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MICROWAVE EXFOLIATION OF VERMICULITE AND PHLOGOPITE

ABDULLAH OBUT[1], İSMAIL GİRGİN[1,*] AND ABDÜLKERİM YÖRÜKOĞLU[2]

[1] Hacettepe University, Mining Engineering Department, 06532, Beytepe, Ankara, Turkey
[2] Mineral Research and Exploration General Directorate, 06520 Ankara, Turkey

Abstract—Vermiculites and phlogopites can be exfoliated by chemical and thermal treatment methods to obtain chemically inert, adsorbent, fire-resistant, low-density materials with excellent thermal and acoustic insulation properties. The water content of the clay generally determines the extent of exfoliation and the presence of interstratification is claimed to increase the rate of exfoliation. Considering the strong interaction between water and microwaves, the effect of microwave power on exfoliation characteristics of vermiculites and phlogopites after treatment with water and hydrogen peroxide solution were studied at 600, 950 and 1300 W for microwave exposure times of 10, 20, 30, 60, 120 and 300 s. It was observed that the water molecules in the interlayers of the individual flakes were driven off quickly by microwave treatment causing layer separation in the samples. The vermiculite sample showed 2.8 and 5.6 times, respectively, the exfoliation ratio of the phlogopite samples, in accord with their water contents.

Key Words—Exfoliation, Microwave Energy, Phlogopite, Vermiculite.

INTRODUCTION

Microwaves are non-ionizing electromagnetic waves of a particular wavelength (1 mm–1 m) and frequency range (300 MHz–300 GHz) situated between infrared (IR) and radio frequencies within the electromagnetic spectrum. Generally, frequencies of 915 MHz and 2450 MHz are used in microwave applications (Haque, 1999). The use of microwaves as a source of thermal energy in many industrial processes as a source of thermal energy is growing rapidly (Osepchuk, 1984) and is considered an alternative to conventional convective and conductive heating. Easy startup and volumetric heating, due to the penetration of microwaves, improve the efficiency and reduce process times, making it an attractive source of thermal energy.

The food industry is the largest consumer of microwave energy for cooking, thawing, tempering, freeze-drying, pasteurization and sterilization (Ayappa *et al.*, 1991) purposes. Microwaves are also used for synthesis of SiC, PbSe, $BaTiO_3$, $CuInS_2$ (Rao *et al.*, 1999), in mineral processing operations (Bluhm *et al.*, 1986; Komarneni and Roy, 1986; Kelly and Rowson, 1995; Kingman and Rowson, 1998, 2000; Wang *et al.*, 2000; Huang and Rowson, 2001; Vorster *et al.*, 2001; Stout and Komarneni, 2002), in textile processing (Griffin and Hendrix, 1986), in environmental remediation techniques (Krause and Helt, 1993), in analytical sample preparations (Smith and Arsenault, 1996), and in assessing the behavior of various materials under microwave heating (Standish *et al.*, 1991; Whittington and Milestone, 1992; Kudra *et al.*, 1993; Abdelghani-Idrissi, 2001; Long *et al.*, 2002).

* E-mail address of corresponding author:
girgin@hacettepe.edu.t r
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The water molecule has an exceptionally high polarity which makes it an ideal material for microwave absorption due to its highly asymmetric configuration. The water dipoles align themselves with respect to the electric field of microwave energy and, after removing microwave energy, thermally-induced disorder in water is restored. At 2450 MHz, the alignment of the molecules followed by their return to disorder occurs 4.9×10^9 times per second and results in very rapid heating (Neas and Colins, 1988). The number of relaxations that correspond to different states of water are a few kHz for ice and water of crystallization and about 10 GHz to a few THz for bulk water (Thuéry, 1992).

Vermiculites and phlogopites can be exfoliated by chemical and thermal treatment methods (Myers, 1963; Mamina *et al.*, 1990; Suquet *et al.*, 1991; Üçgül, 1997; Obut and Girgin, 2002; Üçgül and Girgin, 2002). The exfoliated materials are chemically inert, adsorbent, fire resistant, low in density and have excellent thermal and acoustic insulation properties (McCarl, 1983; Meisinger, 1985; Suquet *et al.*, 1991; Hindman, 1994). The water content of the clay generally determines the extent of exfoliation and the presence of interstratification is claimed to increase the rate of exfoliation (Mamina *et al.*, 1990; Justo *et al.*, 1993).

Considering the strong interaction between water and microwaves, the aim of this work was to establish the exfoliation characteristics of phlogopites and vermiculites after treatment with water and hydrogen peroxide solution under an applied microwave field.

MATERIALS AND METHODS

Crude samples of Phalaborwa (South Africa) phlogopite (PP), Phalaborwa vermiculite (PV) and Sivas-Yıldızeli-Karakoç (Turkey) phlogopite (KP) were used in the experiments.

Table 1. Chemical compositions (wt.%) of the samples.

	SiO_2	MgO	Al_2O_3	K_2O	Fe_2O_3	TiO_2	CaO	Na_2O	F	LOI
KP	36.28	16.99	16.37	7.98	12.05	2.90	1.68	0.38	1.39	4.29
PP	41.90	24.21	9.64	10.92	6.66	1.41	0.84	0.33	0.14	2.58
PV	38.00	27.91	9.46	4.42	2.94	1.12	0.74	0.18	0.20	13.70

LOI: loss on ignition

The chemical compositions of the samples were determined by X-ray fluorescence (XRF) analysis (Philips PW 1480 spectrometer) and the results are given in Table 1. The mineralogical compositions of the samples were determined by X-ray diffraction (XRD) analysis (Philips PW 3710 diffractometer) and the patterns of the samples are given in Figure 1. The low-intensity extra scattering in the patterns of samples treated with ethylene glycol showed that only sample KP has a minor amount of vermiculite in its structure.

The thermogravimetric/differential thermal analysis TG/DTA analyses were performed between 25ºC and 1100ºC on the raw materials using a Rigaku Model No: 2.22E2 analyzer and the resultant data are given in Table 2. The low-temperature weight losses are related to the adsorbed and interlayer water of which there is more in the PV sample. Sample KP has greater low-temperature weight loss than sample PP because of its small vermiculite content.

The microwave exfoliation characteristics of the three clay samples were studied in a domestic White Westinghouse (Model KM-90 VP) microwave oven with a working frequency of 2400 MHz. In all exfoliation tests, 2 g of square-shaped samples with an average size of 2×2 cm and thickness of 0.1–0.4 cm equilibrated at atmospheric conditions for 15 days were used. The samples were placed in the center of the microwave oven.

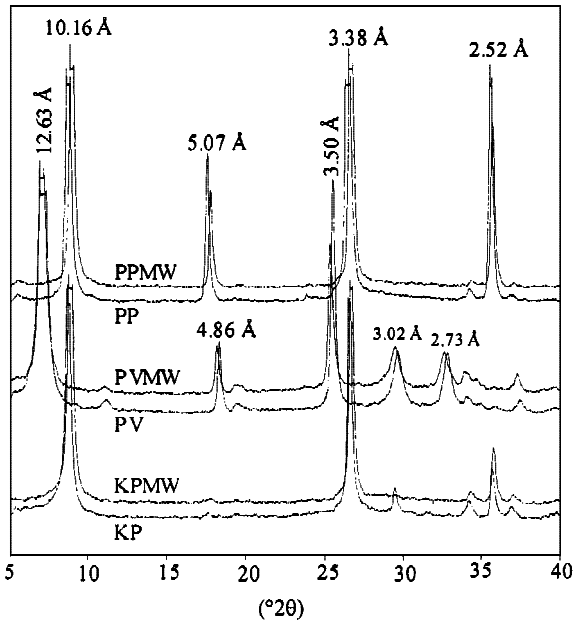

Figure 1. XRD patterns of crude and microwave-treated (MW) samples.

Since the interlayer water content, which changes with the relative humidity, and the type of interlayer cation are the most important factors in exfoliation, the crude samples were treated separately for 30 min with water, 10% H_2O_2 and 20% H_2O_2 aqueous solutions in order to increase their interlayer water contents for hydration of interlayer cations and silicate layers. After this treatment, the outer surfaces of the hydrated samples were dried quickly with tissue paper and subjected to microwave radiation. Hydrogen peroxide solution was used due to its known chemical exfoliation effect on vermiculites and phlogopites (Mamina *et al.*, 1990; Obut and Girgin, 2002; Üçgül and Girgin, 2002).

The crude samples were treated separately with 1 N chloride solutions of Li and Ca at 50ºC for 24 h at a solid/liquid ratio of 1/50 (g/mL) to exchange the initial interlayer cations with highly hydrated Li and Ca cations to increase the interlayer water contents. After this treatment, the samples were dried at room temperature and then subjected to microwave exfoliation.

The crude samples were also heated for 1 h at 400ºC in a muffle furnace to remove the interlayer water so as to reveal the effect of interlayer water on exfoliation. Then, the heated samples were cooled to room temperature in a desiccator and subjected to microwave radiation at 1300 W for 1 min.

In the experimental work, the effect of microwave power on exfoliation was studied on crude and treated samples at 600, 950 and 1300 W for microwave exposure times of 10, 20, 30, 60, 120 and 300 s. After each exposure time, the degrees of exfoliation (*i.e.* the thickness of exfoliated material/the thickness of original

Table 2. TG-DTA data of the crude samples.

	DTA data Peak temp (ºC) and type				TG data Temp range (ºC)	Weight loss (%)
KP	101 endo	193 endo	778 endo	1000 exo	20–255 580–830	2.5 1.8
PP	80 endo	459 endo	1065 endo	1100 exo	20–255 255–830	1.2 1.1
PV	162 endo	273 endo	827 endo	999 exo	20–325 742–1075	8.5 4.3

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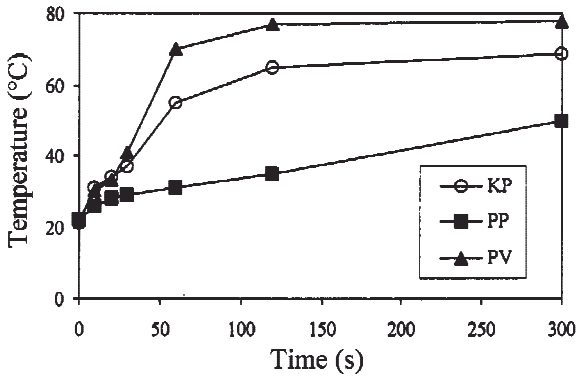

Figure 2. Sample temperatures at 600 W.

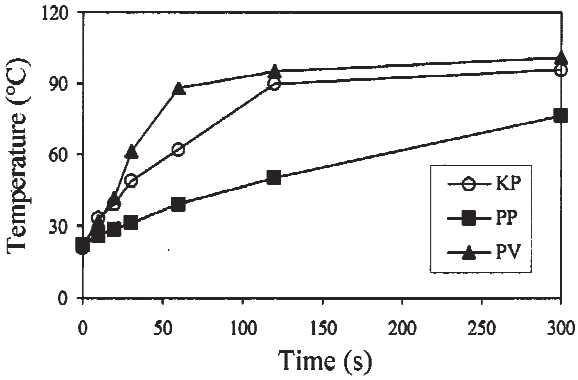

Figure 3. Sample temperatures at 950 W.

material) and the weight losses were determined and the temperatures of the samples were measured using a Raytek Raynger (Model R3iLTDL26) IR sensor.

RESULTS

The temperatures of the samples after various microwave exposure times measured at different power levels are given in Figures 2–4 for samples KP, PP and PV, respectively, showing that sample PV reaches the highest temperatures of 78, 101 and 110ºC for 600, 950 and 1300 W at 300 s of exposure time, respectively. In general, for all the studied microwave powers and exposure times, sample PP has the lowest temperature values.

The effects of microwave radiation on exfoliation and weight loss were studied at 1300 W with continuous microwave energy, and the exfoliation and weight loss values for various exposure times at this power are given in Figures 5 and 6 which show that samples PV, KP and PP have 28-, 10.1- and 5-fold exfoliation values at 1300 W for 300 s of exposure time, respectively. Of these, the exfoliation values of PV for exposure times >30 s are commercially acceptable.

Each crude sample treated separately with water, 10% H_2O_2, 20% H_2O_2, 1 N LiCl and $CaCl_2$ solutions and heated at 400ºC was exfoliated at 1300 W for 1 and 5 min and the results are given in Table 3 which shows that the hydration of the PV and KP samples caused by treatment with water, H_2O_2, Li and Ca increase the exfoliation values in the order: original < water < 10%H_2O_2 < Ca < 20%H_2O_2 < Li for both 60 and 300 s exposure times. The exfoliation behavior of the PP sample is very limited; it increases slightly with exposure time but no significant improvements in exfoliation values are observed for the treated samples. On the other hand, heat treatment at 400ºC disrupts the exfoliation behavior of the samples for all the studied microwave powers and exposure times.

DISCUSSION

The results show that the extent of exfoliation is related mainly to the degree of water loss from the samples as shown in Figure 7.

The water molecules in the interlayers of the individual flakes are driven off quickly as steam by microwave treatment that causes the layer separation or exfoliation of the samples. As vermiculites contain more water than phlogopites (Table 2), the extent of their exfoliation is expected to be, and is, greater, as shown by the data in Figure 5.

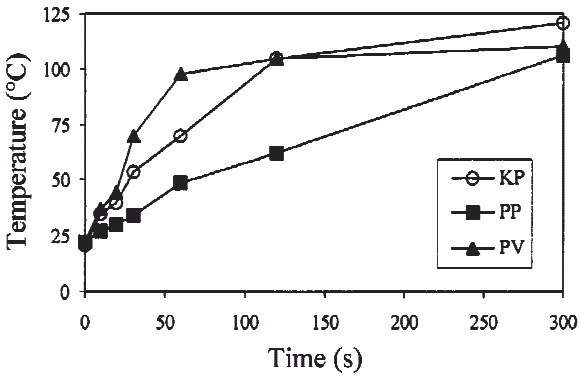

Figure 4. Sample temperatures at 1300 W.

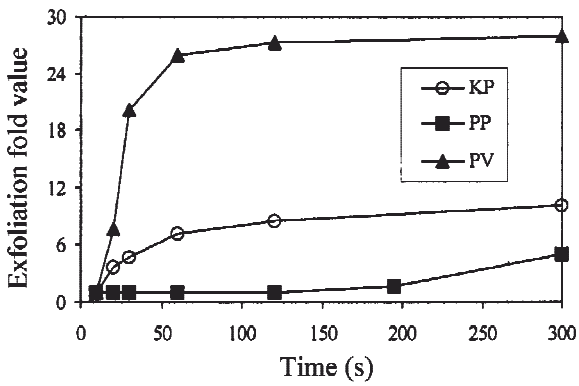

Figure 5. Exfoliation characteristics of samples at 1300 W.

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Table 3. The effect of water, H_2O_2, Li, Ca and heat treatment on exfoliation at 1300 W.

Sample	Original		Water		10% H_2O_2		20% H_2O_2		Ca-exchanged		Li-exchanged		400°C heat
Treatment time (s)	60	300	60	300	60	300	60	300	60	300	60	300	treated
KP	7.2	10.1	7.9	10.2	9.1	10.4	10.5	11.3	9.5	10.5	10.9	12.4	1.0
PP	1.0	5.0	1.0	5.0	1.0	5.0	1.0	5.1	1.0	5.0	3.5	5.2	1.0
PV	26.0	28.0	27.6	30.2	29.2	32.6	31.6	35.3	31.1	33.0	34.2	36.9	1.0

Figure 1 shows that the first peak for the PV sample appears at ~12 Å which is an indication that the sample still contains water molecules in its interlayers, indicating that exposure to microwaves cannot remove all the water molecules between the layers. 72% of water is removed from sample PV, and ~68% from samples PP and KP. As this water layer is held very tightly by the tetrahedrally charged clays, and the properties such as viscosity, structure, *etc.* of this water are very different from those for the bulk water (Low and Margheim, 1979; Stucki *et al.*, 1984; Bishop *et al.*, 1994), microwave radiation cannot remove this last layer of water from the sample even for treatment times up to 5 min.

The treatment of the samples with water, 10% H_2O_2, 20% H_2O_2, Li and Ca increase the interlayer water contents due to hydration which in turn increases the exfoliation behavior of the samples. This is substantiated by heat treatment of the samples at 400°C prior to microwave application which removes the interlayer water (see Table 2) with the result that there was no exfoliation in the samples at any microwave power or exposure time.

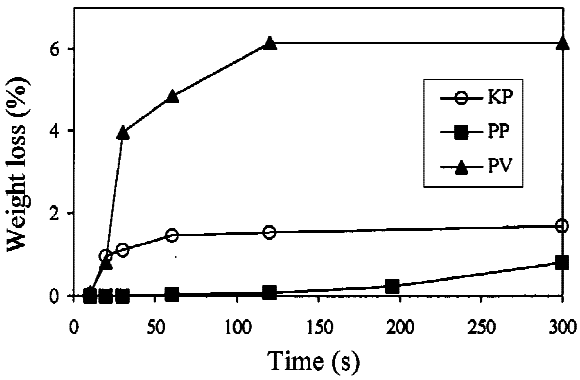

Figure 6. Weight losses in samples at 1300 W.

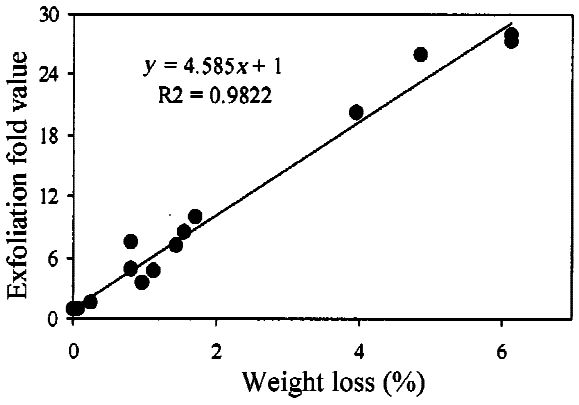

Figure 7. % weight loss *vs.* exfoliation values for the samples.

The higher exfoliation values obtained for samples treated with 10% and 20% H_2O_2 solutions can be explained by the separation of silicate layers by the vigorous release of oxygen, formed by the decomposition of H_2O_2 (Muromtsev *et al.*, 1990), this is accelerated by the increase in temperature (Üçgül and Girgin, 2002) during microwave treatment.

The maximum particle-size of the raw material is generally limited to 12.5 mm in conventional thermal treatment methods and, although there is no such a limitation in the H_2O_2 treatment method, the exfoliated material does need to be dried. On the other hand, it seems that in microwave processing coarser particles are suitable for exfoliation without additional treatments.

CONCLUSIONS

The ratio between exfoliation and loss on ignition obtained from DTA/TG data is a constant value for all the samples, which shows that the microwave exfoliation of vermiculites and phlogopites is mainly related to interlayer water; other factors seem to be of little importance.

Microwave treatment causes no structural changes in the sample as no major changes are observed in the XRD patterns of treated and untreated samples (Figure 1).

Maximum exfoliation values of 10- and 28-fold were reached in microwave treatments of phlogopite and vermiculite, respectively, comparable with 10- to 30-fold exfoliation values in conventional (900–1100°C) thermal methods.

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