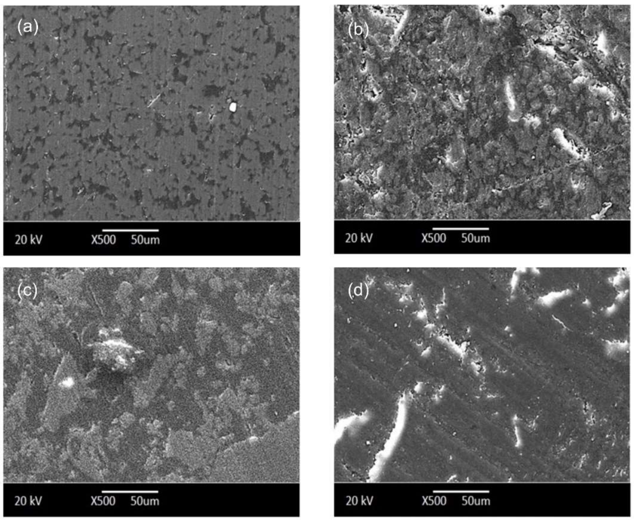

Figure 4. SEM images at X500 of PVC/SW composites and PVC/SG composites; a) 5 wt.% PVC/SW, b) 10 wt.% PVC/SW, c) 5 wt.% PVC/SG, d) 10 wt.% PVC/SG.

The FTIR-ATR spectra analysis of SW and SG are not presented within because of the limitations reported within [12, 22, 26]. However, it is necessary to understand that the nature of calcinated sepiolite chemical interactions in order to compare to other composites, which will be discussed below. In summary, the results demonstrated that both powders had an Mg_3OH band at 3600 cm^{-1}. The band had little bonding strength, because of the OH groups stretching out from the external surface of the sepiolite. In the middle of spectra, the peak located at 1650 cm^{-1} (OH stretching) was attributed to coordinated water for both powders. The last significant peak corresponded to stretching of the Si-O band at 1100 cm^{-1} and 970 cm^{-1} for both powders, which originated from the Si-O-Si group. Many studies have revealed the FTIR transmittance of PVC as O-H (3500-3700 cm^{-1}), C-H (2800-3000 cm^{-1}), nitride groups (2000-2250 cm^{-1}), C-H aliphatic bending bond (1400-1600 cm^{-1}), C-H bending bond (1100-1250 cm^{-1}), C-C aliphatic bending bond (1000-1100cm^{-1}) and C-Cl (600-650cm^{-1}) stretch bond [8, 12, 18]. Fig. 5 and 6 show the chemical structure of PVC/SG and PVC/SW composites for the spectrum between 4000 cm^{-1} and 500 cm^{-1}. According to Fig. 5, the peaks in the ranges of 3500-3700 cm^{-1} (O-H), 2800-3000 cm^{-1} (C-H), 1400-1600 cm^{-1} (C-H aliphatic bending bond) and 1100-1250 cm^{-1} (C-H bending bond) decreased with the addition of SW powders. This was especially true for the peak located at 3700 cm^{-1}, which was eliminated after 15 wt.% addition of SW. The intensity of the peak at 600-650 cm^{-1} (C-Cl) increased with the amount of SW added. Turhan et al. [12] explained this rise by the release of HCl molecules from the PVC, which caused the generation of double bonds. A new peak at 2200 cm^{-1} appeared after the 10 wt.% addition of SW that was due to C-O bonding. The peaks of O-H, C-H, and C-C were not observed in the PVC/SG composite as illustrated in Fig. 6. The peaks at 2000 - 2200 cm^{-1} assigned to C-O groups intensified with the addition of SG.

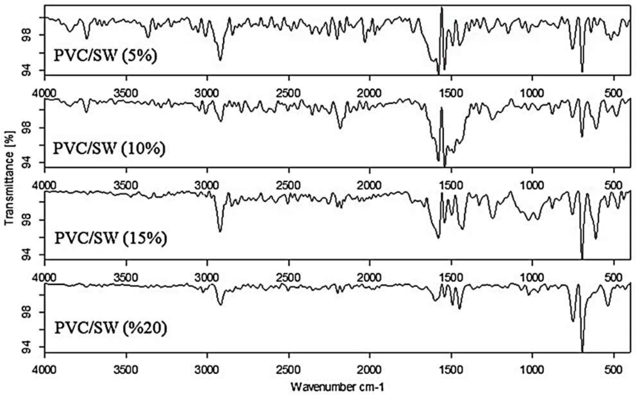

Figure 5. FTIR analysis of PVC/SW composites.

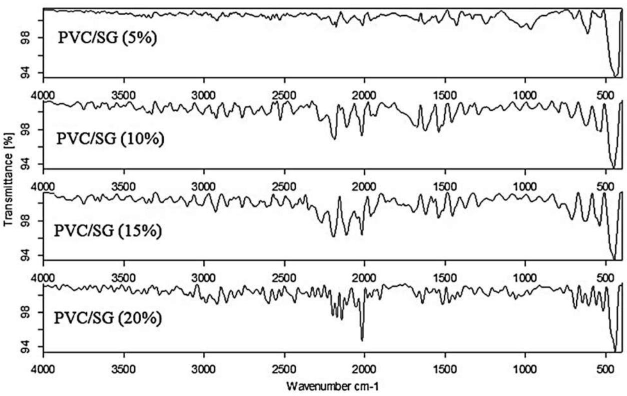

Figure 6. FTIR analysis of PVC/SG composites.

The mechanical performance of composite materials was evaluated by tensile testing. Fig. 7 and Fig. 8 show the effect of sepiolite concentration on the strength of PVC composites. It is well understood that unfilled PVC is brittle. With the addition of sepiolite powders to the matrix, composites have shown ductile behavior, most significantly with PVC/SG composites filled with 15-20 wt%. The results also confirmed that addition of sepiolite powder stiffened the PVC. In general, addition of a lower quantity (5 wt.%) of sepiolite increased the strength and rigidity of composites. The elastic modulus was also higher for PVC/SG, which resulted in increased rigidity when compared to PVC/SW. This difference can be explained by higher amount of SiO_2 in the PVC/SG that improve adhesion of the surface to the matrix. For both composites, higher tensile strength was obtained, at 35 MPa with the addition of 5 wt.% sepiolite.

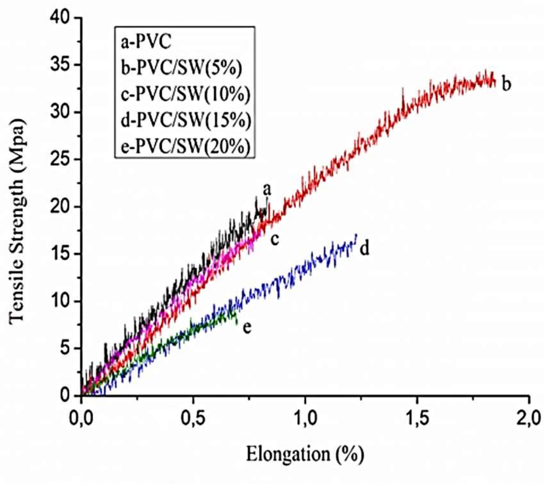

Figure 7. The tensile strength of 5-20 wt.% PVC/SW composites versus unfilled PVC.

This result was 10 MPa lower than the PVC/Nano-$CaCO_3$ [19, 30]. Higher concentrations of sepiolite powders in the composites decreased the strength and rigidity. Thus, increasing the amount of sepiolite powders in the matrix did not transfer the stress from the matrix to the powder, because of weak interface adhesion. As cited in the literature, the interface adhesion between matrix and particle, and the filler quantity both play a major role in the strength of the composite. A special surface treatment of the sepiolite powders could be applied to enhance the interface adhesion between matrix and particles, in order to increase strength.

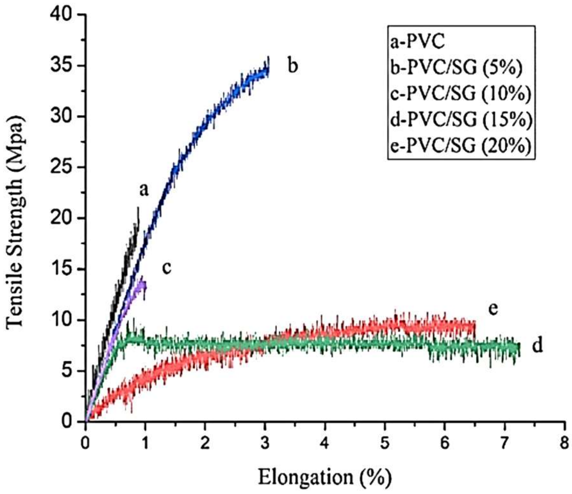

Figure 8. The tensile strength of 5-20 wt.% PVC/SG composites versus unfilled PVC.

4. CONCLUSION

Two different sepiolite powders (SW and SG) were used to fill PVC composites. The powder analyses demonstrated that SW contained dolomite with higher CaO concentrations, while SG contained zeolite with dominant SiO_2. The average particle size of SW was d_{50}= 0.22 µm, which was seven times smaller than SG. The SEM study of extruded composites showed that 5 wt.% SW particles were spread homogeneously in the PVC matrix. The findings demonstrated that increasing the quantity of SG powder increased the peaks of C-O bonding. However, the O-H and C-H groups decreased when SW powders were added. The mechanical analysis of composites confirmed that a smaller addition of powders was better to obtain higher strength. For both composites, a strength of 35 MPa was obtained with the addition of 5 wt.% of sepiolite. Above this quantity, high ductility with lower strength was observed.

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