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RESEARCH ARTICLE

Investigation of Physicochemical Properties and Specific Heat Capacity of TiO_2 Doped- Polydimethylsiloxane Composites

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ABSTRACT

In this study, a series TiO_2-doped–polydimethylsiloxane composite (PDMS-TiO_2) were synthesized at constant amount of PDMS and different amount of TiO_2 particles. For this purpose, TiO_2 structures were synthesized by the hydrothermal method. Morphology and chemical structure of the obtained TiO_2 particles were investigated by scanning electron microscope (SEM), Energy Dispersive X-ray (EDX), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy techniques. Prepared particles were directly dispersed in PDMS wax with melted. The obtained composite structures were examined structurally by SEM, FTIR, and XRD spectroscopy techniques. The intense peaks at 13° and 16.5° visible in the XRD spectrum confirm the desired composite structure. For the pure PDMS structure, 0,523 and 1,740 KeV was observed for O_2 and Si in the EDX spectrum. Peaks at 0.452 (K_α) and 4.510 KeV (K_β) were observed for the composite structures. Then, the thermal properties of the composite structures obtained were investigated by DSC analysis. The study of the specific heat capacity of obtained products is attained by using a DSC. Depending on the amount of doped TiO_2 particles, the specific heat capacity value increased significantly in PDMS-TiO_2 composite structures. Specific heat capacity study' of TiO_2- polydimethylsiloxane composites is original and opened a new area about PDMS.

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1. Introduction

Polydimethylsiloxane (PDMS) is a polymer in the group of polymeric materials called organosilicones or silicones in general and used in many industrial applications [Sun et al 2020; Wolf et al 2018; Xuan et al 2017; Yang et al 2013]. Additionally, due to its adaptability and good qualities, PDMS is the most popular organic silicone polymer [Hwang et al 2019; Sun et al 2020; Xuan et al 2017; Yang et al 2013]. It is particularly well known for its peculiar rheological (or flow) characteristics. In general, PDMS is inert, non-toxic, and flammable in addition to being optically transparent [Wei et al 2017]. This is one of several varieties of silicone oil (polymerized siloxane). Due to its exceptional and distinctive physical and chemical properties, the PDMS product can be used in many applications [Wei et al 2017; Xu et al 2022]. They are highly permeable, adaptable, and mobile structures. It can adhere to some surfaces without breaking because of its numerous Si-CH_3 groups. It can be found in a variety of products, including elastomers, contact lenses, medical equipment, food (antifoam), shampoos (because it makes hair shiny and slippery), sealants, lubricants, and heat-resistant tiles [Bergeron et al 1997; Colas & Curtis 2013; Deborah 2019; Ounoughene et al 2019; Tottey et al 2019]. Polydimethylsiloxane is an essential industrial product, especially in cosmetics and adhesive industries [Abtahi-naeini et al 2018; He et al 2018]. It is also a polymer used for fusing plastic parts with an easy and simple process. Heat treatment is critical processing and assembling plastic parts, and therefore it is necessary to give heat in a controlled manner. For the heat not to damage the polymer structure during these processes, it is required to adjust the thermal properties of some nanostructures and PDMS. For this purpose, clay minerals, graphene, carbon black, carbon nanoparticles and some nanoparticles are used to prevent PDMS from melting more slowly and from thermal deformation. Adjusting the number of additives allows for the desired softening and thermal properties. Especially in composite materials, TiO_2 particles draw attention as an essential additive [Dahl et al 2014; Fujishima et al 2000; Kumar, Ghosh & Kumar 2016; Shojaee & Mohammadizadeh 2009]. Since PDMS is a polymeric material widely used in molding and the production of shock-absorbing surfaces, it is particularly highly exposed to thermoforming and molding processes. During these processes, thermal degradation and deformations are common [Camino, Lomakin & Lazzari 2001] [19]. However, it is possible to reduce these deformations by adjusting the specific heat capacity of the PDMS main structure. For this reason, different additives are tried and many studies are conducted to measure, determine and adjust the specific heat capacity, especially in industrial and commercial applications. Therefore, in this study, TiO_2 particles were used to tune the PDMS main matrix's heat capacity without changing the essential properties.

The most abundant titanium compound in nature is titanium dioxide (TiO_2). TiO_2 is widely used in paints, cosmetics, food products and the pharmaceutical industry. With the discovery of the photocatalytic activity feature of TiO_2, the usage areas of this material have expanded further [Fujishima et al 2000]. Current and future, TiO_2 materials are expected to be used in paint, toothpaste, protection from UV light, photocatalysis, photovoltaics, sensors, electrochromic and medicine [Abel et al 2021; Çeşmeli & Avci 2018; Fujishima et al 2000; Lee et al 2005; Rompelberg et al 2016; Wu 2021]. TiO_2 materials are a material with an electron band gap higher than 3eV and high absorption within the UV area [Manoj Karkare 2014] TiO_2 materials are highly stable, non-toxic and inexpensive [Dar, Saeed & Wu 2020]. Its other optical and biological properties allow it to be used in UV light protection applications. TiO_2 materials are used in glasses, mirrors, and superhydrophilic, superhydrophobic surfaces with their anti-fog functions in glass production [Howarter & Youngblood 2008; Lam et al 2008]. Titanium, also known as titanium dioxide, can be found in many crystal structures in nature, but it has two basic structures, rutile and anatase polymorphic phases. While both have a tetragonal structure, their usage areas vary due to density differences. Titanium; It has semiconductors, non-toxic, white color, low cost, high chemical stability, high photocatalytic activity [Siddiquib 2019]. Thanks to its surface–OH groups, TiO_2 provides different functional properties by interacting with matrix polymers in the composite industry.

For this reason, making strong interactions with some polar polymers shortens the spaces between the chains and reduces the polymer's glass transition temperature. However, when added to polymers with high apolar character, they behave as inert structures and cause an increase in the free volume value of the polymer and a decrease in the glass transition temperature. The amount of doped TiO_2 also significantly affects the polymeric structure's thermal stability and other thermal properties [Li 2009]. Within the scope of this study, the thermal properties and heat capacity of the PDMS structure were adjusted by doping TiO_2 particle structures at different rates. The resulting structures were characterized by FTIR, XRD, SEM and thermal analysis. The specific heat capacity value was determined by DSC analysis. As a result, it is seen that the thermal properties of the PDMS structure can be adjusted depending on the amount of TiO_2.

2. Materials and Method

2.1. Reagents and Instrumentation

The chemicals used for the synthesis, PDMS were analytical grade, and no further purification was employed. Titanium (IV) isopropoxide, i-propanol and HCl were obtained from Merck (Schuchardt, Germany).

The samples' crystalline structure, average particle size, and concentration of impurity compounds were all examined using XRD. A Rigaku Rad B-Dmax II powder X-ray diffractometer was used for the XRD models of these samples. Cu K radiation (λ value 2.2897 Å) was used to measure the 2 θ values between 20° and 110° at a division rate of 0.04°/min. The dried samples were dusted onto low-bottomed plates. A small amount of 30 (±2) mg spread over an area of 5 cm^2 was used to minimize the error at the peak position; additionally, the sample's thickness-related peak broadening was decreased. This data shows the crystal structure of the as well as the inter-planar space, d. According to Scherrer's formula, the peak broadening was proportional to the particle's average diameter (L), that is to say, $L = 0.9\lambda/\Delta\cos\theta$, where λ is the wavelength of the X-rays, Δ is the line enlargement measured at half height, and θ is the Bragg angle of the particles.

Attenuated Total Reflectance (ATR)–Fourier Transform Infrared (ATR–FTIR) analyses were carried out using one Perkin Elmer Spectrum Two model FT-IR spectrometer SiO_2-TiO_2 composite structures and determine if there is any TiO_2 present in the composite matrix in the range 4000 - 400 cm^{-1}. The average spectral resolution was 4 cm^{-1}. Differential scanning calorimeter (DSC) was carried out with Shimadzu DSC-60. DSC measurements were performed from 30 °C to 300 °C with a heating rate of 5°C/min in an air atmosphere condition.

The chemical composition of the samples was analysed by energy dispersive X-ray spectroscopy and; Rönteck xflash detector analyser in combination with a scanning electron microscope (SEM, Leo-Evo 40xVP). Particle beam incident energies from 3 to 30 KeV were used. The EDX spectra were corrected with the ZAF correction, which considers the matrix material's influence on the obtained spectra.

2.2. Preparation of TiO_2 particles

Titanium (IV)-isopropoxide (TIP) was added to 10% by mass in i-propanol, and the mixture was stirred for 10 min using a magnetically stirrer to form a clear sol. After stirring, a mixture of HCl and i-propanol was added to the TIP/i-propanol mixture as a catalyst. The molar ratio of HCl/TIP was 0.05. Stirring occurred at room temperature for 10 min. T_o initiate the hydrolysis-condensation reaction, a mixture of water and i-propanol was added dropwise the alkoxide solution and the molar ratio of $H_2O/Ti(OPr^i)_4$ ratio (mol/mol) of 3. The mixture was stirred at ambient temperature for 10 min. The sol solution was then transferred to an autoclave made of stainless Teflon. The autoclave was kept at 200 °C for 4 hours; it was removed from the hydrothermal unit and cooled to room temperature. The powders produced by the hydrothermal process were centrifuged and dried in a vacuum sterilizer at 40ºC for 3 hours.

2.3. Preparation of TiO_2 - polydimethylsiloxane composites

Nano-TiO_2-PDMS composites were done by mixing and casting. A certain amount of dimethyl siloxane was melted in a Teflon container, and the synthesized TiO_2 particle was added at 1%, 5%, and 10% by mass. Melted dimethyl siloxane was mixed homogeneously with the synthesized TiO_2 particles, and the mold was poured into the siloxane molds.

3. Results and Discussions

3.1. Characterization of PDMS-TiO_2 composites

Within the scope of the study, TiO_2 was doped at different rates to prevent the PDMS structure's structural deformation in heat treatments, delay its rapid fluidization and regulate its thermal properties. The structural and chemical properties of the obtained TiO_2-PDMS composites were determined by XRD and FTIR spectra. Fig. 1 presents the powder XRD patterns for the DMS and DMS-nano-TiO_2 composites. All the diffraction patterns of DMS and composites are similar, offering three diffraction peaks: a first one located at around 13°, which is the characteristic amorphous nature of PDMS and the second, more extensive and broader at 16.5° and the last and smallest at 25.2°. It was noted that all particle XRD profiles are quite similar. The decrease in the 12.1° peak intensity of the membrane prepared from a higher concentration of doping materials might imply a higher deposition of TiO_2 in the support layer.

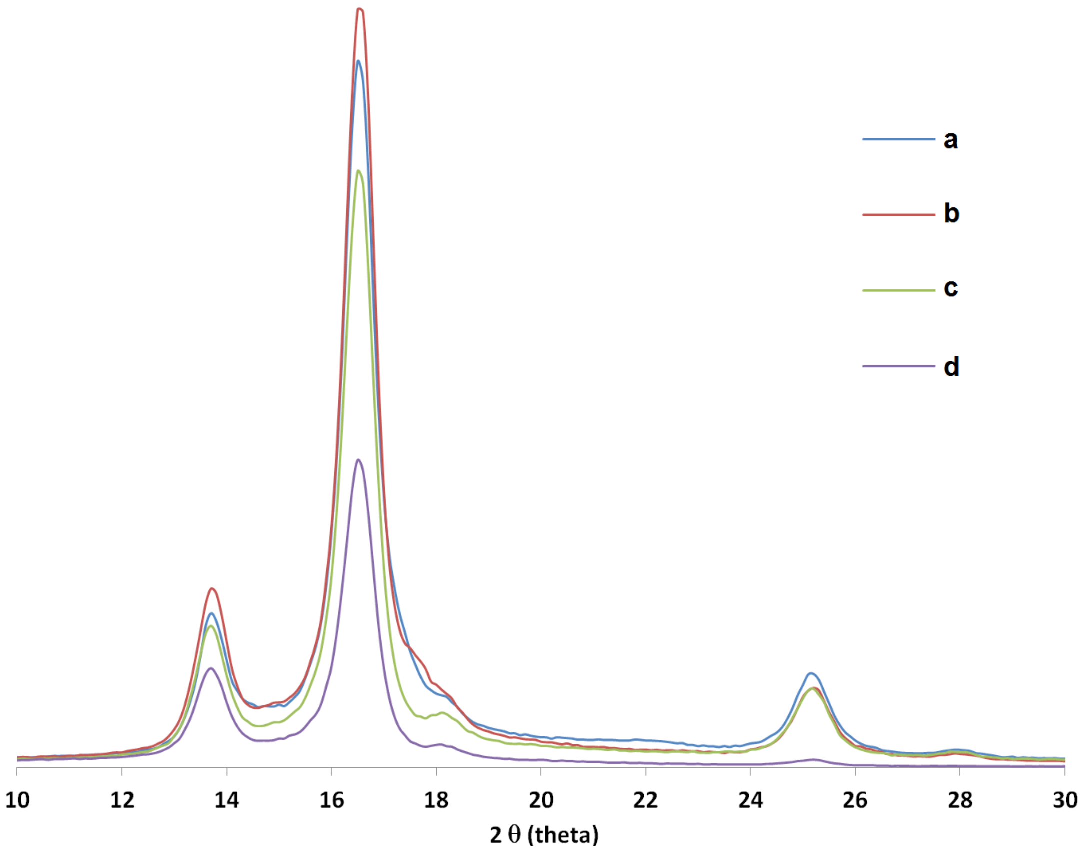

Figure 1. XRD pattern of pure PDMS **(a)**, PDMS-1%TiO_2 **(b)**, PDMS-5%TiO_2 **(c)** and PDMS-10%TiO_2 **(d)**.

The spectrum of the PDMS membrane exhibits typical Si-CH stretching and -CH_3 vibrations at 873 and 1246 cm^{-1}, as shown in Fig. 2. The Si-CH_3 of the PDMS membrane can be used to assign the symmetric and asymmetric stretching vibrations of the -CH_3 groups at 2963 and 2856 cm^{-1}, respectively. The symmetric stretching and bending vibrations of the Si-O in the straight Si-O-Si straight chain are identified by the spectral peaks at 1019 and 604 cm^{-1}.

Within the scope of the study, first of all, TiO_2 structures with particulate structures were synthesized using the hydrothermal synthesis strategy. SEM images and particle size distribution of the obtained TiO_2 structures are given in Fig. 3 (a and b). TiO_2 particles of different sizes with spherical structures can be clearly seen in this figure. Particle structures show a size distribution of 50 nm to 5 A°. The mean size distribution was seen to be around 150 nm. These TiO_2 particles obtained were doped into the PDMS structure, and a series of PDMS-TiO_2 composite structures were prepared.

Fig. 4 shows SEM images of pure PDMS structure and PDMS-TiO_2 composite structures. In these SEM images, the pure PDMS structure appears to be relatively flat and smooth. The ductile regions of this structure draw attention. It was observed that the composite structure became more fractal and the tensile property decreased as TiO_2 was added at different rates to this structure. Fractured surfaces and voids formed on the surface were detected in excessive TiO_2 loading.

The fundamental structure of the PDMS-TiO_2 composites prepared within the scope of the study and the elemental structure that changes depending on the increasing TiO_2 amount were investigated with EDX spectra. Fig. 5 shows EDX spectrum and EDX images of pure PDMS (a), PDMS-1%TiO_2 (b), PDMS-5%TiO_2 (c) and PDMS-10%TiO_2 (d). Peaks of Si, O, and C elements are seen in the EDX spectrum of pure PDMS. In the EDX spectra of PDMS-TiO_2 composites, in addition to the peaks of Si, O, and C elements, there is a peak of Ti element. Depending on the increasing amount of TiO_2, the intensity of the

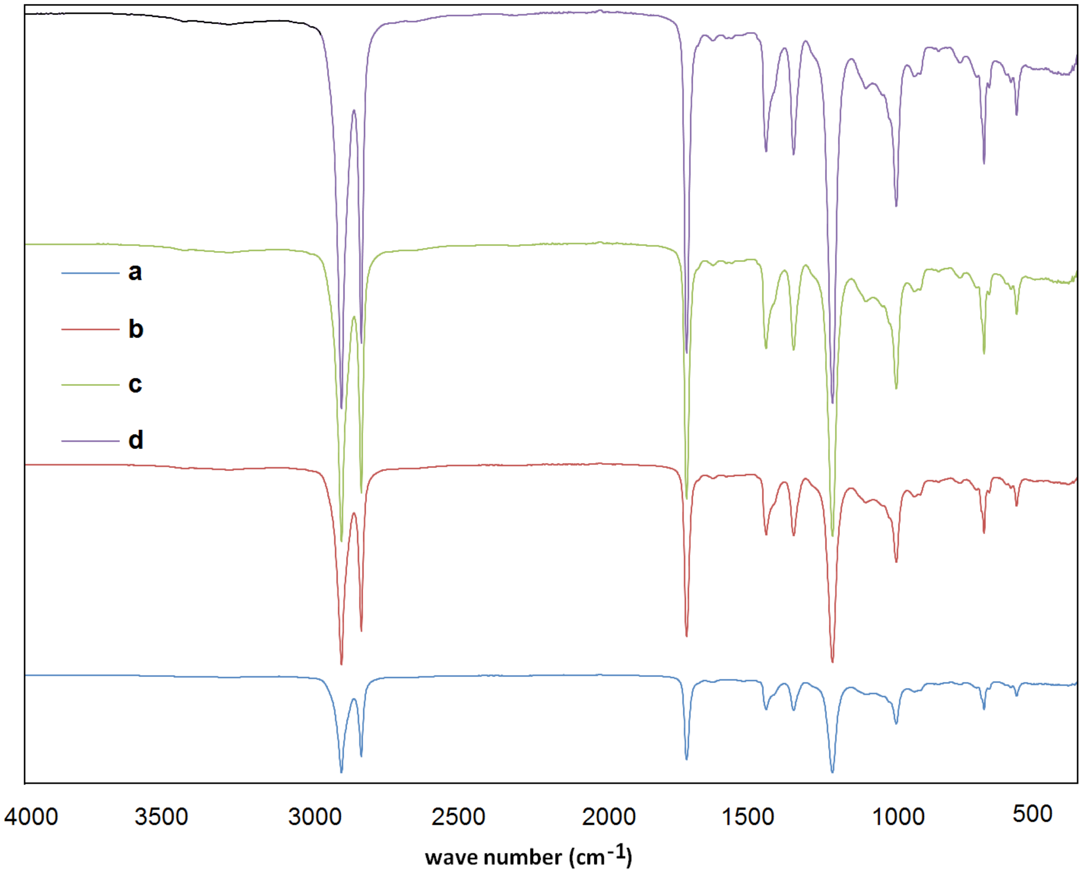

Figure 2. FT-IR spectrums of pure PDMS **(a)**, PDMS-1%TiO_2 **(b)**, PDMS-5%TiO_2 **(c)** and PDMS-10%TiO_2 **(d)**.

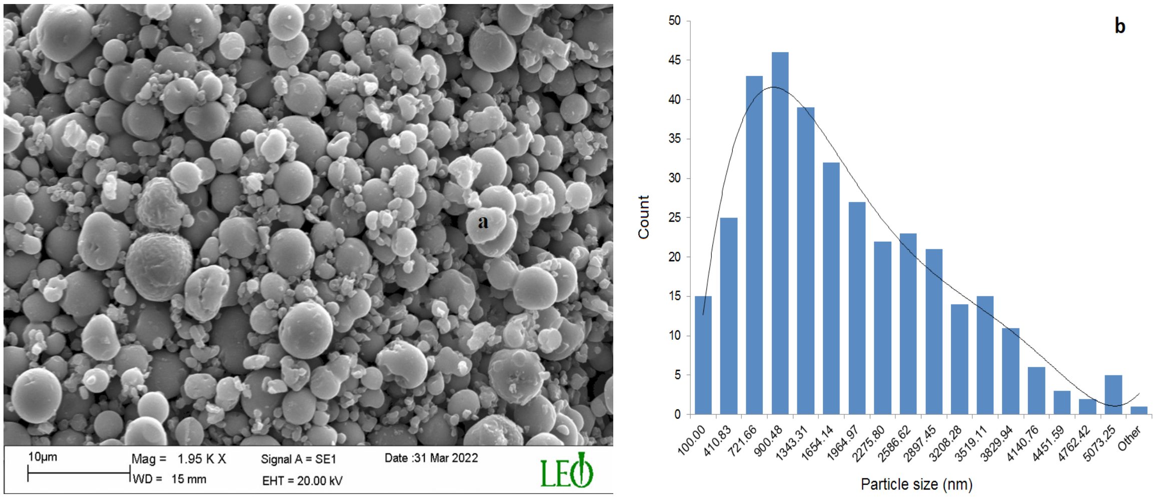

Figure 3. **(a)** SEM image of the synthesized TiO_2 structure, **(b)** particle size distribution of TiO_2 structure

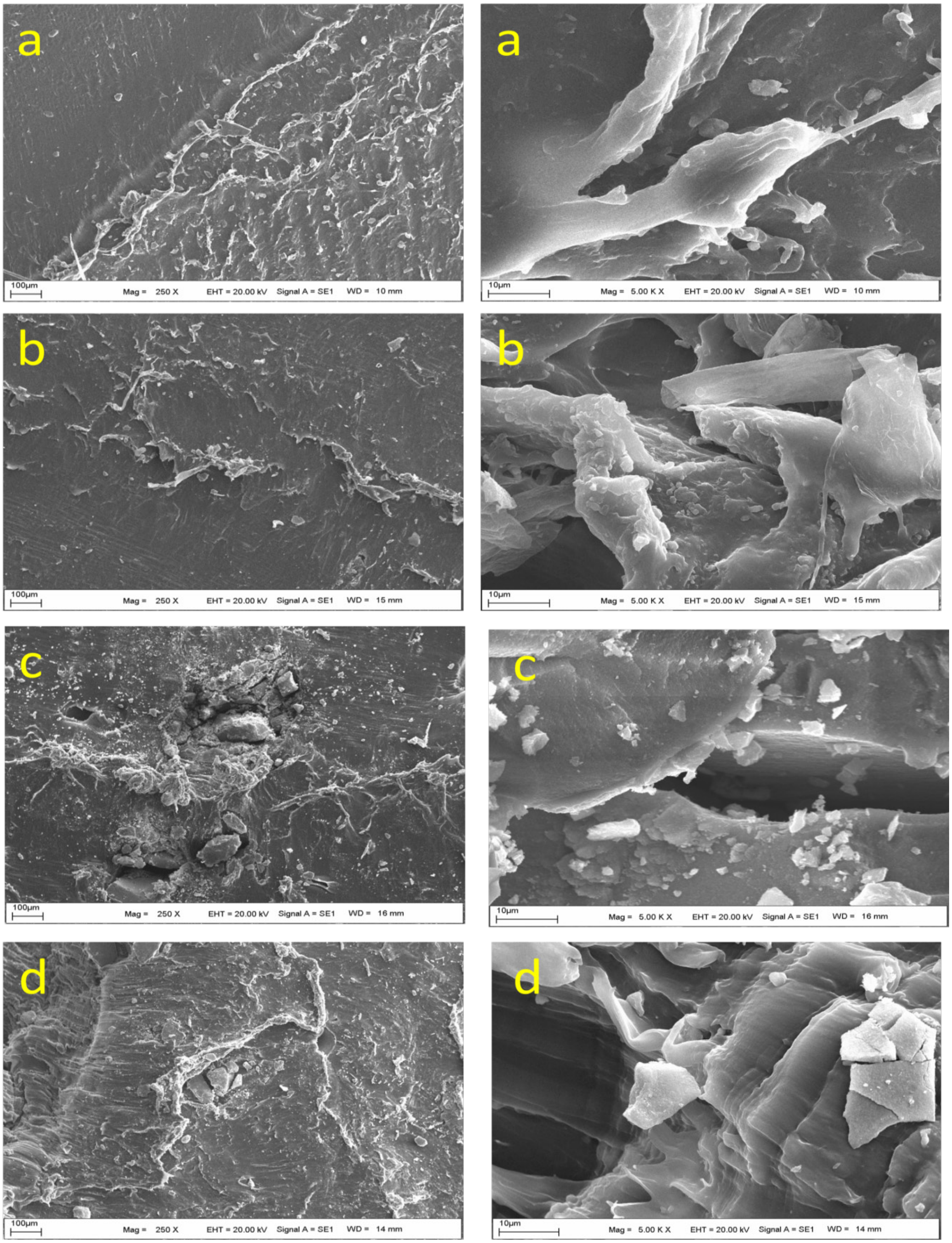

Figure 4. SEM images of pure PDMS **(a)**, PDMS-1%TiO_2 **(b)**, PDMS-5%TiO_2 **(c)** and PDMS-10%TiO_2 **(d)**.

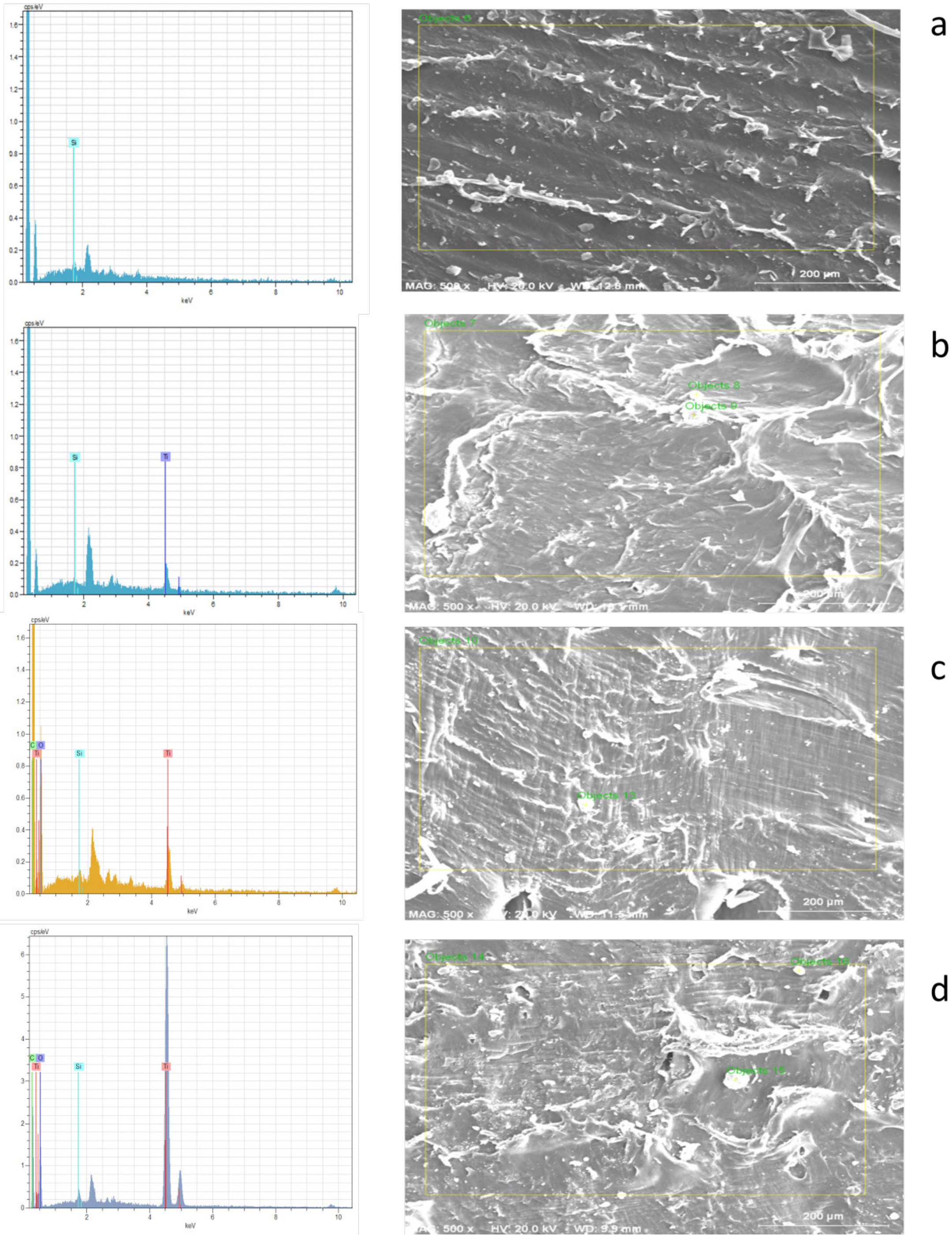

Figure 5. EDX spectrum and EDX images of pure PDMS **(a)**, PDMS-1%TiO_2 **(b)**, PDMS-5%TiO_2 **(c)** and PDMS-10%TiO_2 **(d)**.

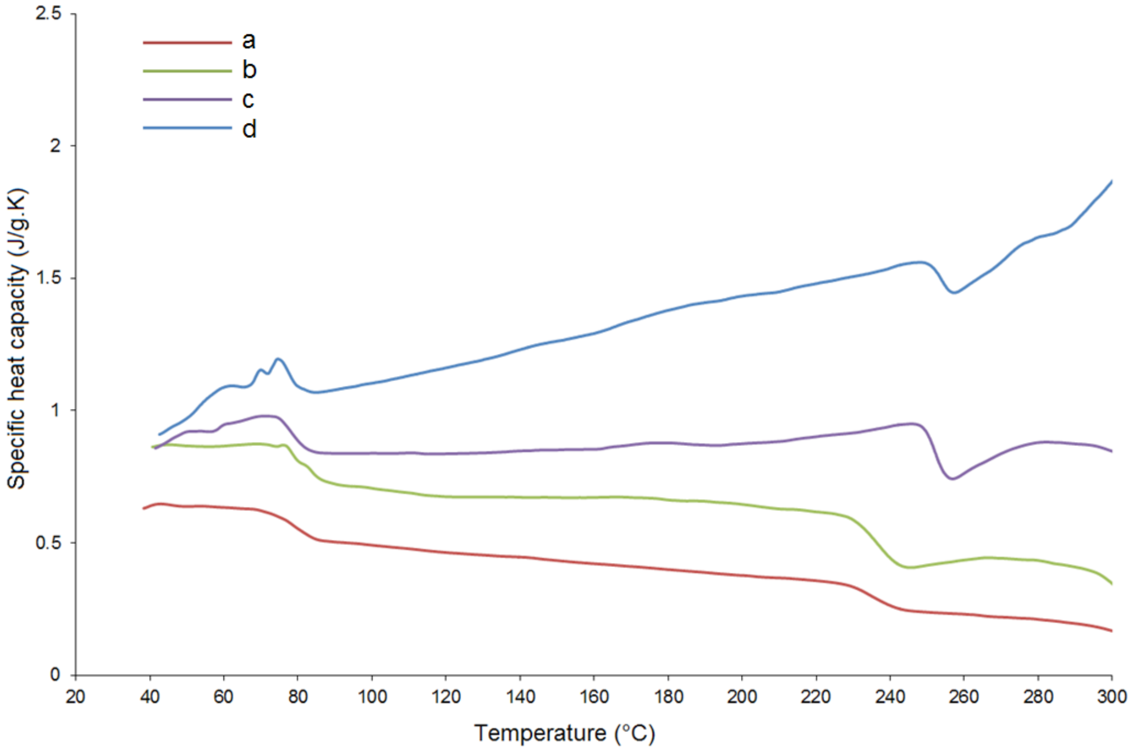

Figure 6. Specific heat capacity of pure PDMS **(a)**, PDMS-1%TiO_2 **(b)**, PDMS-5%TiO_2 **(c)** and PDMS-10%TiO_2 **(d)**.

Ti peak also increases. All these findings prove that the desired PDMS-TiO_2 composite structure was obtained.

3.2. Specific Heat Capacity of PDMS and PDMS-TiO_2 Composites

The specific heat capacity of the obtained composite was determined by the DSC analysis technique. It was carried out in a 25 mL/min air atmosphere with 10°C/min heating between 30 °C and 350 °C (Fig. 6).

The experimental values of the specific heat capacity of TiO_2 reinforced composite and pure PDMS according to temperature are shown in Fig. 6. The specific heat capacity of the pure PDMS structure varies between 0.6 and 0.28 J/g.K. It has been observed that the specific heat capacity values of the composites increase almost linearly with temperature. This value can go up to approximately 0.9 J/g.K at room temperature in composite structures. Even at high temperatures, the specific heat capacity increased to about 1.7 J/g.K. The variation is less during the melting of the composite and is attributed to the reduction of the mean free path length of the phonons. However, the increase in specific heat capacity becomes much more pronounced at high temperatures. This change can be attributed to reduced TiO_2 interaction with the polymer in the melt. As a result, the specific heat capacity of the PDMS structure increased with TiO_2 doping. This amount of increase can be easily adjusted with the amount of TiO_2.

4. Conclusion

This study synthesised TiO_2 with spherical morphology and nanometric size using the hydrothermal synthesis technique. Diffraction peaks in the XRD spectra of the synthesized TiO_2 structures indicate the anatase crystalline TiO_2 phase. TiO_2 particles synthesized from SEM images consist of sphere 50 to 5000 nm nanoparticles. The effect of the synthesized TiO_2 powders on this polymer's morphological and thermal performances was investigated by adding to the PDMS structure. The presence of TiO_2 particles in the obtained composite structures was determined by chemical, morphological and thermal analysis methods. Ideal surface structure and particle-polymer interface interaction were determined in SEM images, especially at 1% and 5% TiO_2 ratios. Pores and microcracks were seen in the polymeric film structures at higher loadings. Therefore, the ideal mixing ratio was determined in the case of 5% TiO_2. The results show that the specific heat capacities of PDMS-TiO_2 composites increase compared to pure PDMS in the obtained structures. In composite structures, specific heat capacity of composites value can go up to approximately 0.9 J/g.K at room temperature. Even at high temperatures, the specific heat capacity increased to about 1.7 J/g.K. This amount of increase can be easily adjusted with the amount of TiO_2.

5. Conflicts of Interest

There are no conflicts of interest for the publication of this research article

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