

# Impact of titanate coated magnetite nanoparticles on the properties of rigid polyurethane foams

## Titanat kaplı manyetit nanopartiküllerin sert poliüretan köpüklerin özellikleri üzerindeki etkisi

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### Abstract

Closed cell polyurethane-based materials represent more than 23% of all polyurethane manufacturing. Unlike to the use of closed cell polyurethane foams in a large variety of applications, these materials exhibit some drawbacks. Their limited mechanical strength and their limited thermal constancy hindering their usage in some areas can be given as examples. In the purpose to overcome and enhance the weaknesses of rigid polyurethane foams and at the same time enlarge the utilization areas of these materials, numerous studies were realized in the literature. The utilization of  $Fe_3O_4$  nanoparticles in various fields, including magnetic resonance, has gained significant attention in recent years. These additives can improve at the same time the thermal and mechanical properties of polyurethane foams. Nevertheless, the development of new methods concerning the surface modification of the nanoparticles is important. The improvement of the interfacial interactions at the polyurethane-filler interface was largely investigated with various agents such as silica, surfactants and precursor metals in the literature. However, the use of a titanate-based coupling agent was not yet researched. In this work, a surface coating of  $Fe_3O_4$  nanoparticles with a titanate-based coupling agent (Ti- $Fe_3O_4$ ) was realized to produce  $Fe_3O_4$  filled rigid polyurethane foam nanocomposites at different filler ratios. Microstructural, mechanical, thermal and electrical conductivity properties of all foam nanocomposites were characterized. The FTIR spectra exhibited only the presence of physical interactions. In addition, an increase of the crystallinity ratio with the increase of the filler content was observed. Concerning the electrical and thermal conductivity results, a noticeable improvement was detected from the pure rigid polyurethane foam to the 50 wt.% Ti- $Fe_3O_4$  filled nanocomposite. From the mechanical test results, a higher performance was observed for the rigid polyurethane foam nanocomposite produced at 12.5 wt.%.

**Keywords:** Polymer composite, Rigid polyurethane foam, Magnetite, Titanate coupling agent.

### Öz

Kapalı hücreli poliüretan bazlı malzemeler, tüm poliüretan üretiminin %23'ünden fazlasını temsil etmektedir. Kapalı hücreli poliüretan köpüklerin çok çeşitli uygulamalarda kullanılmasının aksine, bu malzemeler bazı dezavantajlar sergiler. Sınırlı mekanik dayanımları ve bazı alanlarda kullanımlarını engelleyen sınırlı termal dayanıklılıkları örnek olarak verilebilir. Sert poliüretan köpüklerin zayıf yönlerinin giderilmesi, geliştirilmesi ve aynı zamanda bu malzemelerin kullanım alanlarının genişletilmesi amacıyla literatürde çok sayıda çalışma gerçekleştirilmiştir. Son yıllarda, manyetik rezonans da dahil olmak üzere çeşitli alanlarda  $Fe_3O_4$  nanopartiküllerinin kullanımı önemli ölçüde dikkat çekmiştir. Bu katkı maddeleri aynı zamanda poliüretan köpüklerin termal ve mekanik özelliklerini de geliştirebilir. Bununla birlikte nanopartiküllerin yüzey modifikasyonuna ilişkin yeni yöntemlerin geliştirilmesi önemlidir. Poliüretan-katki arayüzündeki arayüz etkileşimlerinin iyileştirilmesi literatürde silika, yüzey aktif maddeler ve prekürsör metaller gibi çeşitli ajanlarla büyük ölçüde araştırılmıştır. Ancak, titanat bazlı bir bağlayıcı ajanının kullanımı henüz araştırılmamıştır. Bu çalışmada, farklı katkı oranlarında  $Fe_3O_4$  katkılı sert poliüretan köpük nanokompozitleri üretmek için  $Fe_3O_4$  nanopartiküllerinin titanat bazlı bir bağlayıcı ajan ile yüzey kaplaması (Ti- $Fe_3O_4$ ) gerçekleştirilmiştir. Tüm köpük nanokompozitlerin mikroyapısal, mekanik, termal ve elektriksel iletkenlik özellikleri karakterize edilmiştir. FTIR spektrumları yalnızca fiziksel etkileşimlerin varlığını göstermiştir. Ek olarak, katkı oranının artmasıyla kristalleşme oranında da bir artış gözlemlenmiştir. Elektriksel ve termal iletkenlik sonuçlarına ilişkin olarak, saf rijit poliüretan köpüğünden ağırlıkça %50 Ti- $Fe_3O_4$  katkılı nanokompozite göre gözle görülür bir iyileşme tespit edilmiştir. Mekanik test sonuçlarından ağırlıkça %12.5 oranında üretilen rijit poliüretan köpük nanokompozitinin daha yüksek performans gösterdiği gözlemlenmiştir.

**Anahtar kelimeler:** Polimer kompozit, Sert poliüretan köpük, Manyetit, Titanat bağlayıcı ajan.

## 1 Introduction

One of the most widely used materials in a wide range of areas such as automotive, bedding, electronic instrument bezels and structural parts, building, construction, textile and coating is polyurethane (PU) [1]. Different types of polyurethanes and especially polyurethane foams can be synthesized as rigid (closed cell) or flexible (open cell), classified according to their cell structure [2],[3]. Among these various cellular structures, it can be mentioned that closed cell or rigid polyurethane foam

possesses the widest application domains in contrast to the different kind of foam [2]. Unlike to the use of closed cell polyurethane foams in a large variety of applications particularly in insulation, adhesion and coating due to their improved properties such as in particular electrical and thermal insulation, lightweight, dimensional stability, moisture resistance, sound resistance, these materials have some drawbacks [3],[4]. These latter can be for instance their limited mechanical strength but also their limited thermal constancy hindering their usage in some areas [5]. For these reasons and

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in the aim to overcome and improve the weaknesses of rigid polyurethane foams and at the same time enlarge the utilization areas of these materials, numerous studies were realized in the literature.

As a consequence, one of the most important ways to enhance the mechanical properties of rigid polyurethane foam was the addition of fillers and particularly nano-sized fillers and produce nanocomposite foams having improved final properties that can be applied in various fields.

Among the different nanofillers, particles having magnetic properties such as  $\text{Fe}_3\text{O}_4$  particles have the potential to be used in specific areas (magnetic resonance imaging, biomedical and radio frequency interference shielding) requiring magnetic response and have attracted attention in the literature. These additives can simultaneously improve the thermal and mechanical properties of PU foams [6]. Nevertheless, magnetic nanoparticles have some disadvantages, in particular agglomeration, chemical reactivity, and oxidation.

For these reasons, the final properties of the particles can vary noticeably with the apparition of oxidation according to the environment where the nanoparticles are used exhibiting a huge reduction of the magnetic properties. As a result, the homogeneity of the filler dispersion is also affected. To resolve this dispersion problem due to the formation of large agglomerates is a critical point, this difficulty hugely affecting the processability of filled polymer foams.

The major way to prevent the apparition of these magnetite agglomerates is to stabilize the nanoparticles by different methods as largely reported in the literature. From these different methods used especially in the case of  $\text{Fe}_3\text{O}_4$  particles filled closed cell polyurethane foams the surface modifications of the nanoparticles is the most widely applied one. In order to enhance the interfacial interactions between the nanofillers and polyurethane matrix various agents such as silica, surfactants, silane and precursor metals were analyzed [7-10]. The purpose of this work is the investigation of the effect of a coupling agent on the interfacial interactions at the filler-matrix interface to enhance the final mechanical properties of the magnetite added rigid polyurethane foam [11].

Among the various coupling agents, titanate-based materials have the possibility to react simultaneously with free protons and hydroxyls at the filler interface, allowing the development of an organic coating on the filler surface. As a result, the use of a titanate-based coupling agent can improve the dispersion of the filler into the polymer matrix and then the final mechanical properties of the nanocomposite [12].

This study aims to coat the surface of  $\text{Fe}_3\text{O}_4$  particles with a titanate-based coupling agent and investigate the impact of this surface modification on the final microstructural, mechanical, thermal and electrical conductivity properties of closed cell polyurethane foam nanocomposites.

## 2 Materials and methods

### 2.1 Materials

Magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles given in Figure 1 were supplied from Nanokar/Türkiye with an average initial particle size of about 30 nm and were used as a reinforcement material for rigid polyurethane foams. Titanate (TYTAN TM CP-219) served as a coupling agent by modifying the surface of magnetite nanoparticles and was procured from Borica/Taiwan. Polyol and isocyanate were used as raw

materials in the production of rigid polyurethane foams. Commercial grade isocyanate (Izokim RD 001) (NCO content of 31%, density of 1.23 g/cm<sup>3</sup> and viscosity of 0.2 Pa.s) and polyol (KIMrigid RD 057) (density of 1.03 g/cm<sup>3</sup> and viscosity of 0.4 Pa.s) supplied from Kimteks/Türkiye were used in this study. The blowing agent used in this formulation is water and it was directly included in the commercial polyol at a water content of 4.4 wt.%.

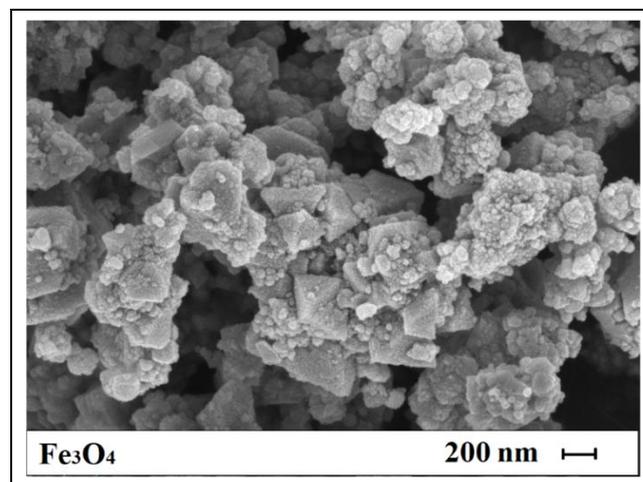


Figure 1. SEM image of magnetite.

### 2.2 Preparation of modified magnetite nanoparticles

First of all, to remove the humidity of  $\text{Fe}_3\text{O}_4$  nanoparticles, the powder was kept waiting at 100°C in an oven for about two hours [13]. Then, an ethanol/ $\text{Fe}_3\text{O}_4$  suspension was prepared using 200 mL of ethanol and a magnetic stirrer. Afterwards, based on the literature, 2.5 wt.% titanate used as coupling agent was added to the ethanol/ $\text{Fe}_3\text{O}_4$  suspension and mixed at 100 rpm for 2 hours and at room temperature [12]. Finally, the residual ethanol was removed from the surface modified magnetite ( $\text{Ti-Fe}_3\text{O}_4$ ) powder in an oven at a temperature of 100°C for 24 hours [13].

### 2.3 Preparation of unfilled and modified magnetite filled rigid PU foam nanocomposites (RPU/ $\text{Ti-Fe}_3\text{O}_4$ )

For the production of RPU/ $\text{Ti-Fe}_3\text{O}_4$  nanocomposites,  $\text{Ti-Fe}_3\text{O}_4$  nanopowders prepared at various weight ratios (12.5, 25, 50 wt.% in polyol) were filled into polyol (Table 1).

Table 1. Compositions of Polyol/ $\text{Ti-Fe}_3\text{O}_4$  suspensions.

RPU/ $\text{Ti-Fe}_3\text{O}_4$ nanocomposites	$\text{Ti-Fe}_3\text{O}_4$ (wt.%)	Polyol (wt.%)
RPU	0	100
RPU/ $\text{Ti-Fe}_3\text{O}_4$ _12.5	12.5	87.5
RPU/ $\text{Ti-Fe}_3\text{O}_4$ _25	25	75
RPU/ $\text{Ti-Fe}_3\text{O}_4$ _50	50	50

The range of filler ratios was determined based on the literature to detect the amount giving the optimum final properties [3],[4]. In a first step, polyol/ $\text{Ti-Fe}_3\text{O}_4$  suspensions were sonicated (40 kHz frequency for 10 minutes) in a cold-water bath to have a better control of the suspension temperature, using an ultrasonic homogenizer (Bandelin/HD 4200). Then, the polyol/ $\text{Ti-Fe}_3\text{O}_4$  suspensions were mixed using a mechanical stirrer (2000 rpm for 1 minute). Finally, isocyanate was mixed with the polyol/ $\text{Ti-Fe}_3\text{O}_4$  suspension for a further five seconds and the final blend was placed in a rectangular mold having the appropriate dimensions for all

characterizations. The weight ratio of the polyol blend to isocyanate was 100:58.4 (isocyanate index = 100). At this stage, all samples were left in the mould for at least 24 hours to allow full curing of the material.

## 2.4 Characterization methods

The scanning electron microscopy analysis of all samples (pure and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites) was carried out using a Carl Zeiss Gemini 300 device. The sections perpendicular to the foaming direction were observed and images were registered to calculate the cell parameters (average cell diameter and average strut thickness) with ImageJ software for at least 100 cells.

Fourier Transform Infrared (FTIR) spectroscopy analysis of pure and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites was conducted by Thermo Scientific Nicolet iS50 device. FTIR analyses, in which the functional groups and the changes in these groups with the addition of fillers were evaluated, were carried out in the wavenumber range of 4000-600 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and a scan number of 16.

X-ray diffraction (XRD) analysis was carried out using a Bruker D8 Discover X-ray diffractometer. Patterns of unfilled and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites were recorded at diffraction angles (2θ) ranging from 5° to 90°. The step time and the increment were 0.02° and 0.5 second, respectively. The level of crystallization (CI) was calculated according to the Segal equation given in Equation (1). In the equation, *I<sub>c</sub>* represents the highest intensity of the crystal area peak and *I<sub>am</sub>* represents the intensity of the amorphous region [14].

$$\% CI = \frac{I_c - I_{am}}{I_c} \times 100 \quad (1)$$

The tensile test was performed using the SHIMADZU-AGS-X instrument based on the ASTM D638 standard. For each nanocomposite, the test was repeated for 5 test specimens.

Thermal conductivity properties of unfilled and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites were measured using a Laser Comp. Fox 314 (TA Instruments) device. The measurement was realized at ten different points for each RPU foam nanocomposite.

The electrical resistivity of all nanocomposites was measured with a Keitley 2400 source meter device and the measurement was repeated for three test samples of 9cm×9cm×3mm dimensions. During the measurement, 1 minute was kept for each sample. The results were recorded every 5 seconds. Then, a graph was created with electrical conductivity values according to the test data obtained.

## 3 Results and discussions

### 3.1 Scanning electron microscope analyses

SEM images of the cross-sectional surfaces of unfilled RPU foam and 12.5, 25 and 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam samples were given in Figure 2 under ×100 magnification rate. Using the SEM images recorded, 100 measurements were realized for each foam with the ImageJ program and as a result of these measurements the changes in mean strut thickness (μm) and mean cell diameter (μm) values were calculated and graphed in Figure 3 and 4, respectively. When Figures 3 and 4 were examined in line with the graphs obtained, it can be observed that with the addition of 12.5 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> to the rigid PU foam structure, the strut thickness and cell diameter increased to a

certain level compared to the unfilled PU foam. However, a decrease at higher filler ratios such as 25 wt.% and 50 wt.% can be seen. This result can be explained by the fact that the addition of magnetite nanoparticles caused the emergence of more nucleation sites, thus rising the cell density [3],[4]. With the use of high weight ratios of Ti-Fe<sub>3</sub>O<sub>4</sub> nanoparticles, agglomeration formation occurred as can be seen in the SEM micrographs obtained at a high magnification ratio (×20000) in Figures 5-7 [15]. SEM images (Figures 5, 6, and 7) revealed that the magnetite particles were well dispersed especially at 12.5 wt.% ratio in the RPU foam matrix, which was in correlation with the mechanical analyses results.

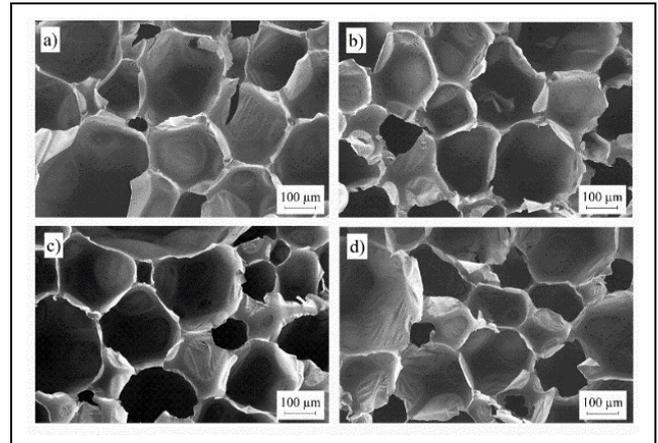


Figure 2. SEM images of a) unfilled RPU foam and b) 12.5 wt.%. c) 25 wt.% and d) 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites.

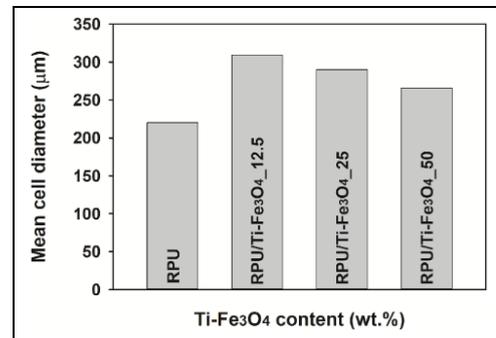


Figure 3. Mean cell diameter of unfilled RPU and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites prepared at different filler ratios (12.5, 25 and 50 wt.%).

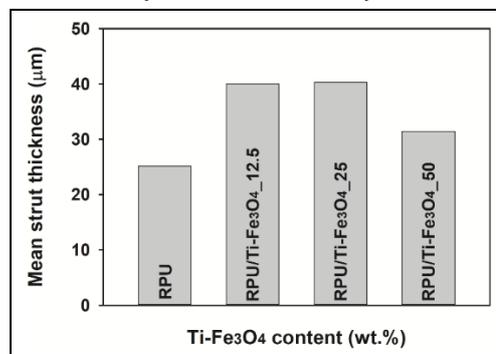


Figure 4. Mean strut thickness of unfilled RPU and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites prepared at different filler ratios (12.5, 25 and 50 wt.%).

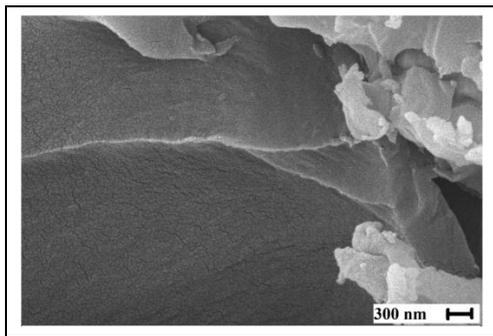


Figure 5. SEM image of Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites prepared at 12.5 wt.%.

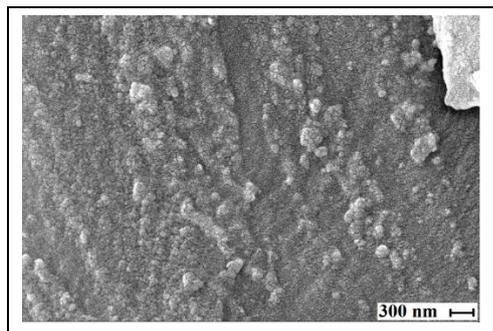


Figure 6. SEM image of Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites prepared at 25 wt.%.

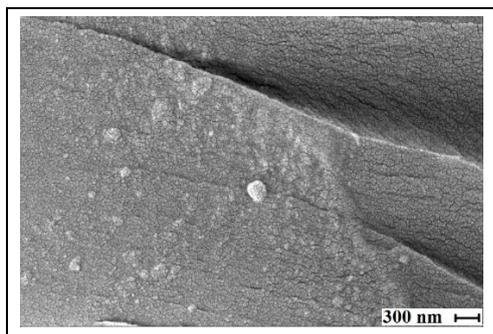


Figure 7. SEM image of Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites prepared at 50 wt.%.

### 3.2 Fourier transform infrared spectroscopy analyses

FTIR spectra of unfilled and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites were presented in Figure 8. In the FTIR spectra of the samples, the N-H stretching vibration peaks at 3300 cm<sup>-1</sup> are the first to be noticed and this peak characterizes the formation of polyurethane [16],[17]. The symmetrical and asymmetrical stretching behaviour of the C-H bond is indicated by the double peaks at 2920 and 2855 cm<sup>-1</sup> [18]. The peak region observed at around 2270 cm<sup>-1</sup> can be associated with the properties of the isocyanate band and the presence of aromatic rings in the isocyanate structure can be characterized by peaks in the 1595 and 1455 cm<sup>-1</sup> wavenumbers [18],[19]. Carboxylic acid derivatives involved in the structure of the polyol were associated with the peak at 1705 cm<sup>-1</sup> [20],[21]. When the FTIR spectra of unfilled and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites were examined, similar peaks and functional groups were observed. The spectra of the Ti-Fe<sub>3</sub>O<sub>4</sub> filled foam nanocomposites generally contain the functional groups detected in the structure of RPU.

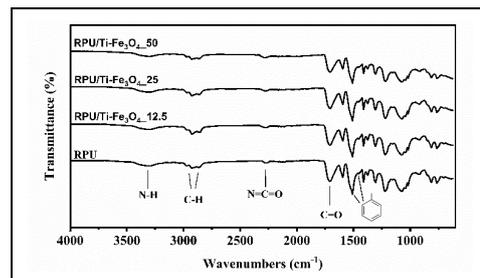


Figure 8. FTIR spectra of unfilled and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites.

This result can be explained by the fact that the added Ti-Fe<sub>3</sub>O<sub>4</sub> fillers do not interact chemically with the RPU matrix and the interactions that occur are only physical interactions. In composite materials, the interface is defined as the boundary between two layers with different chemical structures. At this interface region, parameters such as chemistry, polymer chain mobility, degree of hardening and crystallinity behaviour may differ [22]. Although interfacial interactions, particularly in carbon fibre reinforced polymer composites, are reported to occur through primary bonds between the two phases, there is no conclusive analytical evidence for this effect. In filler reinforced composite systems, interactions are reported to occur mainly through secondary bonds such as hydrogen bonding and van der Waals interactions [23]. In polymer matrix composites, the interphase refers to those portions of the long chain polymers of the matrix that are degraded by interaction with the filler phase. These interactions can occur at functional groups located at the end or along the chains, and molecular conformational changes as a result of interaction with the filler phase affect the interface and interphase formation. In addition, particle size has a direct effect on the volume fraction required to form a continuous interphase [24].

### 3.3 X-ray diffraction analyses

Diffractograms of unfilled and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites were given in Figure 9. When Figure 9 was analyzed, no sharp peak was observed in the unfilled RPU sample and the plateau regions indicated the amorphousness of the sample [25].

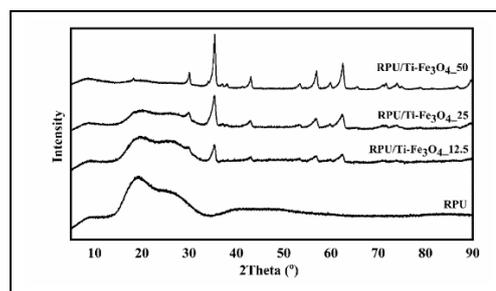


Figure 9. XRD diffractograms of unfilled and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites.

In the 12.5 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled sample, crystal peaks started to appear and as the ratio increases, the intensities of the peaks around  $2\theta = 35.426, 62.515, 56.923, 30.041,$  and  $59.872^\circ$  increased significantly. These peaks, which reached the highest intensity at 50 wt.% filler ratio, can be related to the increase in crystallinity caused by the addition of inorganic additives [26]. After determining the amorphous and crystalline phases of the samples, the level of crystallization (CI) was calculated with the help of diffractograms. According to the Segal Equation (1)

used, the crystallinity ratio of the unfilled RPU sample could not be determined, while the CI values of RPU foam composites prepared with 12.5, 25, and 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filler were determined as 4.3, 14.3, and 43.5%, respectively. In composite systems where there is compatibility between filler and matrix, it is stated that the crystallinity values increase as the filler ratio increases. In cases where the filler and matrix are compatible and interfacial interactions are high, it is stated that the fillers added to the composite structures provide nucleation sites for the regular stacking of polymer chains, thus increasing the crystallinity of the composite structures [27],[28]. It has been reported in the literature that an increase in crystallinity can lead to a decrease in hardness and elongation at break [29]. It was observed that this change in crystallinity values was also compatible with the mechanical strength values.

### 3.4 Mechanical analyses

The tensile strength and elongation at break results of the unfilled and 12.5, 25 and 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam samples were given in Figures 10 and 11, respectively. When the tensile strength results in Figure 10 were examined, it can be observed that the RPU foam structure with the highest tensile strength value was 12.5 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam, and an increase of approximately 23% in tensile strength value was achieved. This increase in tensile strength values, obtained for a 12.5 wt.% filler rate, is a result of the homogeneous distribution of the titanate coated magnetite filler in the structure [30]. This can be associated with the fact that titanate acts as a molecular bridge between the filler and the polymeric foam matrix, reacting with both the magnetite nanoparticles and the surface atoms of the polyurethane, positively affecting the interfacial properties.

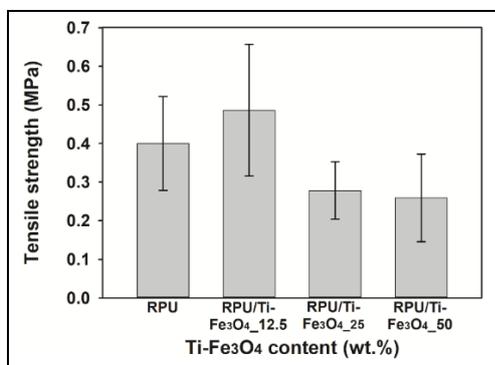


Figure 10. Tensile strength variations of unfilled and 12.5 wt.%, 25 wt.% and 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam samples.

On the other hand, 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam exhibited the lowest tensile strength and this decrease can be related to the agglomerations observed for a high percentage of nanofillers in the foam structure, as demonstrated in SEM images given in Figures 7 [31]. According to these mechanical test results, it can be stated that the use of 12.5 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> exhibited a critical filler content. This situation can be expressed by the percolation threshold achieved at a certain point, as widely interpreted in the literature [3],[4].

As can be seen in Figure 11, with the increase in the Ti-Fe<sub>3</sub>O<sub>4</sub> nanoparticles ratio, the elongation at break values decreased as expected. Based on these results, when a comparison was made according to the filler ratios, the sample giving the lowest elongation at break value was 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam. The highest percentage of elongation at break was obtained for the unfilled RPU foam.

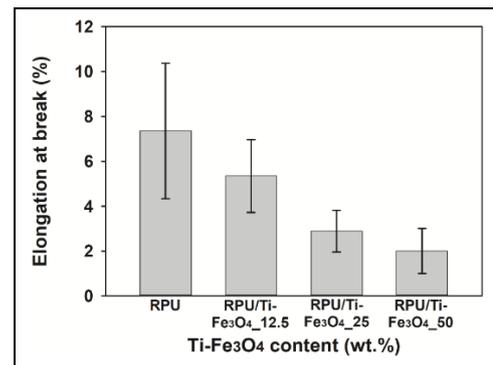


Figure 11. Elongation at break variations of unfilled and 12.5 wt.%, 25 wt.% and 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam samples.

### 3.5 Thermal conductivity analyses

The thermal conductivities recorded for the unfilled RPU foam and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites obtained at various Ti-Fe<sub>3</sub>O<sub>4</sub> ratios (12.5, 25, 50 wt.%) were gathered in Figure 12. An improvement from 0.02431 W/m.K for the unfilled RPU foam to 0.02646 W/m.K for the 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposite can be detected from the results. As a consequence, the thermal conductivity of RPU/Ti-Fe<sub>3</sub>O<sub>4</sub> foam nanocomposites demonstrated a higher increase of nearly 9% for the 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU nanocomposite. Considering the error bars detected, it can be stated that an increase of the filler ratio engendered an increase tendency of the thermal conductivity. This evolution was in correlation with the cell size evolution. From the comparison of these results with the cell diameter variations, it can be noticed that as the filler ratio increases in RPU foam nanocomposites an augmentation of the cell diameter and thermal conductivity was observed. This behavior is in correlation with the literature where a similar effect has been detected for magnetite filled foams composites [1],[12],[32],[33].

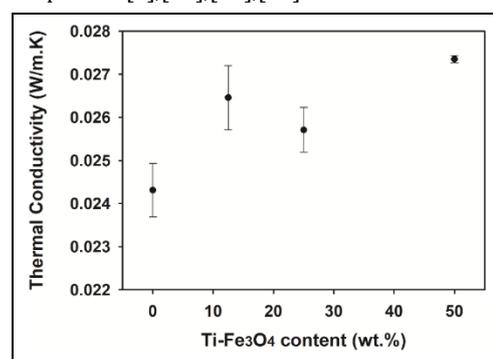


Figure 12. Thermal conductivity of unfilled and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites.

### 3.6 Electrical conductivity results

The electrical conductivity values of unfilled RPU foam and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites obtained at various Ti-Fe<sub>3</sub>O<sub>4</sub> ratios (12.5, 25, 50 wt.%) and calculated as the inverse of the electrical resistivity values were detected experimentally and represented in Figure 13. It can be seen from this Figure 13 that a visible improvement of the value from the unfilled foam to the 12.5 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam is observed and then a more constant evolution of the electrical conductivity was obtained between 12.5 wt.% and 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled foam nanocomposites.

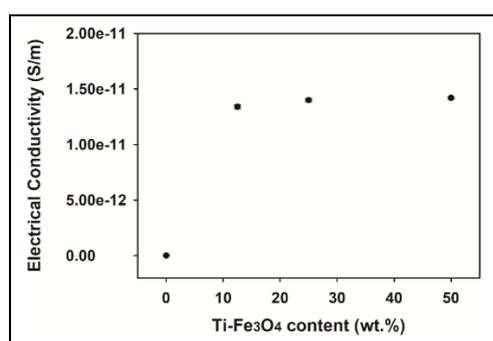


Figure 13. Electrical conductivity of unfilled and Ti-Fe<sub>3</sub>O<sub>4</sub> filled RPU foam nanocomposites.

As a result, with an increase of the Ti-Fe<sub>3</sub>O<sub>4</sub> content to 50 wt.% a rise from  $1.64 \times 10^{-14}$  to  $1.42 \times 10^{-11}$  was seen. The presence of a critical Ti-Fe<sub>3</sub>O<sub>4</sub> ratio of 12.5 wt.% in this work can be interpreted by the presence of a percolation threshold as discussed in the literature [11],[12], this critical point showing the apparition of a conductive pathway formed by Ti-Fe<sub>3</sub>O<sub>4</sub> nanoparticles into the RPU foam.

#### 4 Conclusions

In this study, titanate coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles were filled to the RPU foams and prepared at three different ratios (12.5, 25 and 50 wt.%). The microstructure, electrical conductivity, thermal conductivity and mechanical properties of unfilled RPU and RPU/Ti-Fe<sub>3</sub>O<sub>4</sub> foam nanocomposites were characterized. The FTIR spectra demonstrated that Ti-Fe<sub>3</sub>O<sub>4</sub> fillers do not interact chemically with the RPU matrix and the interactions are only physical interactions. Furthermore, an increase of the crystallinity ratio with the increase of the filler content was observed. The results exhibited an increase in the average strut thickness and the average cell diameter for the foam nanocomposite filled at 12.5 wt.% representing the percolation threshold in this study. Afterwards, a reduction of these parameters was observed with the augmentation of the Ti-Fe<sub>3</sub>O<sub>4</sub> weight ratio. Concerning the electrical and thermal conductivity results, a noticeable improvement was detected from the pure RPU foam to the 50 wt.% Ti-Fe<sub>3</sub>O<sub>4</sub> filled nanocomposite. From the mechanical test results, a higher performance can be seen for the RPU foam nanocomposite produced at 12.5 wt.%.

#### 5 Authors contribution statements

In the scope of this study, Buse Fem Yılmaz contributed to the design of the work, experimental study, data analysis, and writing the manuscript. Meral Akkoyun Kurtlu contributed to the design of the work, experimental study, data analysis, formal editing, visualization, writing the manuscript, review and editing. Sibel Tuna contributed to the data analysis, visualization, and writing the manuscript. All authors read and approved the final manuscript.

#### 6 Ethics committee approval and conflict of interest statement

"There is no need to obtain permission from the ethics committee for the article prepared".

"There is no conflict of interest with any person/institution in the article prepared".

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