

# Silane Coupling Efficiency on Thermal Properties of Volcanic Ash Filled PPS Composites

T. KUTLUK<sup>a,\*</sup>, O. ÇOBAN<sup>b</sup>, M.Ö. BORA<sup>b</sup>, S. FIDAN<sup>b</sup> AND T. SINMAZÇELİK<sup>c</sup>

<sup>a</sup>Kocaeli University, Department of Chemical Engineering, 41380, Umuttepe-Kocaeli, Turkey

<sup>b</sup>Kocaeli University, Faculty of Aeronautics and Astronautics, 41285, Kartepe-Kocaeli, Turkey

<sup>c</sup>Kocaeli University, Department of Mechanical Engineering, 41380, Umuttepe-Kocaeli, Turkey

Thermal properties of volcanic ash filled polyphenylene sulfide (PPS) composites have been investigated with respect to surface treatment that was conducted with 3-aminopropyltriethoxysilane (3-APTS) which had an organic functional group. Volcanic ash/PPS composite samples were prepared by using DSM Xplore 15 ml twin screw microcompounder and DSM Xplore 12 ml injection molding machines. The content of volcanic ash in composite samples was varied as 10 and 15 wt%. Volcanic ash filler dispersion and adhesion between volcanic ash particles and PPS matrix were examined by scanning electron microscopy. Thermal properties such as crystallization and melting behavior were investigated by TA Instruments Q200 differential scanning calorimeter. According to the test results, the relation between the thermal properties and surface treatment was determined as a function of melting temperature and melting enthalpy. Additionally, crystallization behavior was investigated according to surface treatment.

DOI: [10.12693/APhysPolA.129.498](https://doi.org/10.12693/APhysPolA.129.498)

PACS/topics: 81.05.Qk

## 1. Introduction

Polyphenylene sulfide (PPS) is a high performance, semicrystalline thermoplastic polymer which is finding increasing use as either unfilled or filled molding resin [1, 2]. It shows superior mechanical properties thermal stability, chemical resistance and precision moldability. However, PPS has some limitations for certain applications requiring superior flame resistance, high glass transition temperature, strength or/and toughness [3]. The addition of fillers into PPS is an attractive strategy to obtain composites with improved performance. For this reason, different inorganic particles such as Al<sub>2</sub>O<sub>3</sub> [4], TiO<sub>2</sub>, ZnO, and SiC [5] have been melt-blended with PPS matrix. Volcanic ash (VA), which is deposited at the surface during volcanic activity, is readily accessible and has the advantage that it can be economically mined, with enormous benefits of low cost and limited negative environmental impact compared with traditional open pit quarry-type clay mining [6, 7]. VA, known as mesoporous material, has high specific surface area, significant porosity and an appropriate pore structure, which enhances its possibility to be filled in PPS.

To the best of our knowledge, very few studies deal with the effect of VA filler in polymer composites. In VA filled composites it is reasonable to expect that the reinforcing VA particles will have some influence on the crystallization process. Thermoplastic matrix composites have been studied extensively in an effort to best utilize

the potential advantages of high fracture toughness, high temperature resistance, repairability and ease of manufacture. It has long been recognized that the modulus, stiffness, hardness, yielding, optical and electrical properties of semicrystalline polymers and the composites made therefrom are dependent on the crystallinity and crystalline morphology [8, 9]. For this reason, in addition to homogeneous dispersion of VA fillers, strong interfacial adhesion between polymer matrix (PPS) and VA filler is essentially crucial to obtain high-performance polymer/filler composites [10]. Surface modification of inorganic particles has attracted a great deal of attention because it produces excellent integration and improved interface between particles and polymer matrices [11–14]. While there have been many studies of PPS crystallization, there is not any report that have dealt with the influence of surface modification of VA particles on crystallization behavior of VA/PPS composites. Therefore, this study aimed to investigate the effect of silane coupling of VA particles on crystallization and melting properties of PPS composites. For this reason, thermal properties were investigated by differential scanning calorimetry (DSC) method.

## 2. Materials and method

### 2.1. Materials

PPS used as the matrix resin for the micro-compounding and injection molding was Fortron 1200L1 provided by Ticona Co. The Fortron 1200L1 is an unfilled grade for extrusion applications and has a density of 1.34 g/cm<sup>3</sup>. VA particles with density of 2.8 g/cm<sup>3</sup> were taken from Güneydag tuff ring, which is located 13 km southwest of Nevşehir/Turkey. SEM and elemental analysis of VA particles were shown

\*corresponding author; e-mail:  
[togayhan.kutluk@kocaeli.edu.tr](mailto:togayhan.kutluk@kocaeli.edu.tr)

in Fig. 1 and Table I. The silane coupling agent called 3-aminopropyltriethoxysilane (3-APTS) is one of the most popular predilections for creating a functional group on an inorganic surface of particle. It involves a short organic 3-aminopropyl group which cap off a primary amine.

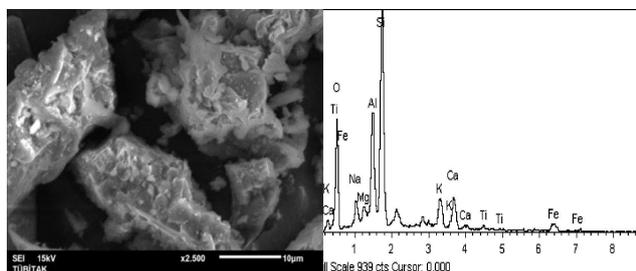


Fig. 1. SEM and elemental analysis of VA particles.

TABLE I

Elemental analysis of VA particles.

Elements	Weight [%]	Atomic [%]
O K	39.44	55.99
Na K	2.95	2.92
Mg K	1.41	1.32
Al K	10.55	8.88
Si K	24.98	20.20
K K	6.19	3.60
Ca K	6.96	3.94
Ti K	1.35	0.64
Fe K	6.17	2.51
O K	51.95	65.60
Na K	2.89	2.54
Al K	6.80	5.09
Si K	34.33	24.69
K K	4.03	2.08
Total	100.00	100.00

### 2.2. Silane coupling

A sum of VA whose particle size was  $< 71 \mu\text{m}$  was added in methanol at overnight by stirring 200 rpm to rip off from miriness and then washed with distilled water when pH reaches up to 7.0. Afterwards 50 ml of 5N NaOH solution was prepared for cleaning the VA particles. The mixture was kept in water bath more than half an hour at  $100^\circ\text{C}$ . VA feculence was removed by filtration and shaken in 1 litre of distilled water for detaches the NaOH on the surface of VA. Pure VA feculence was dried at  $110^\circ\text{C}$  in oven during 24 h. Powdered dry VA particles were mixed in recently prepared 3-APTS 1–3–5 % (v/v) in distilled water. The mixture was shaking at  $75^\circ\text{C}$  in 200 rpm on magnetic stirrer. At last, the VA feculence was filtered with whatman filter paper in filtering flask to obtain the silanized VA particles.

### 2.3. Sample preparation

All silane coated and original VA/PPS composite materials were prepared by melt compounding and injection molding processes. The content of VA in composite samples was varied as 10 and 15 wt%; DSM Xplore 15 ml micro-compounder was used for melt compounding and DSM Xplore 12 ml injection molding machine was used for injection molding of compounded melt. All the samples were extruded at  $340^\circ\text{C}$  of mixing temperature and 75 rpm of screw speed and then injected into the mold at  $150^\circ\text{C}$  with an injection pressure of 12 bar.

### 2.4. Differential scanning calorimetry

For DSC measurements, samples were prepared by shaving approximately 10 mg from the injection molded samples and sealed in aluminum pans. The melting behavior of VA/PPS composites was investigated by TA Instruments DSC Q200 differential scanning calorimeter at a heating rate of  $10^\circ\text{C}/\text{min}$  from  $25^\circ\text{C}$  to  $340^\circ\text{C}$  and under a nitrogen gas flow of 50 ml/min. The  $T_m$  was taken as the peak temperature of the melting endotherm. The degree of crystallinity,  $X_c$ , was calculated according to the following equation:

$$X_c = \frac{\Delta H_m 100}{\Delta H_m^0 \omega}, \quad (1)$$

where  $\Delta H_m$  is the melting enthalpy of the samples,  $\Delta H_m^0$  is the melting enthalpy for 100% crystalline PPS polymer ( $\Delta H_m^0 = 80 \text{ J/g}$ ) and  $\omega$  is the mass fraction for PPS in the VA/PPS composites [3, 15, 16].

## 3. Results

It is well known that DSC is a useful method to determine thermal properties of polymers such as melting temperature ( $T_m$ ), melting enthalpy ( $\Delta H_m$ ) and degree of crystallinity (%). To measure the effect of silane coupling of VA particles on the thermal properties of PPS, these measurements were employed for both silane coated and uncoated VA filled PPS. Silane coupling effect on the thermal properties of PPS composites that has 10 and 15 wt% VA loading content was illustrated in Fig. 2. As seen in Fig. 2a, the melting point of neat PPS is approximately  $280^\circ\text{C}$  for both 10 and 15 wt% VA contents. It was clear that silane coupling had no significant effect on  $T_m$  values of both 10 and 15 wt% VA filled PPS composites. It can be said that silane coupling did not change lamella thickness and spherulite size. Effect of silane coupling on melting enthalpy and degree of crystallinity was illustrated in Fig. 2b. For both 10 and 15 wt% uncoated VA filled PPS composites melting enthalpy values were obtained as approximately 43.7 and 44.1 J/g, respectively. On the other hand, degrees of crystallinities were obtained as 51.9 and 51.7 J/g for both 10 and 15 wt% uncoated VA filled PPS composites, respectively. Silane coupling up to 3 vol.% was significantly increased the melting enthalpy and degree of crystallinity such as from 52% to 58%. However, further

increment of silane coupling agent decreased these values. It can be noticed that 3 vol.% silane coupling of VA for PPS composites achieved significant increment in crystallinity and rigidity.

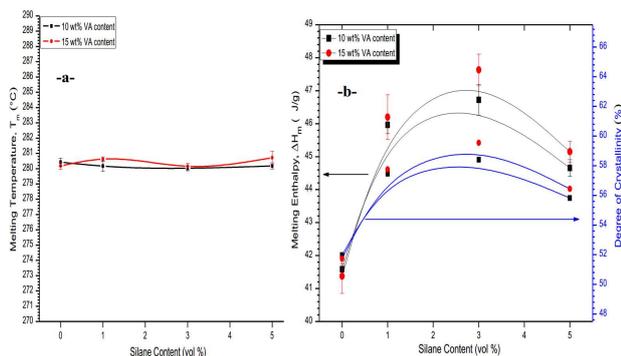


Fig. 2. Silane coupling effect on the thermal properties of VA/PPS composites: (a) melting temperature, (b) melting enthalpy and degree of crystallinity.

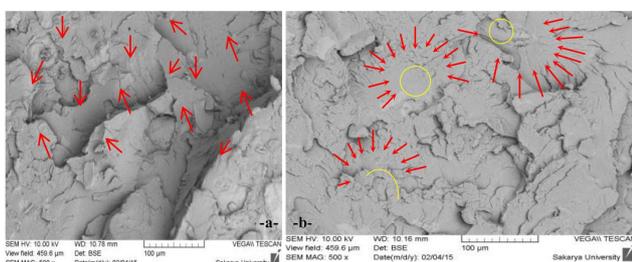


Fig. 3. Distribution and adhesion of VA particles in PPS composites: (a) original 15 wt% VA/PPS, (b) 3 vol.% silane coupled 15 wt% VA/PPS.

VA particles dispersion and adhesion with PPS of 15 wt% VA/PPS composite were investigated on three point bending fractured surfaces as shown in Fig. 3.

Almost all seen particles were marked with red arrows in Fig. 3a. It was clearly seen that a good distribution of VA particles in composite samples was obtained. Due to particle size, agglomeration was not expected. After silane coupling, a good adhesion was obtained between VA particles and PPS matrix as shown with yellow circle and red arrows in Fig. 3b. This phenomenon is supporting the increment of crystallinity degree.

#### 4. Conclusion

The effect of VA particles silane coupling on thermal properties such as melting temperature and crystallinity of VA/PPS composites was investigated. The results showed that degree of crystallinity of VA/PPS composites increased approximately by 6% with increase of silane coupling agent up to 3 vol.% content. According to the SEM analysis, strong adhesion was obtained between VA particles and PPS matrix after silane coupling. However,  $T_m$  values of VA/PPS composites did not change by silane coupling.

#### Acknowledgments

This work was supported by TUBITAK, “The Scientific and Technological Research Supporting Program 1001” under contract number of 213M563.

#### References

- [1] L.C. Lopez, G.L. Wilkes, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **C29**, 83 (1989).
- [2] L.I. Minkova, M. Paci, M. Pracella, P. Magagnini, *Polym. Eng. Sci.* **32**, 57 (1992).
- [3] A.M. Díez-Pascual, M. Naffakh, *Compos. Part. A- Appl. Sci.* **54**, 10 (2013).
- [4] C.J. Schwartz, S. Bahadur, *Wear* **237**, 261 (2000).
- [5] S. Bahadur, C. Sunkara, *Wear* **258**, 1411 (2005).
- [6] E. Avcu, O. Çoban, M.O. Bora, S. Fidan, T. Simmazçelik, O. Ersoy, *Polym. Compos.* **35**, 1826 (2014).
- [7] P.N. Lemougna, U.F.C. Melo, M.P. Delplancke, H. Rahier, *Ceram. Int.* **40**, 811 (2014).
- [8] S.L. Gao, J.K. Kim, *Compos. Part. A- Appl. Sci.* **31**, 517 (2000).
- [9] A.M. Díez-Pascual, J. Guan, B. Simard, M.A. Gomez-Fatou, *Compos. Part. A- Appl. Sci.* **43**, 997 (2012).
- [10] N. Ning, S. Fu, W. Zhang, F. Chen, K. Wang, H. Deng, Q. Zhang, Q. Fu, *Prog. Polym. Sci.* **37**, 1425 (2012).
- [11] H. Skaff, T. Emrick, *Angew. Chem. Int. Edit.* **43**, 5383 (2004).
- [12] Q. Peng, D.M.Y. Lai, E.T. Kang, K.G. Neoh, *Macromolecules* **39**, 5577 (2006).
- [13] Y. Taniguchi, M. Ogawa, W. Gang, H. Saitoh, K. Fujiki, T. Yamauchi, N. Tsubokawa, *Mater. Chem. Phys.* **108**, 397 (2008).
- [14] R. Walter, K. Friedrich, V. Privalko, A.J. Savadori, *J. Adhesion* **64**, 87 (1997).
- [15] Y. Yang, H. Duan, S. Zhang, P. Niu, G. Zhang, S. Long, X. Wang, J. Yang, *Compos. Sci. Technol.* **75**, 28 (2013).
- [16] S. Zhou, Q. Zhang, C. Wu, J. Huang, *Mater. Des.* **44**, 493 (2013).