

PACS numbers: 62.23.Pq, 62.25.Mn, 68.37.Hk, 78.30.Jw, 81.70.Bt, 81.70.Pg, 83.80.Tc

Study of Nano-Titanium-Dioxide Effect on Mechanical, Thermal, and Morphological Properties of Polypropylene–Low-Density Polyethylene Blend

Abeer Adnan Abd¹ and Zainab S. Al-Khafaji^{2,3}

¹*Polymer Department,
College of Materials Engineering,
Babylon University,
Hillah, Babil, Iraq*

²*Department of Civil Engineering,
Faculty of Engineering and Built Environment,
Universiti Kebangsaan Malaysia,
43600 UKM Bangi, Selangor, Malaysia*

³*Imam Ja'afar Al-Sadiq University,
Qahira, Baghdad, Iraq*

The study is aimed to improve the mechanical and thermal properties of a low-density polypropylene–polyethylene blend mixed at 80–20 wt.%. Titanium dioxide is added at different percent ratios: 0, 2, 4, 6, 8 wt.%. Particle sizes and melt processing of the low-density polyethylene–polypropylene blending play a significant role in thermoplastic arrangements. The composite material is prepared using the composite by the melt mixing technique in a screw extruder. The results show that the mechanical properties are improved, when TiO₂ particles are added at an average particle size of 0.201. The tensile strength and hardness increase with the increase in filler content. The tensile modulus increases due to the higher surface area of the filler. The bending strength decreases due to the decrease in elasticity and the increase in tensile strength. The impact strength decreases by 2% and then increases. FT-IR results show the physical bonds between the filler particles and the blend. DSC-test results indicate two glass transition temperatures, making the blend immiscible. SEM results show that ethylene–propylene–diene monomer (EPDM) rubber (as a type of synthetic thermoset elastomeric copolymers produced from a terpolymer of ethylene, propylene and a diene monomer) coupling agents enhance the adhesion between the titanium dioxide and the blended composite.

Метою дослідження було поліпшення механічних і термічних властивостей суміші поліетилену низької густини та поліпропілену, замішаної з вмістом 80–20 мас.%. Діоксид Титану додавали в різних відсоткових співвідношеннях: 0, 2, 4, 6, 8 мас.%. Розміри частинок та оброблення ро-

зтопу суміші поліетилену низької густини та поліпропілену відіграють значну роль у термопластичних композиціях. Композитний матеріал був виготовлений з використанням композиту методом змішування розтопу в шнековому екструдері. Результати показують, що механічні властивості поліпшилися із додаванням частинок TiO_2 із середнім розміром частинок 0,201. Міцність на розрив і твердість зростають зі збільшенням вмісту наповнювача. Модуль пружності збільшується завдяки більшій площі поверхні наповнювача. Міцність на вигин зменшується через зменшення еластичності та збільшення міцності на розрив. Ударна в'язкість зменшується на 2%, а потім зростає. Результати ІЧ-спектроскопії з Фур'є-перетвором проявили фізичні зв'язки між частинками наповнювача та сумішшю. Результати ДСК-тестів показали дві температури склування, що робить суміш незмішуваною. Результати СЕМ показали, що сполучна речовина «синтетичний каучук на основі сополімеру етилену, пропілену з добавкою дієнового мономера» (СКЕПТ) підсилює адгезію між діоксидом Титану та змішаним композитом.

Key words: titanium dioxide, polypropylene, polyethylene, blend, EPDM.

Ключові слова: діоксид Титану, поліпропілен, поліетилен, суміш, СКЕПТ.

(Received 4 February, 2024; in revised form, 22 March, 2024)

1. INTRODUCTION

In recent years, a significant focus has been on the study and development of composites, which incorporate nanoparticles [1–3]. These nanocomposites have garnered significant interest due to their impressive enhancements in various characteristics, such as mechanical strength, optical clarity, and thermal conductivity [4, 5]. In addition, they have shown great potential for a wide range of applications. Nevertheless, a significant hurdle in polymer nanocomposite technology is inhibiting particle aggregation [6–8]. Surface modification can help overcome this issue by improving the interfacial interaction between the polymer matrix and inorganic particles, which, in turn, can enhance the general properties of nanocomposites [9–13].

Polyethylene (PE) and polypropylene (PP) were developed recently due to low cost, good mechanical properties, lightweight, and desirable applications. PE in two kinds, of low and high density, may be added to PP to develop mechanical PP properties [14]. The blend of PP and PE is used because PP and PE have similar characteristics, such as reasonable wear and mechanical, thermal, electrical, and chemical resistance, used in pipes. PE has more moisture and depredation resistance than PP; therefore, it was blended with it [15, 16]. The characteristics of the PP–PE blend are refined by several additives, which are mixed

with them, like adding nanofillers, which improve the properties such as TiO_2 , CaO , Al_2O_3 , ZrO_2 , and SiO_2 have [17].

Inorganic particles like clay, silica, CaCO_3 , layered silicate nanoparticles, and titanium dioxide (TiO_2) have garnered significant attention as inorganic materials for inorganic–organic nanocomposites. One material that stands out is TiO_2 , which has significant potential in various applications, such as photocatalytic activity and photoelectric conversion in solar cells. In addition, TiO_2 nanoparticles also exhibit antibacterial properties, help prevent odours, and have a self-cleaning mechanism [18, 19]. The numerous benefits of TiO_2 make it a highly desirable inorganic component for creating nanocomposite materials. These materials offer exceptional mechanical properties, low density, and protection against the UV and thermal degradation, critical in regions with intense sunlight, high temperatures, and humidity, including Vietnam's tropical climate. Various polymers can be effectively combined with TiO_2 nanoparticles through different processing techniques, including sol–gel or polymerization in solution. These polymers include poly(methyl methacrylate), epoxy, polyethersulphonate, poly(ethylene terephthalate), and polystyrene [20].

By adding small amounts of nanoparticles, polymer nanocomposites improve the mechanical properties, heat resistance, thermal resistance, degradation, and elastic modulus. Besides, other characteristics like melt processing, polymer crystallization, and electrical and thermal conductivities can be modified [21]. Nanofillers like SiO_2 , TiO_2 , Al_2O_3 , and ZrO_2 reinforce the polymers by embedding them in the polymer matrix. TiO_2 is very important due to particular characteristics like low density, thermal degradation, hydrophilic and photocatalytic degradation, and a large surface ratio, which makes them aggregate easily; therefore, styrene ethylene butylene styrene (SEBS) can be used as a coupling agent [22].

SEBS showed good attributes, as found by Sajad and Farmarz's desperation of titania nanoparticles in the matrix, and increased the samples' thermal stability. Another coupling agent used with ethylene and propylene is PDEM (propylene diethylene monomer) to prevent filler agglomeration [23].

The current work aims to enhance the mechanical, thermal, and morphology properties of polypropylene–low-density polyethylene blend by preventing filler agglomeration in nanocomposite material by using EPDM coupling agents.

2. EXPERIMENTAL WORK

The polypropylene purchased from Sabic Company is produced in Saudi Arabia, and the low-density polyethylene purchased from

Amber Kabir Petrochemical Company is made in Iran. The polypropylene and polyethylene pellets were mixed with TiO nanofiller with PDEM as coupling agent, then, put in the twin-screw extruder with a speed of 35 cycles/min at 170°C to mix, then, roll through the roller to get the sheet of 5-mm thickness. The samples are then cut into the required shapes.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties Tests Results and Discussion

The tensile strength test results (stress–strain curve for the composite) are represented in Fig. 2. The results show that the tensile strength increases, when titanium oxide increases due to high sur-

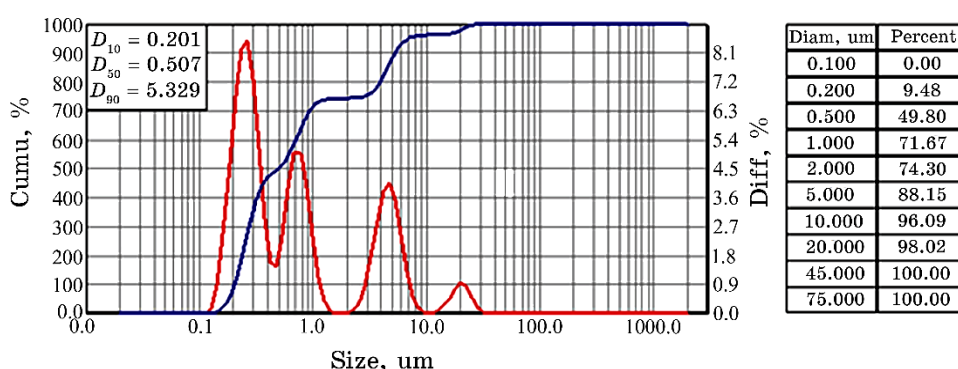


Fig. 1. LBZA average particle size of titanium dioxide.

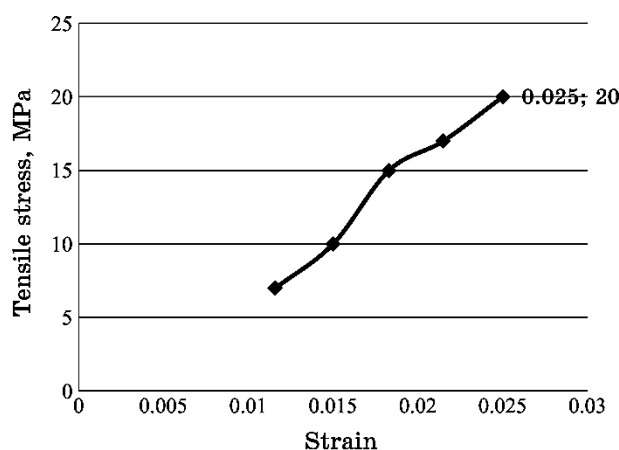


Fig. 2. Tensile strength *versus* strain.

face activity between the filler and the coupling agent PDEM and polypropylene and polyethylene that is due to reduction in interfacial tension, stabilization of morphology, enhancements adhesion between faces in the solid state facilitating the stress transfer, hence improving the mechanical properties of the product.

The tensile strength modulus increases, when the titanium dioxide percentage increases, as shown in Fig. 3, due to the maximum surface area, aspect ratio, and loading, which all will increase the modulus. Through active sites or coupling agents, fillers with strong chain attachments resist the chain extension most.

The hardness increases to 6% of titanium dioxide. Then, it decreases, as shown in Fig. 4, because titanium dioxide has higher hardness than the polypropylene–polyethylene blend and has a high

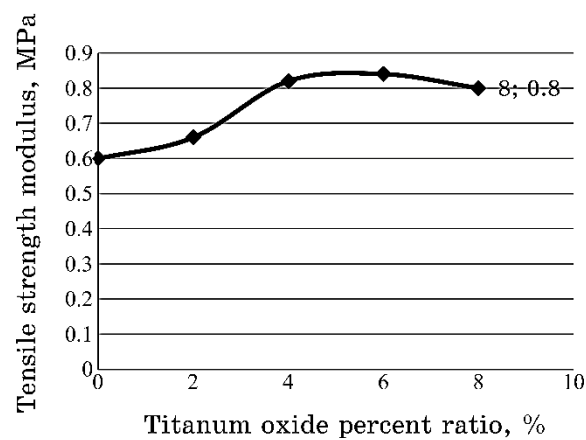


Fig. 3. Tensile modulus *versus* titanium oxide content.

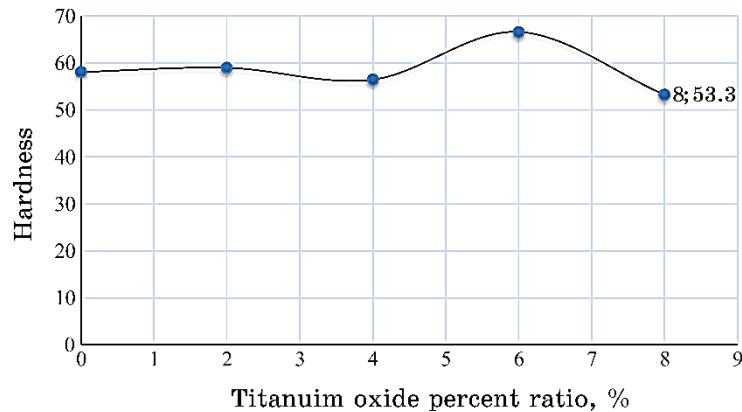


Fig. 4. The total percent hardness *versus* titanium oxide content.

surface area due to the small particle size of the filler. The reason behind the hardness increases is that the density increases. The different shapes of particles, which are irregular, including pentagonal and rectangular shapes, and have high surface area, aspect ratio, and high loading; therefore, the surface area increases.

The flexural strength test was used with the machine at the 2-mm/min speed applied at 3 points. A load was applied at the central axis until fracture occurred. The bending strength decreases, when filler content increases (Fig. 5) due to the high modulus-strength increase of blend material and the elasticity decrease, and it has a brittle fracture. When the filler content is increased, the distance between polymer chains is increased, hindering the movements of chains.

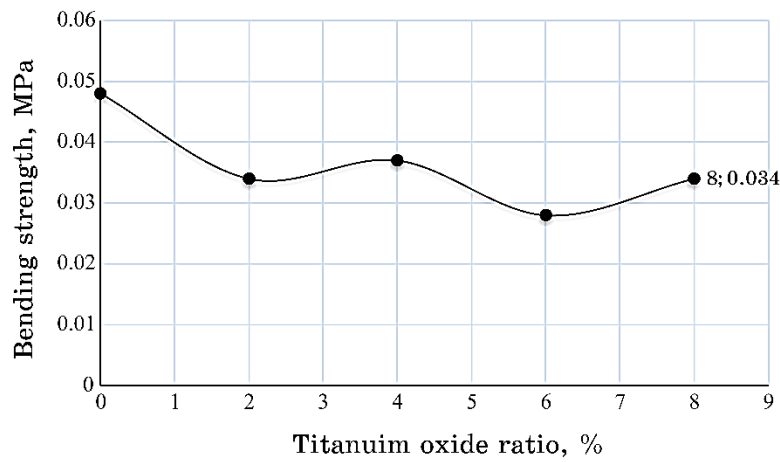


Fig. 5. Bending strength *versus* titanium oxide content.

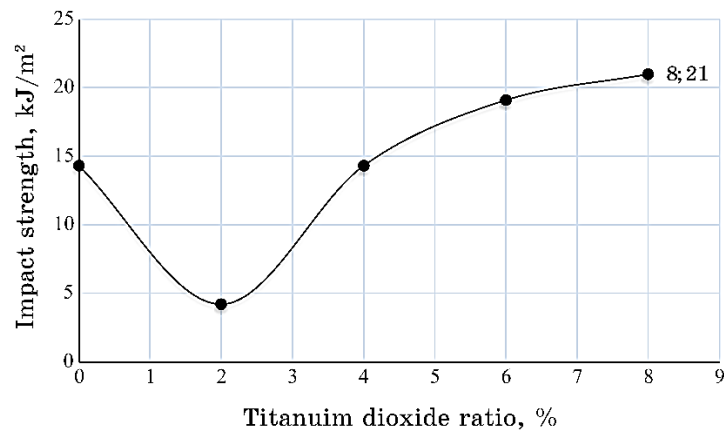


Fig. 6. Impact strength *versus* titanium dioxide ratio content.

The impact strength decreases to 2%, as shown in Fig. 6, because the elasticity decrease is related to PP having a methyl group, which is rigid and attached to a carbon atom of the polymer main chain, limiting the spin of the chain, producing a stronger but less flexible material; then, the impact strength increases; due to the high surface area of filler and high hardness, also titanium dioxide has high surface activity with higher content.

3.2. DSC-Test Results and Discussion

The thermal properties were indicated by the DSC test for the samples. As shown in Figure 7, there are two T_g , 125.59°C and 155.82°C; so, it is an immiscible blend. The glass transition temperature T_g is decreased for the sample 2 and, then, increased in other samples due to the filler-particles' (TiO₂) substantial spaces in the structure performance as strengthening filler between chains due to small average particle size (D50:0.507) and making van der Waals bonds, as shown in Figs. 7–11.

3.3. FT-IR Results and Discussion

As shown in Figure 12, there is a physical attraction between titanium-dioxide particles and the PE–PP blend.

In sample 1, there is no titanium dioxide. Titanium dioxide was

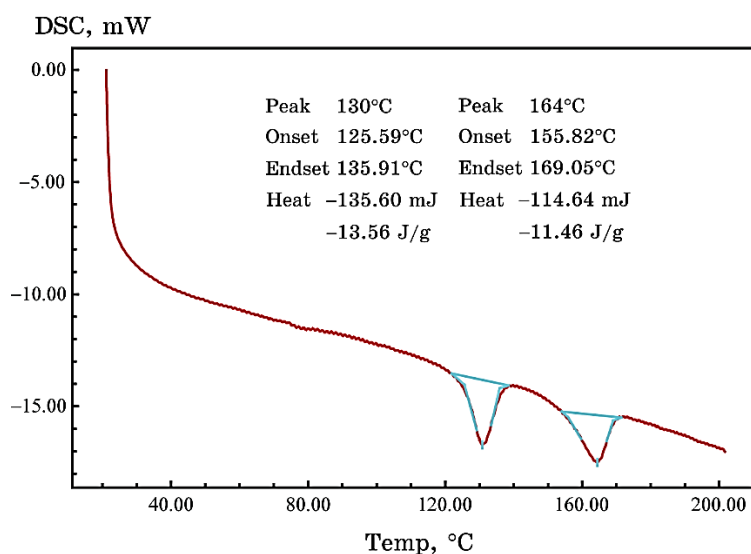


Fig. 7. The DSC test for sample 1.

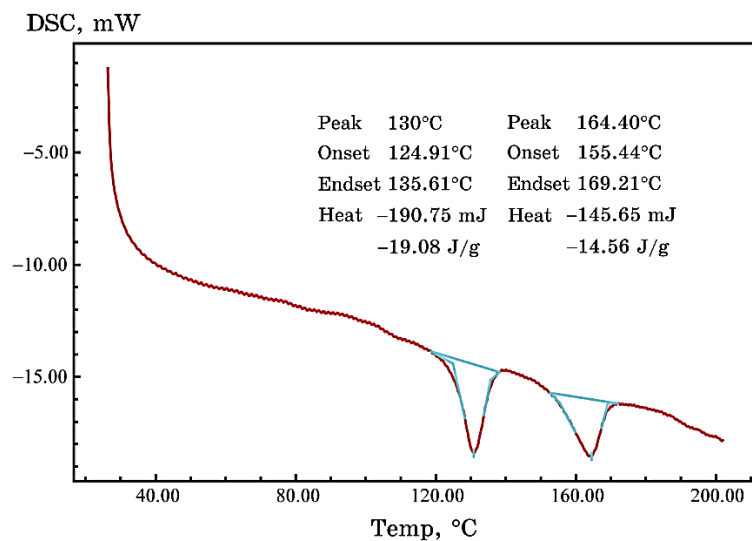


Fig. 8. The DSC test for sample 2.

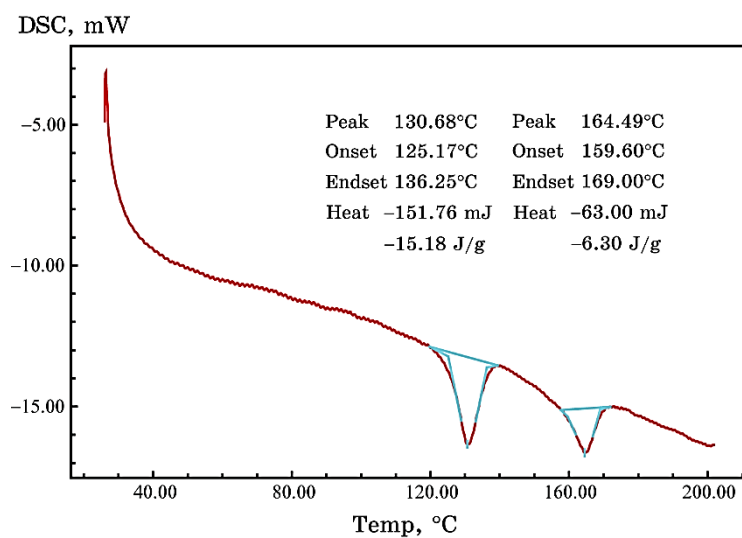


Fig. 9. The DSC test for sample 3.

added in other samples at different ratios 2, 4, 6, 8%. The transparency intensity increases, when the titanium-dioxide filler content increases, because titanium-dioxide particles far apart the distance between chains, and the light can pass through the chains.

Then, the transparency intensity decreases because the content of filler particles increases, and the distance between chains increases.

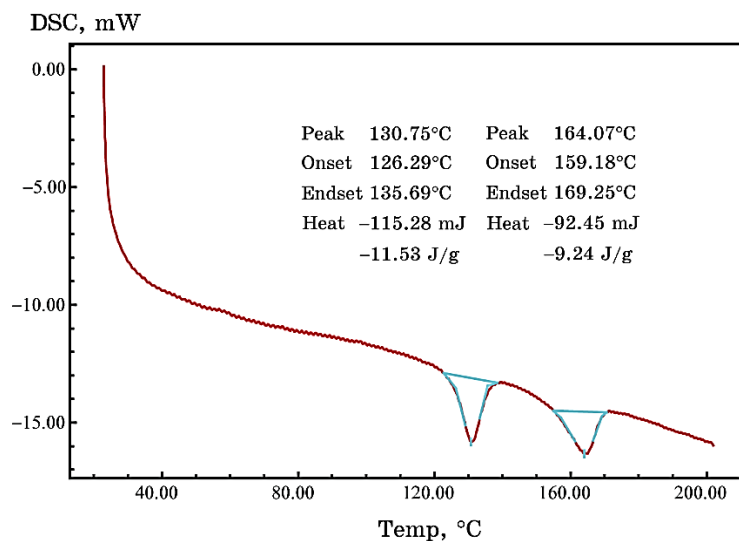


Fig. 10. The DSC test for sample 4.

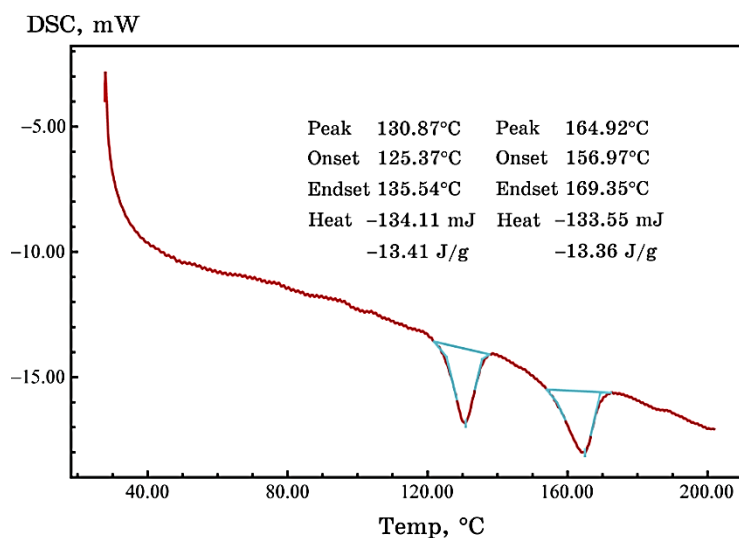


Fig. 11. The DSC test for sample 5.

The light cannot pass through the chains. There is vibration in the range of $466\text{--}700\text{ cm}^{-1}$ due to the single bond between the titanium and oxygen atoms, Ti-O, and often present in the stretching of the titanium-dioxide molecule.

The bond at 1410 cm^{-1} and 1375 cm^{-1} occurred due to the symmetric bending of the -CH_3 group and the scissoring of an extended

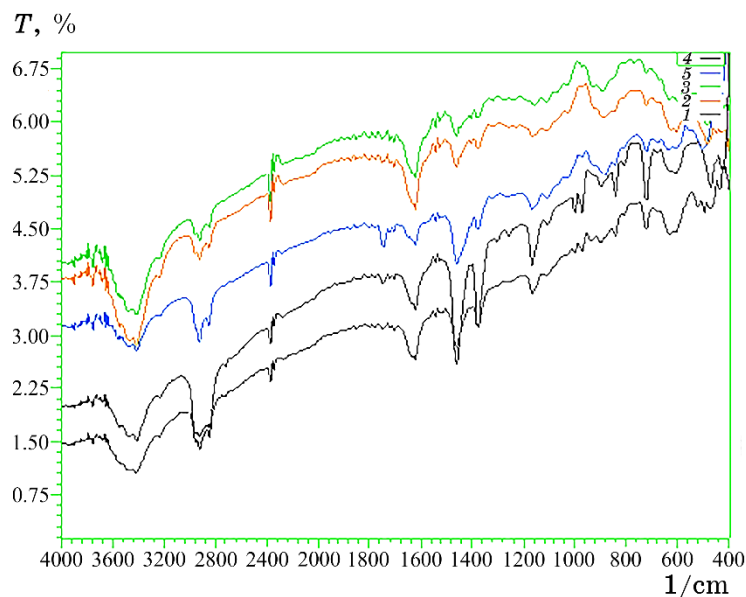


Fig. 12. Transparency *versus* the wavelength for the samples.

chain alkyl group. In addition, the peak at 1462 cm^{-1} is attributed to the vibrational changes occurring in the C–H bond.

3.4. SEM Results and Discussion

The morphology of the specimens shown in Fig. 13 in sample 1 is a pure blend containing 70–20% of PP–PE blend without titanium dioxide, as shown in Fig. 13. There are little delaminations of the PP–PE blend and immiscible blend. In sample 2, there is more delamination and white colour in most of the regions than in sample 1 due to TiO_2 addition. The homogenous structure appears in the sample 3. As shown in the sample 3, there is no delamination due to good adhesion between TiO_2 particles and the blend, because the EPDM coupling agent enhances the adhesion. As shown in samples 3, 4, the filler particles were distributed evenly due to good adhesion, when the titanium-dioxide filler increased. There is no evidence of agglomeration of filler particles in the samples. In the sample 5, there are separation between titanium-dioxide particles, as shown in white dots, and delamination due to the high fraction of filler content.

4. CONCLUSIONS

1. The tensile stress is improved at 5 wt.% titanium-dioxide con-

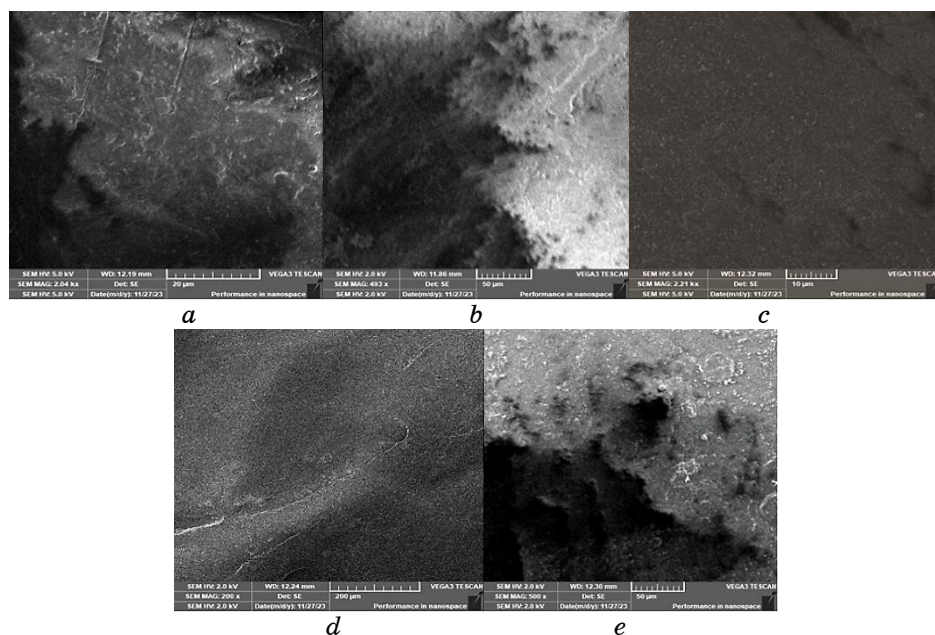


Fig. 13. SEM for the samples (*a*—sample 1 (0% TiO_2); *b*—sample 2 (2% TiO_2); *c*—sample 3 (4% TiO_2); *d*—sample 4 (6% TiO_2); *e*—sample 5 (8% TiO_2).

tent, when compared with neat blend samples.

2. The tensile strength modulus is improved at 5 wt.% titanium-dioxide content.
3. The bending strength has a minimum value of 4%, in which the elasticity is decreased to the minimum value, and the tensile modulus is increased to the maximum value.
4. SEM tests reveal the enhanced morphology in samples 3 and 4 due to the EPDM coupling agent, which enhances the adhesion.
5. The titanium-dioxide particles increase the temperature of the nanocomposites' glass transition. DSC results indicate that the blend is immiscible.

REFERENCES

1. N. S. Radhi and Z. S. Al-Khafaji, *Proc. 6th International Scientific Conference on Nanotechnology, Advanced Materials and Its Applications (May 13–14, 2018, Iraq)*, p. 1–9.
2. S. Sattar, Y. Alaiwi, N. S. Radhi, Z. Al-Khafaji, O. Al-Hashimi, H. Alzahrani, and Z. M. Yaseen, *J. King Saud Univ. Sci.*, **35**, No. 8: 102861 (2023); doi.org/10.1016/j.jksus.2023.102861
3. N. M. Dawood, N. S. Radhi, and Z. S. Al-Khafaji, *Mater. Sci. Forum*, **1002**, No. 1: 33 (2020); doi.org/10.4028/www.scientific.net/MSF.1002.33

4. N. S. Radhi, H. H. Jamal Al-Deen, R. Safaa Hadi, N. Al-Ghaban, and Z. S. Al-Khafaji, *J. Nanostruct.*, **14**, No. 1: 1 (2024); https://jns.kashanu.ac.ir/article_113861.html
5. A. J. Salman, Z. F. Jawad, R. J. Ghayyib, F. A. Kareem, and Z. Al-Khafaji, *Energies*, **15**, No. 18: 6808 (2022); <https://doi.org/10.3390/en15186808>
6. H. A. Sallal, M. H. Mahboba, M. S. Radhi, A. Hanif, Z. S. Al-Khafaji, S. Ahmad, and Z. M. Yaseen, *J. King Saud Univ. Sci.*, **36**, No. 2: 103061 (2024); <https://doi.org/10.1016/j.jksus.2023.103061>
7. A. M. Humad, A. J. Dakhil, S. A. Al-Mashhadi, Z. Al-Khafaji, Z. A. Moham-med, and S. F. Jabr, *Res. Eng. Struct. Mater.*, **10**, No. 1: 1 (2024); <http://dx.doi.org/10.17515/resm2023.43me0806rs>
8. I. A. U. Kadhim, H. A. Sallal, and Z. S. Al-Khafaji, *ES Mater. Manuf.*, **21**, No. 1: 828 (2023); <https://dx.doi.org/10.30919/esmm5f828>
9. A. H. Jasim, N. S. Radhi, N. E. Kareem, Z. S. Al-Khafaji, and M. Falah, *Open Eng.*, **13**, No. 1: 20220472 (2023); <https://doi.org/10.1515/eng-2022-0472>
10. N. S. Radhi, A. H. Jasim, Z. S. Al-Khafaji, and M. Falah, *Nanosistemi, Nanomateriali, Nanotehnologii*, **21**, Iss. 4: 769 (2023); <https://doi.org/10.15407/nnn.21.04.769>
11. N. D. Fahad, N. S. Radhi, Z. S. Al-Khafaji, and A. A. Diwan, *Heliyon*, **9**, No. 3: 14103 (2023); <https://doi.org/10.1016/j.heliyon.2023.e14103>
12. S. Sattar, Y. Alaiwi, N. S. Radhi, and Z. Al-Khafaji, *Acad. J. Manuf. Eng.*, **21**, No. 4: 86 (2023); https://ajme.ro/current_issue.php
13. E. Mohammed and Z. Al-Khafaji, *Acad. J. Manuf. Eng.*, **21**, No. 3: 1 (2023); <https://ajme.ro/content.php?vol=21&year=2023&issue=3&offset=0>
14. M. Awang and W. R. Wan Mohd, *IOP Conf. Ser.: Mater. Sci. Eng.*, **342**, Iss. 1: 012046 (2018); DOI:10.1088/1757-899X/342/1/012046
15. C. Rosales, C. Bernal, and V. Pettarin, *Polym. Test.*, **90**, No. 1: 106598 (2020); <https://doi.org/10.1016/j.polymertesting.2020.106598>
16. J. A. Vallejo-Montesinos, J. A. L. Martínez, J. A. Montejano-Carrizales, E. Perez, J. A. B. Pérez, A. A. Almendárez-Camarillo, and J. A. Gonzalez-Calderon, *Mech. Mater. Sci. Eng.*, **8**, No. 1: 1 (2017); doi:10.2412/mmse.96.48.950
17. O. Kaymakci and N. Uyanik, *Mater. Plast.*, **57**: 309 (2020); <https://doi.org/10.37358/Mat.Plust.1964>
18. B. Al-Zubaidy, N. S. Radhi, and Z. S. Al-Khafaji, *Int. J. Mech. Eng. Technol.*, **10**, No. 1: 776 (2019); https://cdnx.uobabylon.edu.iq/research/repository1_publication14452_28_816.pdf
19. S. A. Hamza and N. S. Radhi, *Acad. J. Manuf. Eng.*, **21**, No. 1: 65 (2023); <https://ajme.ro/content.php?vol=21&year=2023&issue=1&offset=0>
20. H. A. Sallal, M. S. Radhi, M. H. Mahboba, and Z. Al-Khafaji, *Egypt. J. Chem.*, **55**, No. 6: 197 (2023); doi:10.21608/EJCHEM.2022.154630.6684
21. B. M. Rudresh, B. N. Ravikumar, and D. Madhu, *Indian J. Adv. Chem. Sci.*, **4**, No. 1: 68 (2016); <https://ijacskros.com/artecles/IJACS-M174.pdf>
22. H. Jones, J. McClements, D. Ray, C. S. Hindle, M. Kalloudis, and V. Koutsos, *Polym.*, **15**, No. 21: 4200 (2023); <https://doi.org/10.3390/polym15214200>
23. S. Daneshpayeh, F. Ashenai Ghasemi, and I. Ghasemi, *Teh. Glas.*, **13**, No. 3: 165 (2019); <https://doi.org/10.31803/tg-20190312191013>