FABRICATION AND STUDY ON PROPERTIES OF POLYPROPYLENE COMPOSITE MATERIALS/SILICA SAND POWDER

CHẾ TẠO VÀ KHẢO SÁT CÁC TÍNH CHẤT CỦA VẬT LIỆU COMPOZIT POLYPROPYLENE/BỘT CÁT SILICA

Dam Xuan Thang[1,*]

DOI: https://doi.org/10.57001/huih5804.2023.230

ABSTRACT

The polypropylene/silica sand powder polymer composite materials were fabricated by using the melt mixing method in a Haake internal mixer at 190°C. The influence of size and BCSi content on melt rheology, mechanical properties, and structural morphology was investigated. The results show the torque of the PP/BCSi composite material decreased as the BCSi content increased from 10 to 30% wt, but then increased at 40% and 50% wt. The tensile strength, elongation, and impact strength of the PP/BCSi composite were lower than that of PP, but the hardness was higher. When comparing PP/BCSi composites made with silica sand powder modified with steric acid (BCSiA) to unmodified (BCSi), those made with BCSiA had higher mechanical properties. By studying SEM images of the composite surface, we observed that BCSiA increased phase interaction, adhesion, and dispersibility of BCSi into the PP plastic substrate.

Keywords: *Poly propylen (PP), silica sand powder, PP/BCSi composite.*

TÓM TẮT

Vật liệu compozit PP/BCSi được chế tạo bằng phương pháp trộn nóng chảy ở 190°C trên máy Haake Rheomixer. Đã khảo sát ảnh hưởng của kích thước, hàm lượng BCSi đến lưu biến nóng chảy, tính chất cơ học và hình thái cấu trúc. Kết quả thu được cho thấy ban đầu khi hàm lượng BCSi tăng từ 10 đến 30% khối lượng, mô men xoắn của vật liệu compozit PP/BCSi giảm sau đó lại tăng khi hàm lượng BCSi trong mẫu chiếm 40%, 50% khối lượng. Độ bền kéo đứt, độ dãn dài khi đứt, độ bền va đạp của compozit PP/BCSi thấp hơn so với PP nhưng độ cứng cao hơn. So sánh tính chất cơ học của vật liệu compozit PP/BCSi sử dụng bột cát silica biến tính bằng axit steric (BCSiA) cao hơn so với chưa biến tính (BCSi). Nghiên cứu ảnh SEM bẻ gãy bề mặt vật liệu compozit cho thấy, BCSiA làm tăng tương tác pha, độ bám dính và khả năng phân tán của BCSi vào trong nền nhựa PP.

Từ khóa: *Poly propylen (PP), bột cát silica, compozit PP/BCSi.*

[1]Faculty of Chemical Technology, Hanoi University of Industry, Vietnam
[*]Email: thangdx@haui.edu.vn
Received: 06/10/2023
Revised: 20/11/2023
Accepted: 25/11/2023

1. INTRODUCTION

Polypropylene (PP) is a commonly used thermoplastic in both daily life and industrial production. While it can be modified to change its flexible properties, its low melting temperature, impact strength, and toughness hinder its use in engineering applications. Several studies have been conducted to improve the melting temperature and hardness of PP. One method is to increase its molecular weight through copolymerization with PS PMMA or by adding inorganic particles like silica or carbon nanotubes [1-3]. Adding inorganic particles has been found to be an effective way to enhance some mechanical properties of pure PP [4].

Silica is an inorganic particle and has been used extensively for its ability to enhance properties like hardness and mechanical strength in thermoplastics such as PE and PP [5]. In studies, pure silica with different sizes and concentrations is often used, but few studies use silica sand powder - a readily available raw material in Vietnam with high silica content - in the production of composite materials with thermoplastic polymer substrates. In particular, PP is a thermoplastic polymer with unique advantages that make it a popular choice for composite materials. This article presents findings on the impact of unmodified and modified BCSi size and content on the fabrication of PP/BCSi composite materials in a molten state, as well as the physical and mechanical properties and structural morphology of these materials.

2. EXPERIMENTAL

2.1. Materials

Polypropylene (PP) resin was used in the form of commercial product granules (Singapore) with a density of 0.903g/cm^3, a flow index of 20g/min at 146°C.

Silica sand powder (BCSi) commercial product (Vietnam) with SiO_2 content 99.0 - 99.8%, with size 5µm (BCSi3), 10µm (BCSi2), 30 µm (BCSi1) and content of Fe_2O_3 $\leq$ 0.03%. Steric acid is a commercial product in China.

2.2. Sample preparation PP/silica sand powder composite

Polypropylene (PP) and silica sand powder (BCSi) were physically mixed with predetermined contents (Table 1).

PP/BCSi samples were prepared using the melt mixing method in a Haake internal mixer with a rotor speed of 50rpm and temperature of 190ºC.

Table 1. Mass composition ratio for fabricating PP/BCSi composite materials

No	Samples	Ratio of ingredients by volume	
		PP resin	Silica sand powder
1	PP	100	0
2	PP/BCSi3	80	20
3	PP/BCSi2	80	20
4	PP/BCSi1	80	20
5	PP/BCSi310	90	10
6	PP/BCSi320	80	20
7	PP/BCSi330	70	30
8	PP/BCSi340	60	40
9	PP/BCSi350	50	50

PP/BCSi composite material samples were injection molded into paddles using Haake MiniJet Pro equipment (Thermo Scientific), following ISO 527 standards, to determine material properties.

2.3. Characterization

2.3.1. Melting rheology

Melting rheology data was collected using Polylab simulating software connected to Hakke polylab os Determine the temperature variation and the force of the rotor following the time, thereby determining the melting rheological state of the material.

2.3.2. Fourier Transform Infrared Spectroscopy

The FTIR spectra of the samples were recorded using Fourier Nexus 670 (USA) at room temperature, in the wavenumber region from 500 to 4000cm^{-1} with a 4cm^{-1} resolution and 32 scans by using the reflexed method.

2.3.3. Field emission scanning electron microscopy (FESEM)

Morphology of the samples were analyzed by using a field emission scanning electron microscopy (JEOL, JSM-6510LV, Japan) at Institute of Materials Science, Vietnam Academy of Science and Technology. The samples were coated with platinum prior to FESEM observation.

2.3.4. Mechanical properties

The tensile properties and elongation at break of the testing samples were performed on a universal testing machine (Zwick V.2.5, Germany) at the room temperature with a crosshead speed of 50mm/min, in standard with ASTM D638M-93/89 for plastic.

2.3.5. Determine firmness properties

The firmness of the material was measured on Durometer device (Germany), shore D according to ASTM D785-08 standard.

2.3.6. Determination of impact resistance

The impact strength of the material was conducted according to ISO 179 standard on the impact measuring device of Olsen Tinus (USA).

3. RESULTS AND DISCUSSION

3.1. Investigate the effect of sad powder size

3.1.1. Rheological studies of PP/BCSi composites

The torque and temperature of the polymer composites were recorded as a function of mixing time, as shown in Figure 1. The results provide qualitative information about the relative melt viscosity and mixing processes [6, 7].

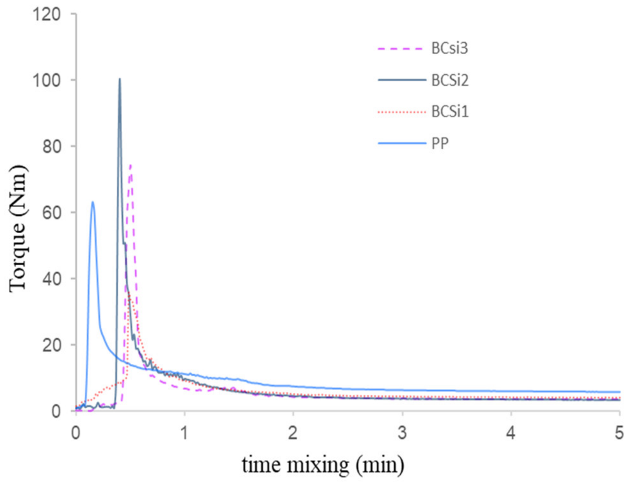


Figure 1. Plots of torque versus time of mixing for PP/BCSi with various sizes

At the beginning of the mixing process, the polymer is in a solid state, then it starts to melt and the measured temperature is recorded. It is clear that the sampled torque initially reaches its maximum when loading and closing the mixing chamber. This can be explained that during the material being in a solid state, resulting in high friction between the particles. However, as the process continues, the torque gradually decreases and stabilizes. This is because the molten PP particles and BCSi particles disperse into the PP matrix, enhancing its flexibility and flow. Additionally, when BCSi is added to the PP matrix, the stabilizing torque of the PP/BCSi material is lower than that of PP. Furthermore, if the BCSi particles are smaller in size, the stabilizing torque will be even lower. This is because smaller BCSi particles are more easily dispersed into the PP matrix and can be interspersed among the PP fiber bundles.

3.1.2. Scanning electron microscope images (SEM)

Figure 2 shows the SEM images of the PP/BCSi at 30% wt with various-size particles.

Observing the SEM image of the fractured material surface, it becomes clear that the smaller BCSi3 particles have a greater capacity to bond with the surface of the PP material compared to the larger-size BCSi2 and BCSi1 particles. Moreover, the BCSi1 and BCSi2 particles display distinct phase separation, resulting in gaps within the PP material.

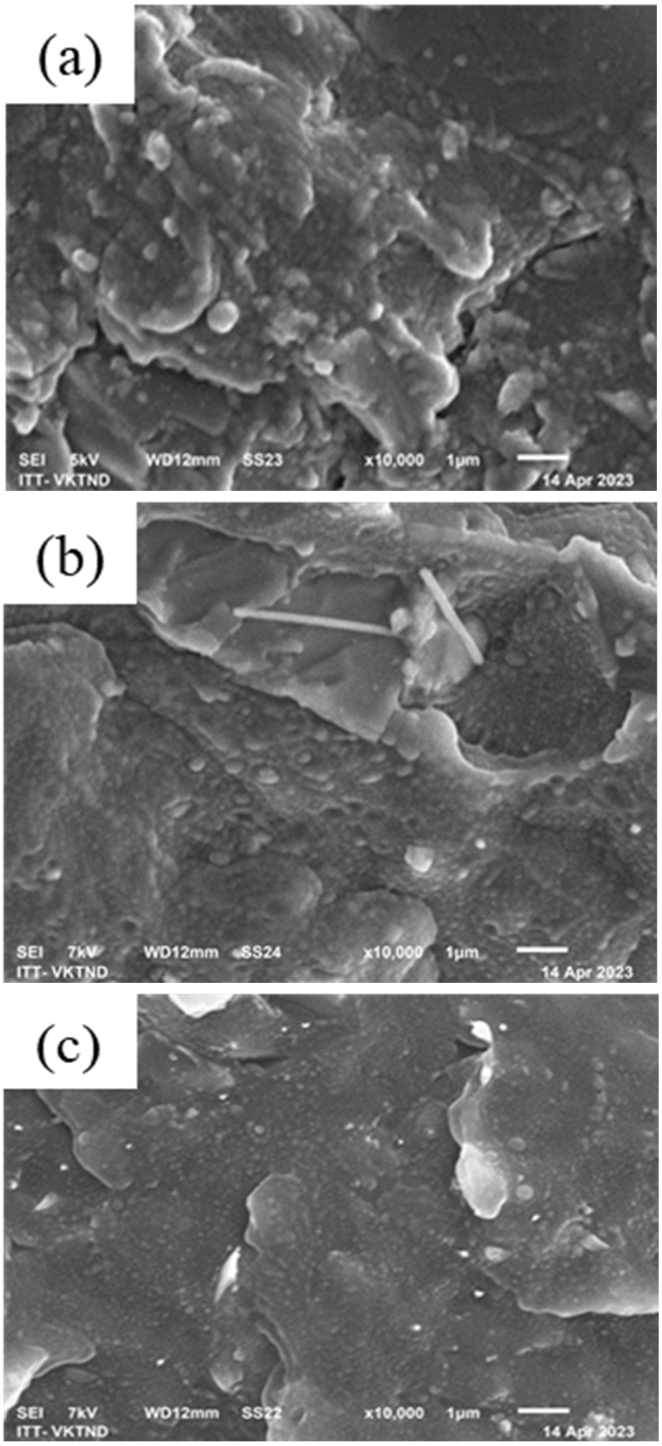


Figure 2. SEM images of PP/BCSi at 30 % wt (a) BCSi1; (b) BCSi2; (c) BCSi3

3.1.3. Mechanical properties of PP/BCSi materials

Table 2 presents the mechanical properties of PP/BCSi composites, which were fabricated at various sizes.

Table 2. Mechanical properties of PP/BCSi at 20 % wt with various-size particles

Samples	Impact strength (kJ/m²)	Tensile strength (MPa)	Elongation at break (%)	Shore D hardness
PP	56.80	35.35 ± 0.5	969.74 ± 1.1	56.00 ± 1.7
PP/BCSi3	43.96	28.81 ± 0.8	731.48 ± 1.9	69.80 ± 2.1
PP/BCSi2	44.12	28.43 ± 1.1	728.32 ± 2.1	69.35 ± 2.4
PP/BCSi1	44.56	28.18 ± 1.3	725.98 ± 2.4	68.76 ± 2.7

According to Table 2, we can observe that the tensile strength and flexural strength of the materials are at their highest level when using BCSi3. This is due to BCSi3 with the size of 5µm, making it easier to mix the silica sand powder evenly into the PP maxtric. In contrast, using BCSi1 and BCSi2 leads to poorer mechanical properties due to reduced mixing ability. The silica sand powder particles in these two types are not evenly dispersed in the plastic matrix, leading to defects in the product's contact surface between PP and BCSi. As a result, when BCSi is added to composite materials, the tensile strength, impact strength, and elongation at break all decrease, while the ductility increases. These changes in mechanical properties align with the phase interactions observed in SEM images of the material.

3.2. Effect of silica sand powder content

3.2.1. Rheological studies of PP/BCSi composites

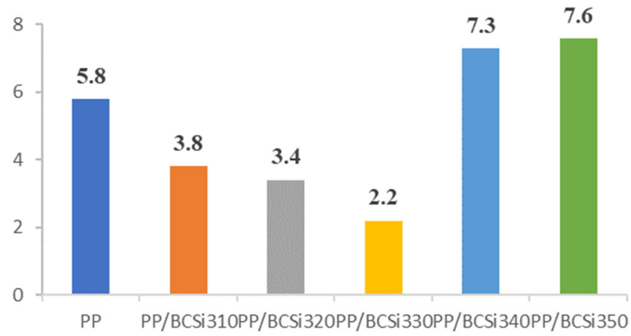


Figure 3. Stable torque of PP and PP/BCSi3 composites with different BCSi3 content

Based on Figure 3, the stable torque of PP/BCSi3 material declines gradually as the weight percentage of BCSi increases from 10% to 30%, which is lower than that of PP. However, when the BCSi3 content is raised to 40% and 50%, the stable torque rises at a faster and larger rate compared to PP. Thus, it can be concluded that the PP/BCSi composite material containing 30% BCSi content is more creatable than the other samples.

3.2.2. Mechanical properties

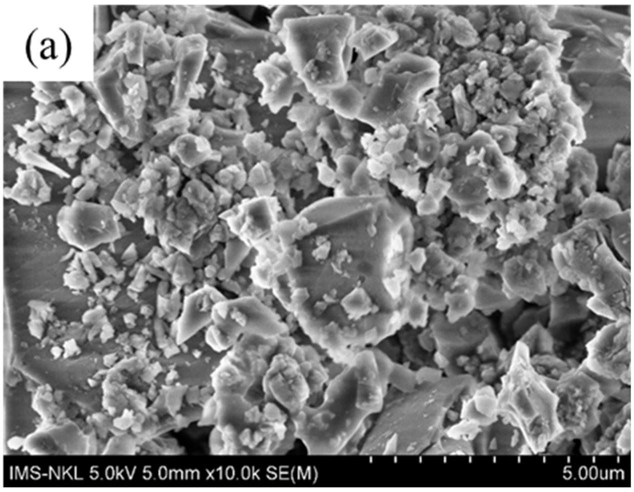
Observing Table 3, increasing the amount of BCSi3 in the material decreases in tensile strength. This indicates that the interaction and bonding between BCSi particles and the PP matrix is weak and that there is agglomeration of BCSi3 particles in the PP matrix at a content level of 50%. As a result, the stress concentrates in the BCSi3 particles when tensile, leading to breakage. This ultimately results in a reduction in the material's tensile strength. The same trend can be observed in the Elongation at break measurement, where a higher BCSi3 content also leads to decreased Elongation at break. This can be attributed to the low polarity of PP as a polymer. When BCSi3 particles, which are inorganic and active, were added to PP, they struggled to blend, which can cause defects within the composite material.

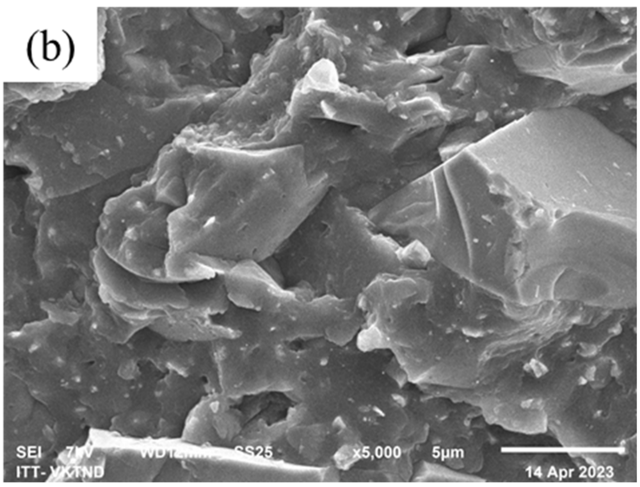
Table 3. Mechanical properties of PP/BCSi with different content

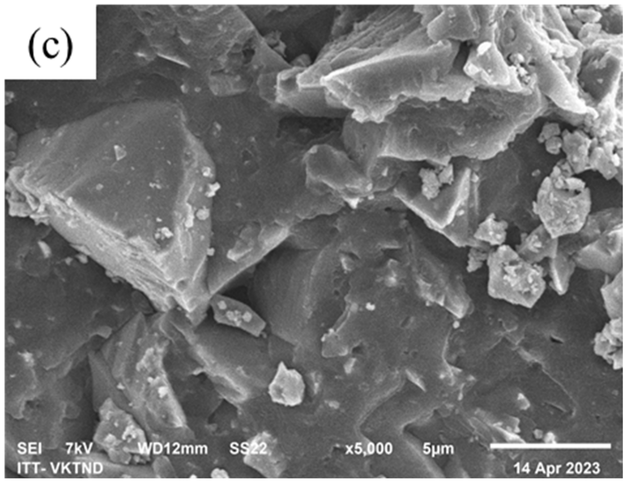
BCSi3 content (%)	Mechanical properties			
	Impact strength (kJ/m^2)	Tensile strength (MPa)	Elongation at break (%)	Shore D hardness
0	56.80	35.35 ± 0.5	969.74 ± 1.1	56.00 ± 1.7
10	47.78	29.54 ± 0.7	859.55 ± 1.5	58.42 ± 1.8
20	43.96	28.81 ± 0.6	731.48 ± 1.3	69.80 ± 1.7
30	27.83	24.00 ± 1.0	414.57 ± 2.3	74.59 ± 2.4
40	21.41	20.73 ± 1.3	195.44 ± 2.4	73.93 ± 2.5
50	12.34	17.25 ± 1.2	43.92 ± 2.2	73.53 ± 2.1

The strength of PP/BCSi3 decreased as the BCSi3 content increased. This shows that samples with high BCSi3 content have more energy absorption centers created in the material, resulting in the formation of holes. These holes help to prevent the propagation of cracks during material destruction. Interestingly, the hardness of the PP/BCSi3 composite material gradually increased until it reached a maximum of 30% content, after which it gradually decreased. This outcome is suitable with the changes observed in tensile strength and elongation at break.

3.2.3. SEM images (SEM)







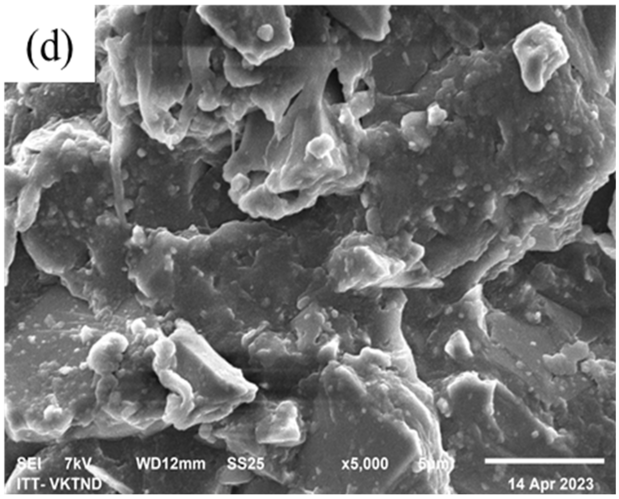


Figure 4. SEM image of BCSi3 (a) and fracture surface of PP/BCSi3 composite material 30% mass (b), 40% mass (c), 50% mass (d)

Figure 4 shows that the composite material sample with 30% BCSi is evenly dispersed in the PP plastic matrix and has good phase interaction. However, when using 40% and 50% BCSi content, phase separation occurs at the internal BCSi grain positions, which weakens the interaction between the phases and creates gaps. Additionally, clusters of BCSi particles appear in the substrate, which leads to a decrease in the mechanical properties of the corresponding composite materials.

3.3. Effects of original and modified silica sand powder

3.3.1. FTIR spectra

From Figure 5, it can be observed that the FTIR spectra of BCSi3 and BCSi3A are different. On the BCSi3A sample, there are characteristic stretching vibrations (ν) of C-H bonds and bending vibrations (δ) at wave numbers 2960cm^{-1}, 2915cm^{-1}, 2848cm^{-1}, and 1466cm^{-1}, the characteristic absorption of the C=O group is present at wavenumber 1698cm^{-1}. In contrast, the FTIR spectrum of BCSi3 does not show the characteristic absorption of the C=O group. This indicates that steric acid is present in the BCSi3A sample, and the denaturation process was successful.

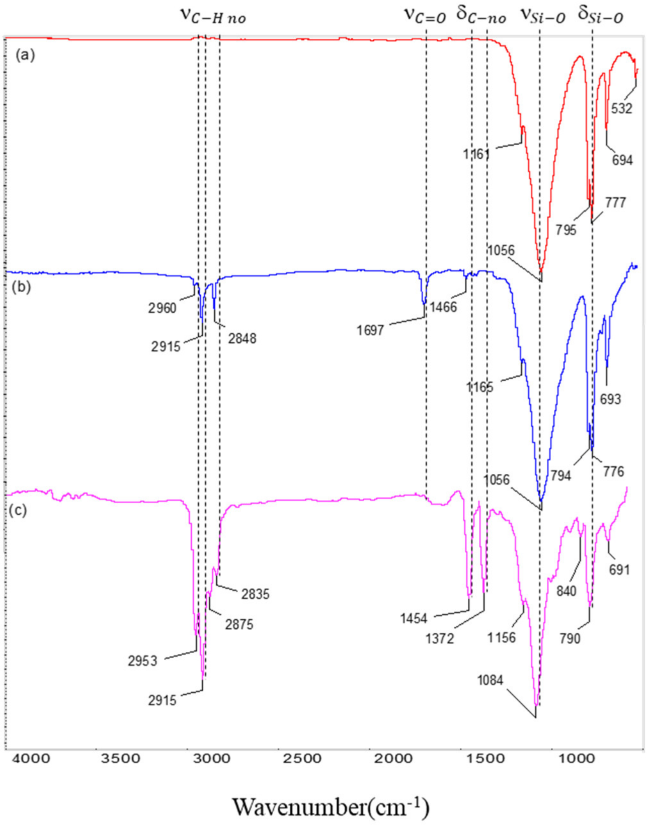


Figure 5. FTIR spectra of (a) BCSi3, (b) BCSi3A and (c) PP/BCSi3A composite

In Figure 5, the FTIR spectrum of the PP/BCSi3A composite displays the characteristic absorption of the PP matrix as the specific absorption bands of PP, such as the stretching vibrations (ν) of C-H bonds at $2953cm^{-1}$, $2915cm^{-1}$, $2875cm^{-1}$, and $2835cm^{-1}$; bending vibrations (δ) of CH_3 at 1454, δ(CH_2) at $1372cm^{-1}$. The characteristic absorptions of BCSi3 and BCSi3A appear at the wavenumbers $1156cm^{-1}$ and $1084cm^{-1}$, which are attributed to stretching (ν) and bending (δ) of Si-O (Si-O-C, Si-O-Si) in spectra of PP/BCSi [8, 9]. This result confirms the presence of BCSi3 and BCSi3A components in the composite material sample, and these particles have dispersed into the PP resin.

3.3.2. SEM images

In this study, the BCSi3 modification method was used with PP plastic to enhance compatibility. Upon observing the fracture surface of the material through an SEM image (Figure 6), it was found that the phase interaction between BCSi3 particles and PP substrate was weak in the initial composite material samples using BCSi3. Almost no adhesion or interaction of PP substrate on the surface of BCSi3 particles was observed.

By modifying the surface of BCSi3 particles with steric acid (BCSi3A), its phase interaction ability was significantly enhanced. The SEM image shows no gap at the contact position between BCSi3A particles and the PP substrate, indicating good adhesion. Additionally, the PP substrate also adheres well to the surface of BCSi3A particles.

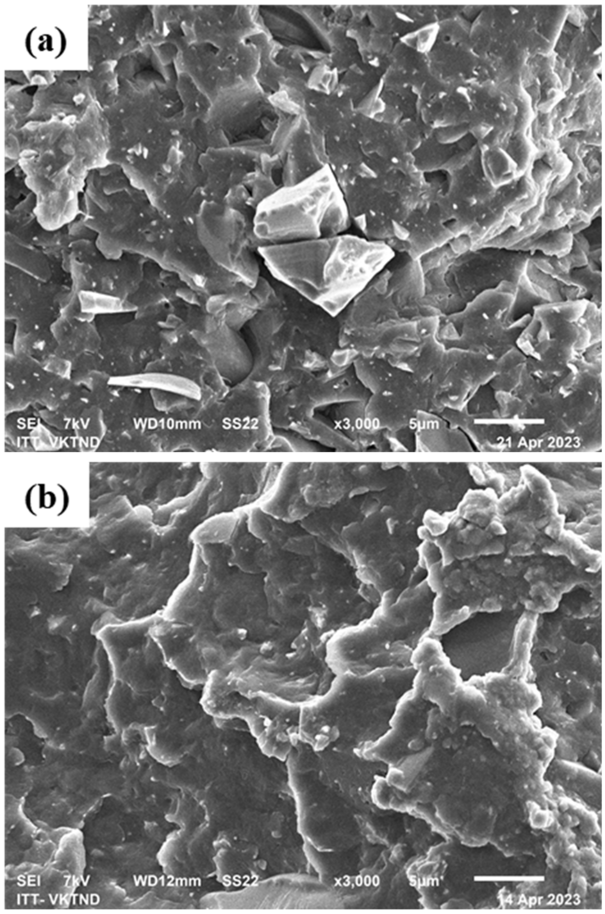


Figure 6. SEM image of the fracture surface of PP/BCSi3 (a) and PP/BCSi3A composite materials

3.3.3. Mechanical properties

Table 4 presents the impact strength, tensile strength, and elongation at break of PP/BCSi materials.

Based on Table 4, it is evident that adding BCSi3 particles to PP reduces the material's tensile strength. However, composite material samples using BCSi3A indicate an increase in tensile strength. This proves that BCSi3, when modified with steric acid, enhances its dispersion ability due to the long-chain hydrocarbon radical in the steric acid molecule interacting with the PP plastic matrix attached to the BCSi3 particle. The rules for the elongation at break of materials are also the same as the tensile strength.

Table 4. Mechanical properties of PP/BCSi

Samples	Mechanical properties			
	Impact strength (kJ/m^2)	Tensile strength (MPa)	Elongation at break (%)	Shore D hardness
PP	56.80	35.35 ± 0.5	969.74 ± 1.1	56.00 ± 1.7
PP/BCSi3	27.83	24.00 ± 1.0	414.57 ± 2.3	74.59 ± 2.4
PP/BCSi3A	26.61	27.82 ± 1.2	661.44 ± 1.9	74.32 ± 2.2

The addition of BCSi to PP composite materials results in a significant decrease in their impact strength. This is

P-ISSN 1859-3585 | E-ISSN 2615-9619

because the insertion of BCSi3 into PP plastic facilitates the process of impact destruction and crack propagation. The interaction between the surface of BCSi3 and the PP resin causes increased rigidity in the overall material structure. Although adding BCSi3 and BCSi3A to the PP plastic matrix increases its hardness, there is no significant difference in hardness between the two material samples using original and modified BCSi3.

This study aimed to improve the versatility of the PP/BCSi composite material, by utilizing granular materials to manufacture helmet shells through injection molding. These products meet TCVN 5756:2017 standards. Furthermore, PP/BCSi composite material was used to create clamps and screws using 3D printing technology. The result is a product with precise and distinct lines.

Figure 7. Helmet shell, clamp, nut made from PP/BCSi composite material

4. CONCLUSION

The impact of BCSi particle size on the mechanical and rheological properties of PP/Bcsi composite materials was conducted. The findings revealed that BCSi with a size of 5µm, is the most effective in enhancing PP materials to achieve optimal mechanical properties. Additionally, it is easy to process at 30% of the volume. Silica sand powder is a mineral that can be utilized as a reinforcing filler for thermoplastic-based composite materials.

When using original silica sand powder (BCSi3) in the production of PP/BCSi3 composite materials at the same content of 30% wt, the tensile strength and elongation at break were lower than those using modified silica sand powder (BCSi3A). However, there was little difference in hardness and impact resistance. Depending on the intended use, unmodified BCSi3 or BCSi3A can be used to create composite materials with PP plastic.

ACKNOWLEDGMENT

This work was completed under financial support from Science and Technology topic at the grassroots level of Hanoi University of Industry under grant number 50-2022-RD/HD-DHCN.

REFERENCES

[1]. Zhai WT, Wang HY, Yu J, Dong JY, He JS, 2008. *Foaming behavior of isotactic polypropylene in supercritical CO_2 influenced by phase morphology via chain grafting*. Polymer 49:3146-56. http://dx.doi.org/10.1016/j.polymer.2008.05.018

[2]. Shuzhao Li, Miaomiao Xiao, Dafu Wei, Huining Xiao, Fuzeng Hu, Anna Zheng, 2009. *The melt grafting preparation and rheological characterization of long chain branching polypropylene*. Polymer 50, 61216128. doi:10.1016/j.polymer.2009.10.006.

[3]. Patricio Toro, Raul Quijada, Omar Murillo, Mehrdad Yazdani-Pedram, 2005. *Study of the morphology and mechanical properties of polypropylene composites with silica or rice-husk*. Polymer International, 54:730-734. doi: 10.1002/pi.1740

[4]. Kyung Hwa Yoon, Sung Park, Youn Cheol Kim, 2012. *Study of the rheological properties and crystallization behavior of branched PP/silicate composites*. Polymer Journal 44, 1098-1104; doi:10.1038/pj.2012.68.

[5]. Rothon R. N., 2003. *Particulate-Filled Polymer Composites*. Rapra Technology Limited, Shrewsbury, UK.

[6]. Luo Z., Jiang J., 2010. *Molecular Dynamics and Dissipative Particle Dynamics Simulations for the Miscibility of Poly (ethylene oxide)/poly (vinyl chloride) Blends*. Polymer 51, 291-299.

[7]. El-Shekeil Y.A., Sapuan S.M., Jawaid M., Al-Shuja O.M, 2014. *Influence of Fiber Content on Mechanical, Morphological and Thermal Properties of Kenaf Fibers Reinforced Poly (vinyl chloride)/thermoplastic Polyurethane Poly-blend Composites*. Materials & Design 58; 130-135.

[8]. T. N. Agayev, N. N. Gadzhieva, S. Z. Melikova, 2018. *Fourier transform IR spectroscopic study of nano-ZrO_2 + nano-SiO_2 + nano-H_2O systems upon the action of gamma radiation*. J. Appl. Spectrosc., 85(2), 365-368.

[9]. Tham Do Quang, Hoang Thai, Giang Nguyen Vu, Kim Dung Nguyen Thi, Chung Ildoo, 2018. *Synthesis and characterization of (4-arm-star-PMMA)/PMMA-g-SiO_2 hybrid nanocomposites.* Green Processing and Synthesis, vol. 7, no. 5, pp. 391-398. https://doi.org/10.1515/gps-2018-0016.

THÔNG TIN TÁC GIẢ

Đàm Xuân Thắng

Khoa Công nghệ Hóa, Trường Đại học Công nghiệp Hà Nội