



Improving the Mechanical Properties of Thermoplastic Polyolefins Using Recycled Low-Density Polyethylene and Multi-Walled Carbon Nanotubes



CrossMark

M A. Ahmed¹, M. El-Shafie¹, U F. Kandil^{1*}, M. M. R Taha²

¹ Petroleum Applications Department, Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt.

² Department of Civil, Construction & Environmental Engineering, University of New Mexico, Albuquerque, NM 87131-0001, USA.

Abstract

Thermoplastic polyolefin (TPO) has gained considerable attention because of having a combination of rubbery and thermoplastic properties and ease of production. Their excellent weather resistance, low density, and relatively low cost make them attractive materials for the automotive, electrical, footwear industries and membranes for water treatment. Their main shortcomings are poor mechanical properties, especially at low temperatures because of the opposing trends of stiffness and toughness. In this paper, recycled low density polyethylene (RLDPE) was integrated with ethylene-propylene-diene rubber (EPDM) incorporating very low content of carboxylated multi-walled carbon nanotubes (MWCNTs-COOH) to improve the mechanical properties of the produced TPO nanocomposite. TPO has been prepared through the combination of 40, 50, and 60 wt.% RLDPE and 40, 50, and 60 wt.% EPDM. The improved TPO composition was then reinforced with 0.1, 0.3, and 0.5 wt.% MWCNTs-COOH to produce TPO nanocomposites. The compounding of TPO and its nanocomposites was done by melt mixing followed by heat pressing. Mechanical and thermal behaviors of the TPO nanocomposites were investigated. Tensile tests showed that the TOP (60-40) is the best improved concentration; the storage modulus of nanocomposites was enhanced by increasing MWCNTs-COOH concentration. In addition, modulus, stress/strain and toughness of TPO were enhanced by adding 0.5 wt.% MWCNTs-COOH. Thus, MWCNTs-COOH reinforced TPO due to not only its large aspect ratios but also due to its interaction with both the TOP matrix and the compatibilizer. The results of microstructural investigations of the prepared TPO nanocomposite using FTIR and TGA confirmed the interaction between MWCNTs-COOH and TPO matrix

Keywords: Thermoplastic Polyolefin, Dynamic Mechanical Analysis (DMA), Nanocomposites, Carbon Nanotubes

1. Introduction

LDPE waste represents a substantial portion of the thermoplastics found in waste streams. However, there is minimal use of a recycled LDPE (RLDPE) alone because of its low mechanical properties. RLDPE waste sources including bags, pallet covers. Nowadays, it was found that LDPE waste can be developed if their low mechanical properties can be improved by adding other materials [1,2]. Efforts by various researchers to modify and blend recycled thermoplastic waste have been investigated so as to obtain finished products with good mechanical properties[3,4].

Thermoplastic polyolefin elastomers (TPOs) are compounds comprising blends of thermoplastics such

as polyethylene (PE), polypropylene (PP) and elastomers such as EPDM (ethylene propylene diene monomer) rubber. It is found in TPOs that the rubber phase is finely dispersed within the continuous thermoplastic polyolefin phase [5]. TPOs have performance properties that are equivalent to conventional thermoset rubbers and can be processed as efficiently as thermoplastics. Therefore, they can be easily processed by injection molding, extrusion or blow molding [6,7,8].

The advantages of TPOs come from its outstanding properties. They are characterized by high impact resistance, low density and good chemical resistance. They are used in applications where there is a requirement for increased toughness

*Corresponding author e-mail: alfa_olefins@yahoo.com.

Receive Date: 10 February 2021, Revise Date: 15 February 2021, Accept Date: 21 February 2021

DOI: 10.21608/EJCHEM.2021.62554.3341

©2021 National Information and Documentation Center (NIDOC)

and durability over the conventional thermoplastics, such as automotive bumpers and dashboards. In addition, it is possible to prepare various TPO compounds for suitable end-use applications by changing the polyolefin and EPDM composition. The most attractive feature of these materials is that they can be processed like thermoplastic while exhibiting the resilience and elasticity characteristics like an elastomer [9].

Their main shortcomings are poor mechanical properties, especially at low temperatures. In this regard, inorganic fillers are commonly added to TPO blends to achieve desired mechanical stiffness and strength. It is known that the traditional reinforcements and fillers must be used at high loading levels [10,11], which increase the weight and cause an adverse effect in automotive applications area, because 90% of the total energy used by automobile during its life cycle is from fuel consumed by its own weight [12]. Consequently, small amount of nanofiller can improve the stiffness of the material substantially, thus cost effective where the weight of the material part is a concern. Therefore, some trials have been made to enhance the mechanical properties of TPOs using montmorillonite nano-clay (MMT) and the resulting polymer nanocomposites generally exhibit enhanced tensile modulus and strength but poor tensile ductility and impact toughness [13].

While MWCNTs have been extensively studied for enhancing the mechanical properties of polymer blends, research on industrially relevant thermoplastic polyolefin TPO/MWCNT composites remains scarce [14,15,16]. Nowadays, the addition of MWCNTs in different polymer matrices has been reported which provide an effective improvement in the overall mechanical properties, especially high tensile strength and stiffness [17,18,19,20]. In contrast, less information is available on the mechanical behavior of the elastomer-rich TPO/MWCNT composite [21,22,23].

This research aims to produce TPO/MWCNTs composite based on LDPE waste and EPDM to achieve an optimum balance of stiffness and toughness in TPO blends. The produced composite was fully investigated through thermal and mechanical behaviors. In this research, the enhanced mechanical properties of TPO will widen its industrial applications.

2. Experimental Methods

2.1. Materials

EPDM, with Mooney viscosity 71 (ML₁₊₄ at 190 °C), and 56.5 ethylene content, was supplied by Kumho Polytechnical Co. (trade name KEP-270) and used as a minor phase. Recycled LDPE denoted

below as “RLDPE” in crushed form was obtained from the Egyptian Saudi Company for Plastic Products; Industrial Zone, 10th of Ramadan, Egypt. Maleated polyethylene (MPE) copolymer was used as a coupling agent (Sigma Aldrich). Carboxy functionalized multiwall carbon nanotubes (MWCNTs-COOH) was supplied by CheapTubes Inc. and had a purity greater than 95%. Its physical dimensions was within a 20 to 30 nm outer diameter, a 5 to 10 nm inner diameter, and a 10 to 30 μm length. The functionalization of the nanotubes was achieved through acid chemistry, and their surface area was approximately 110 m²/g.

2.2. Compounding and blend preparation

A two-step compounding process was used to prepare the TPO blends and its nanocomposites with various compositions [24]. Firstly, TPO with different RLDPE/EPDM compositions was melt blended in weight ratios of 40/60, 50/50 and 60/40 of RLDPE and EPDM, respectively, in an internal mixer (Haake Rheomix; HBI SYS 90) at a temperature of 190°C and a rotor speed of 60 rpm. Each of these percentages contains a 3.7 wt.% coupling agent (MPE) with respect to the total weight of both RLDPE and EPDM [25,26,27]. Then, the optimum RLDPE/EPDM mixing ratio was used to prepare RLDPE/EPDM/MWCNTs-COOH composites with MWCNTs-COOH loadings of 0.1, 0.3, and 0.5 wt%, using the same preparation conditions. A hindered phenol antioxidant, Irganox B225, was added to each formulation at 0.2 wt% to prevent thermal degradation. TPO (neat) and TPO/MWCNTs-COOH nanocomposite blends obtained from the mixer were then heat pressed into sheets (3mm thick) in a compression mold (Mini Test Hydraulic Press) at 190°C and 10MPa for 5 min. Then, TPO nanocomposite blends were left for cooling at room temperature.

2.3. Characterization

Dynamic mechanical analysis (DMA) was performed to investigate the mechanical properties of the prepared nanocomposites by the Triton Technology instrument [28]. Storage modulus and stress-strain results were measured using tension mode (ASTM D-4065) at 1Hz frequency in a temperature range from -85 to 130 °C with a heating rate of 3°C/min. The sample dimensions were 25, 10, and 1 mm for length, width, and thickness, respectively. For the thermal properties, thermal gravimetric analysis (TGA) was performed for all composites by TGA 55 TA instrument through heating to 800 °C with a heating rate of 5°/min. Under N₂ gas. Microstructural analysis for RLDPE-EPDM(60/40) and RLDPE-EPDM(60/40)/MWCNTs-COOH (0.5Wt%) was performed by Fourier Transform Infrared - Attenuated Total Reflection

(FTIR-ATR, Alpha Bruker Platinum, 1-211-6353) spectroscopy, using a zinc selenide crystal with an incident angle of $45 \pm 15^\circ$ and 560 scan time (24 s) at 4 cm^{-1} resolution. The spectral range used for FTIR was $650\text{--}4,000 \text{ cm}^{-1}$.

3. Results and discussion

The optimum ratio of RLDPE/EPDM was first performed to produce TPO. Selection of the optimized ratio of TPO depends on measuring the modulus values for samples of blank RLDPE, weight ratios of RLDPE/EPDM (60/40, 50/50, 40/60) and blank EPDM using DMA. Consequently, the effect of adding EPDM to RLDPE was firstly investigated by DMA. In **Fig.1**, blank RLDPE, shows the highest modulus in the whole temperature range (2 GPa), which is attributed to the stiffer property of polyethylene. However, adding the elastic EPDM polymer to RLDPE starts to reduce the modulus value, especially with the 40-60 percentage which recorded the lowest modulus (0.93 GPa), compared with other mixing percentages, but still has a little bit higher value compared with the blank EPDM (0.91 GPa). In other words, the stiff RLDPE can enhance the modulus of the highly elastic EPDM during all temperature scale. This effect is more apparent with the 60-40 mixture that having the highest modulus (1.35 GPa) compared with other percentages.

By taking the 60/40 mixture as an enhanced mixture (reference), different MWCNTs-COOH percentages (0.1, 0.3, and 0.5 wt.%) were added, as shown in **Fig.2**. All nanocomposites have a higher modulus than that of the reference one as expected. The moduli values of TPO treated with 0.1, 0.3 and 0.5 wt.% MWCNTs-COOH were 2.0, 2.2, and 2.7 GPa, respectively. It is clear that the least treating percentage of MWCNTs-COOH enhanced TPO from 1.35 to 2.0 GPa. This modulus value is similar to that of pure RLDPE. Consequently, TPO treated with only 0.1 wt.% MWCNTs-COOH has similar mechanical properties of the stiff RLDPE.

For $\tan \delta$ curves of the mixtures in **Fig.3**, the different polymeric TPO mixtures show similar curves, compared with the version RLDPE and EPDM. This indicated the smooth surface, good mixing, and the other thermal behavior in case of mixing the two polymeric components together, which is different from RLDPE or EPDM alone. However, all $\tan \delta$ curves of the prepared nanocomposites in **Fig.4** indicate a typical behavior with the same T_g temperature.

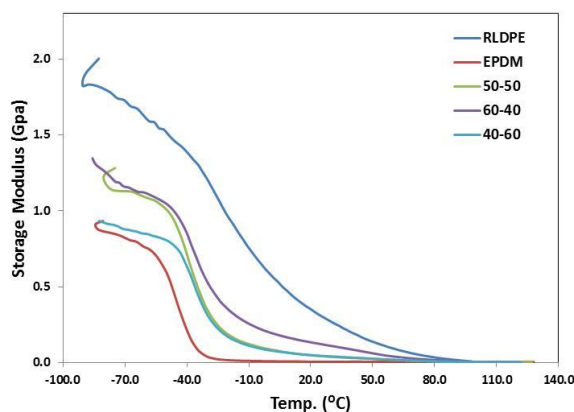


Fig.1: Storage modulus of RLDPE and RLDPE-EPDM composite with different EPDM mixture ratios.

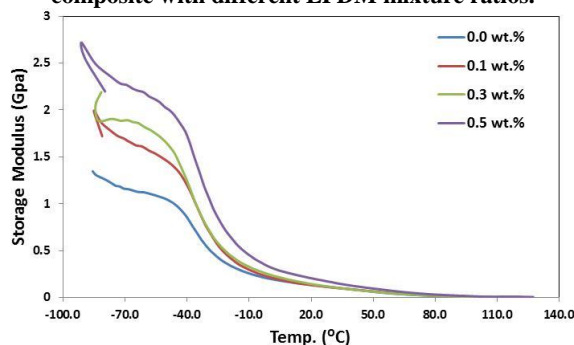


Fig.2: Storage modulus of RLDPE-EPDM composite reinforced with different weight contents of MWCNTs-COOH.

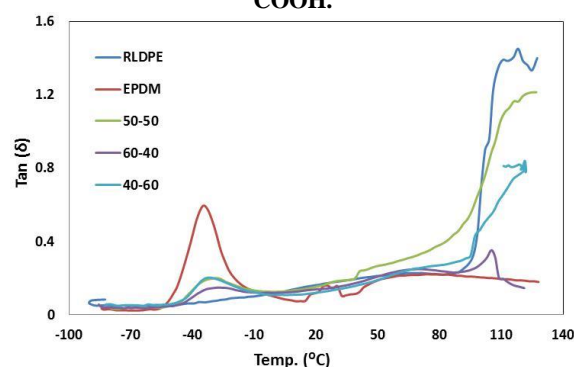


Fig.3: $\tan \delta$ for RLDPE and RLDPE-EPDM composite with different EPDM mixtures ratios.

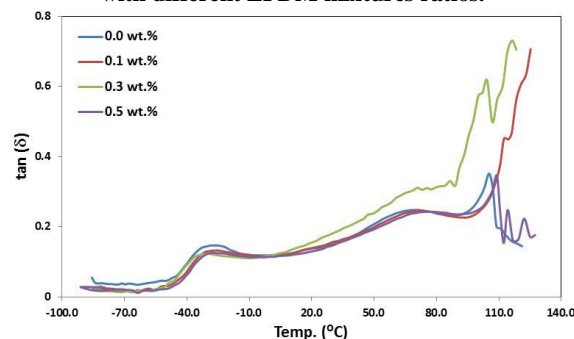


Fig.4: $\tan \delta$ for RLDPE-EPDM composite reinforced with different weight contents of MWCNTs-COOH.

The stress-strain behavior of TPO control sample (60/40) and its nanocomposites is shown in **Fig.5**. The control sample shows the least stress and strain values due to its poor mechanical properties compared with all nanocomposite concentrations. Adding different MWCNTs-COOH concentrations as 0.10, 0.30 and 0.50 wt.% led to different effects on stress and strain. 0.1 wt.% MWCNTs-COOH nanocomposite shows higher stress and strain values, however, the highest stress (around 2×10^5 Pa) is achieved by 0.3 wt.% MWCNTs-COOH nanocomposites but the strain became to reduce compared with 0.1 wt.% MWCNTs-COOH. The highest strain (0.024) is achieved by the 0.5 wt.% MWCNTs-COOH concentration, where the stress is almost the same as 0.3 wt.% MWCNTs-COOH. It is concluded that the 0.5 wt.% MWCNTs-COOH nanocomposite has high stress and advanced strain property, which makes it the more ductile TPO-MWCNTs-COOH nanocomposite concentration that can bear more external loads. Furthermore, it has improved toughness property due to the increased area under the obtained stress-strain line.

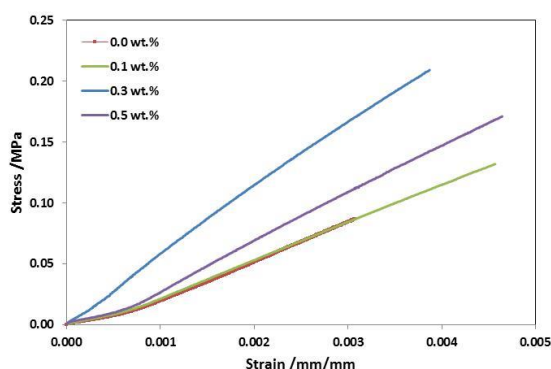


Fig.5: Stress-strain curve for RLDPE-EPDM composite reinforced with different weight contents of MWCNTs-COOH

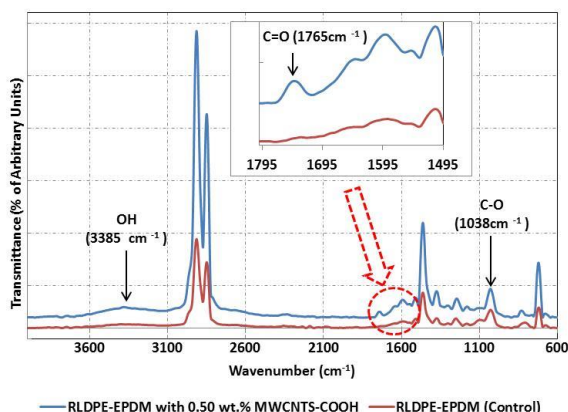


Fig.6: FTIR of RLDPE-EPDM (Control) and RLDPE-EPDM with 0.50 wt.% MWCNTs-COOH

The enhancement in moduli and toughness values of the prepared TPO (LPPE/EPDM/MWCNTs-COOH) could be attributed to the enhancing effect correlated to the interfacial interaction between the functionalized MWCNTs and TPO through its coupling agent (MPE). One reason for such enhancement is attributed to π - π interaction between the unsaturation units in the EPDM part and the nanotubes [29]. Besides, enhancing scenario could also be related the chemical interaction (hydrogen bonding) between the anhydride groups of the coupling agent (MPE) and the carboxyl groups of the functionalized MWCNTs. Microstructural investigations of the prepared TPO/MWCNT-COOH using FTIR and TGA were performed to confirm these interactions.

The FTIR spectra of neat TPO (PE-EPDM) (60/40) and TPO (LPPE/EPDM/MWCNTs-COOH) (0.5wt.%) are shown in **Fig. 6**. In both curves, the main TPO structure shows the main peaks of the skeleton structure. The stretching peaks of C-O and (C-O-C) of the coupling agent (MPE) appear at 1038 cm^{-1} and 1250 cm^{-1} , respectively [30]. The peaks at 1385 cm^{-1} and 1466 cm^{-1} are assigned for the bending vibration of CH_3 . The peaks appear in the region of 2800 to 3080 cm^{-1} are assigned for C-H stretching vibrations in both saturated and unsaturated regions and a peak at 1608 cm^{-1} is assigned for C=C of the EPDM component [31,32,33,34]. In case of TPO (LPPE/EPDM/MWCNTs-COOH), the peak at 1765 cm^{-1} is assigned to the C=O stretching vibration, and the broad peak present at 3385 cm^{-1} is the stretching vibration of the O-H functional group in MWCNTs-COOH [35,36,37,38,39].

Thermal degradation of neat TPO samples with different LDPE/EPDM weight ratios and the TPO (60/40)/ MWCNTs-COOH was assessed using thermogravimetric analysis (TGA) as shown in **Figs7&8**, respectively. By comparing the thermal stability through the temperatures for 10% (T10) and 50% (T50) of weight loss (**Table 1**) for the TGA curves of neat TPO (**Fig.7**), it is apparent that RLDPE starts 10% (T10) degradation at 431°C and 50% (T50) at 473°C , while the thermal stability is shifted higher for EPDM and for all RLDPE/EPDM weight ratios. It is reported that polyethylene started degradation by thermal scissions of C-C chain bonds following the formation of radical species through a molecular weight reduction by depropagation and inter/intra-transfer reactions [40,41]. In general, the LDPE displays lower thermal stability than the corresponding TPO blends. This may be due to the fact that LDPE has higher branch content than EPDM, and branches reduce the thermal stability of a

polymeric material because they are more labile sites for degradation [42,43,44,45]. Consequently, this is an indication of a good compatibility between both components in the TPO blends, which is also attributed to the presence of the coupling agent.

In TGA curves of TPO (60-40)/ carbon nanotube composite (Fig. 8), it could be noticed that TPO(60/40/05) reaches 10% (T10) degradation at 465°C and 50% (T50) at 486°C. By comparing values of neat TPO (60-40) with the other MWCNTs-COOH weight ratios, it becomes clear that increasing wt.% of MWCNTs-COOH raises the thermal stability of the TPO/MWCNTs-COOH composite. As a result, TPO/MWCNTs-COOH nanocomposites exhibit enhanced thermal stability in comparison with the neat TPO blend. This is an indication of the successful chemical interfacial interaction between the functionalized MWCNTs-COOH and the TPO matrix. More importantly, this is a distinct proof for the successful MWCNTs-COOH dispersion in the TPO matrix, and is strongly consistent with enhanced mechanical properties and FTIR results.

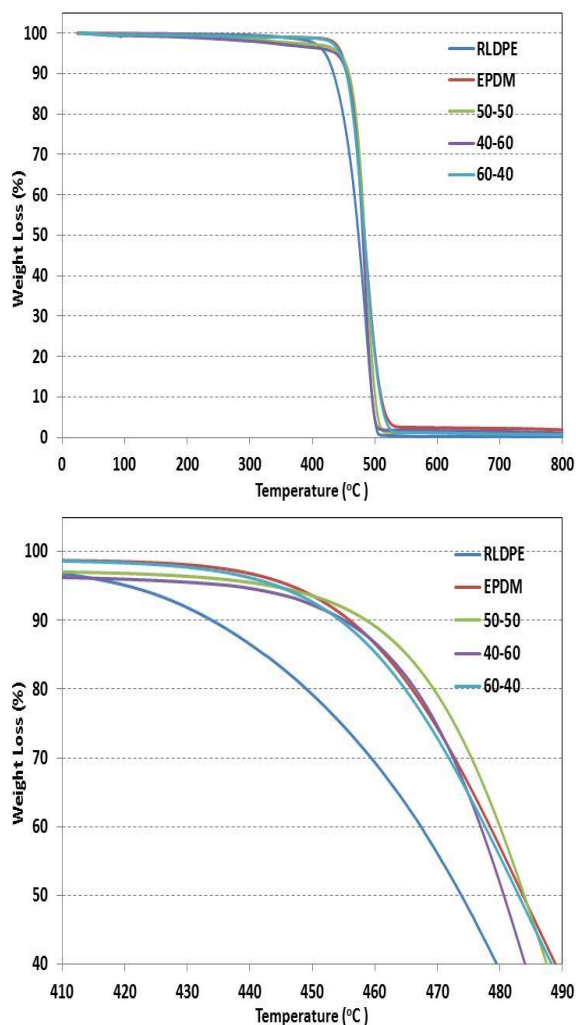


Figure 7: TGA of various TPO samples with different RLDPE/EPDM weight ratios

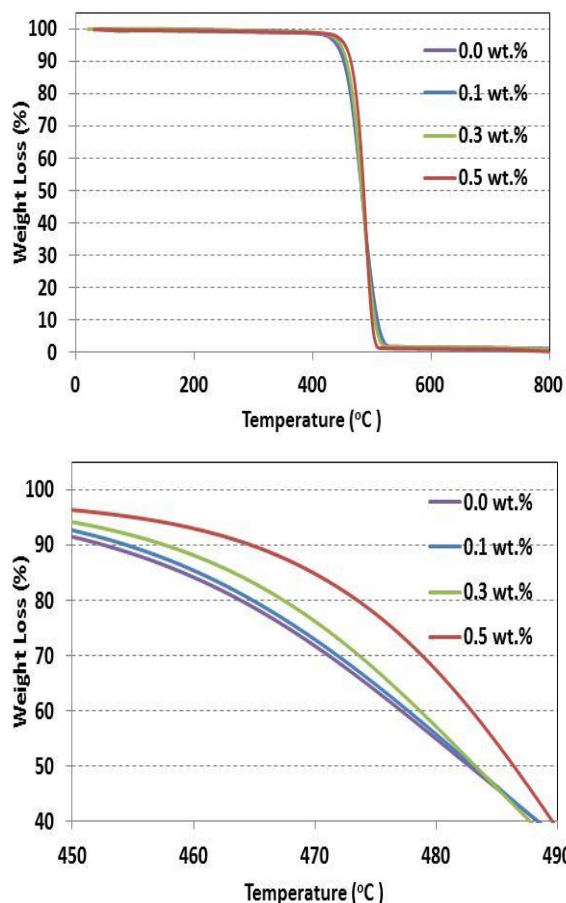


Figure 8: TGA of RLDPE-EPDM composite reinforced with different weight contents of MWCNTs-COOH

Table 1: Decomposition temperature of TPO and TPO/MWCNT composites.

LDPE/EPDM (Wt%)	T10 (°C)	T50 (°C)	LDPE/EPDM/MWCNT (wt%)	T10 (°C)	T50 (°C)
100/0	431	473	60/40/0	453	481
0/100	453	481	60/40/0.1	453	482
50/50	458	483	60/40/0.3	457	483
60/40	453	481	60/40/0.5	465	486
40/60	454	480			

As a result, the thermal stability of the modified TPO was significantly enhanced in comparison with the neat TPO blend.

Conclusion

Thermoplastic polyolefin (TPO) has been prepared by thermal blending of waste low density polyethylene (RLDPE) and ethylene-propylene-diene rubber (EPDM) in wt.% ratios of 40/60, 50/50, and 60/40, respectively, in the presence of maleated polyethylene as a coupling agent. Dynamic mechanical analysis (DMA) was performed to select

the optimum mixing ratio of TPO blends. It is found from the results that the ratio of 60/40 is the best. Then, this specific mixing ratio was treated with MWCNTs-COOH in different ratios (0.1, 0.3, and 0.5 wt.%) to produce TPO/MWCNTs-COOH nanocomposites. From DMA results, modulus, stress-strain and toughness of TPO/MWCNTs-COOH are mechanically enhanced where the ratio of 0.5 wt.% was the best. The mechanical enhancement was confirmed with microstructural using FTIR and TGA. Consequently, incorporating a very few percentages of MWCNTs-COOH significantly improved the mechanical properties of TPO composite and also enhanced the thermal stability in comparison with the neat TPO blend. In addition, it is a cost effective composite since the starting matrix is a recycled polyethylene. As a result, this modified TPO composite will widen its industrial applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This paper is based upon work supported by Science, Technology & Innovation Funding Authority (STDF) under grant (BARG Call7 - Project ID 37200). The authors greatly acknowledge this funding.

References

- [1] Bertin S., Robin J.; *European Polymer Journal*, 38 2255–2264(2002).
- [2] Alnajjar H.M., Naguib H.M., Shaker N.O, Ahmed H., Farag A.A., Kandil U.F.; Enhancement of Recycled WPC with Epoxy Nanocomposite Coats; *Egyptian Journal of Chemistry*; 62(3); 555-563(2019).
- [3] Khan M.A., Kumar S.S., Raghu T.S., Kotresh T.M., Sailaja R.R.N.; Commingled nanocomposites of LDPE/PP/Nylon 6/EPDM reinforced with MWCNT and Kenaf Fiber with enhanced mechanical, thermal and flammability characteristics; *Materials Today Communications*, 4, 50–62(2015).
- [4] Saber E., El-Sayed N.S., Nagieb Z.A., Ismail A., Kamel S.; Characterization of Plastic Composite Based on HIPS Loaded with Bagasse; ; *Egyptian Journal of Chemistry*; 60(6); 1101-1110(2017).
- [5] Growth in thermoplastic polyolefin elastomeric compounds set to soar; *Plastics, Additives and Compounding*, 2(3), 30-31(2000).
- [6] Ruan Y.H., Tjong S.C.; Mechanical Properties of Thermoplastic Polyolefin (TPO)/Clay Nanocomposites; *Mater. Res. Soc. Symp. Proc., Materials Research Society*, 1056, 2008.
- [7] Abitha V.K., Rane A.V.; A review on EPDM/polyolefinic blends and composites; *Research & Reviews in Polymer*; 5(3), 102-114(2014).
- [8] Petrie K.G., Osazuwa O., Docoslis A., Kontopoulou M.; Controlling MWCNT partitioning and electrical conductivity in melt compounded polypropylene/poly(ethylene-co-octene) blends; *Polymer*, 114, 231-241(2017).
- [9] Mishra J.K., Hwang K.J., Ha C.S.; Preparation, mechanical and rheological properties of a thermoplastic polyolefin (TPO)/organoclay nanocomposite with reference to the effect of maleic anhydride modified polypropylene as a compatibilizer; *Polymer*, 46, 1995–2002(2005).
- [10] Abd El-Hakim A.A., El-Sawey A.A., Motawie A.M., Eid A.I., Mahruos N.S.; Study of Some Polypropylene Nanocomposite Properties; *Egyptian Journal of Chemistry*; 61(5); 825-842(2018).
- [11] Dief Allah M.M., Ali Z.M., Rozik N.N., Raslan M.A.; Sadek K.U.; Electrical and Mechanical Properties of Nitrile Rubber (NR) Filled with Industrial waste and by Product from Manufacture of Ferrosilicon Alloys in Egyptian Chemical Industries Company; *Egyptian Journal of Chemistry*; 60(5); 905-918(2017).
- [12] Graces J, Moll D, Bicerano J, Fibiger R. *Adv Mater.*;12,18352000.
- [13] Ruan Y.H, and Tjong S.C.; Mechanical Properties of Thermoplastic Polyolefin (TPO)/Clay Nanocomposites; *Mater. Res. Soc. Symp. Proc. Materials Research Society*, 1056, 2008.
- [14] Li C., Zhao Q., Deng H., Chen C., Wang K., Zhang Q., Chen F., Fu Q., Preparation, structure and properties of thermoplastic olefin nanocomposites containing functionalized carbon nanotubes, *Polym. Int.*, 60, 1629-1637(2011).
- [15] Valentini L., Biagiotti J., Kenny J.M., Manchado M.A.L., Physical and mechanical behavior of single-walled carbon nanotube/polypropylene/ethylene - propylene - diene rubber nanocomposites, *J. Appl. Polym. Sci.*, 89, 2657-2663(2003).
- [16] Farouk K; El-Nemr M; Masoaud E; Abdullah E; Hanko Z; Ablation and thermal properties of ethylene propylene diene rubber/carbon fiber composites cured by ionizing radiation for heat shielding applications; *Egyptian Journal of Chemistry*; 64(3); 10-11(2021).
- [17] Bal, S., and Samal, S. S. *Bull. Mater. Sci.*, 30, 379 (2007).
- [18] Alexander, M., and Dubios, P. *Mater. Sci. Eng.*, 28, 1 (2000)
- [19] Douba, A.E., Emiroglu, M, Tarefder, R.A., Kandil, U.F., Reda Taha, M.M. Use of Carbon Nanotubes to Improve Fracture Toughness of Polymer Concrete; *Transportation Research Record: Journal of the Transportation Research Board*, 2612(1)96–103, (2017)
- [20] Douba A.E., Emiruglo M., Kandil U.F, and Taha M.M.R.; Very Ductile Polymer Concrete Using Carbon Nanotubes; *Construction & Building Materials*, 196, 468–477(2019).
- [21] Lee H.S., Fasulo P.D., Rodgers W.R., Paul D.R., *Polymer*, 46, 11673-11689 (2005)
- [22] Mishra J.K, Hwang K.J., Chang S H, *Polymer*, 46, 1995-2002 (2005)
- [23] Lee H.S, Fasulo P.D., Rodgers W.R., Paul D.R., *Polymer*, 47, 3528-3539 (2006)
- [24] Ahn Y. C., Paul D.R., *Polymer*, 47, 2830-2838 (2006)
- [25] Lu J. Z., Negulescu I. I., and Wu Q., Maleated Wood-Fiber/High-Density-Polyethylene Composites: Coupling Mechanisms and Interfacial Characterization *Composite Interfaces* 12(1–2), 125–140(2005).

- [26] Mohamed, M.R., Naguib, H.M., El-Ghazawy, R.A., Shaker, N.O., Amer, A.A., Soliman, A.M., and Kandil, U.F., Surface Activation of Wood Plastic Composites (WPC) for Enhanced Adhesion with Epoxy Coating, *Journal of Materials Performance and Characterization*, 8(1), 22–40(2019).
- [27] Abolkassem S.A., Elkady O.A., Ewais E.M.M., Hussein W.A.; Studying the Microstructure and Mechanical Properties of (WC – TiC - Co) /ZrO₂ Composite Prepared by Powder Technology; *Egyptian Journal of Chemistry*; 63(4); 1241- 1254 (2020)
- [28] Eldesouki M; Abo-shanab Z; Mohammedy M; Elshafie M; Abo Riya M; Elkholy S; Evaluation of the dynamic mechanical analysis, water absorption and chemical resistance properties of sulfur/epoxy composites; *Egyptian Journal of Chemistry*; 64(1); 107-115(2021).
- [29] Petrie K.G., Osazuwa O., Docoslis A., Kontopoulou M.; Controlling MWCNT partitioning and electrical conductivity in melt compounded polypropylene/poly(ethylene-co-octene) blends, *Polymer*, 114, 231-241(2017).
- [30] Ozdemir T; Gamma irradiation degradation/modification of 5-ethylidene 2-norbornene (ENB)-based ethylene propylene diene rubber (EPDM) depending on ENB content of EPDM and type/content of peroxides used in vulcanization; *Radiation Physics and Chemistry*, 77, 787–793(2008).
- [31] Li C., Zhao Q., Deng H., Chen C., Wang K, Zhang Q, Chen F. and Fu Q.; Preparation, structure and properties of thermoplastic olefin nanocomposites containing functionalized carbon nanotubes; *Polym Int*; 60, 1629–1637(2011).
- [32] Hwang G.L., Shieh Y.T. and Hwang K.C., *Adv Funct Mater*, 14, 487–491(2004).
- [33] Li W.H., Chen X.H., Yang Z. and Xu L.S., *J Appl Polym Sci*, 113, 3809–3814(2009).
- [34] Roucoules V. , Siffer F., Ponche A. , Egurrola U., Vallat M.F.; Strengthening the Junction Between EPDM and Aluminium Substrate via Plasma Polymerization, *The Journal of Adhesion*, 83(10), 875-895(2007).
- [35] Li C., Zhao Q., Deng H., Chen C., Wang K., Zhang Q., Chen F. and Fu Q.; Preparation, structure and properties of thermoplastic olefin nanocomposites containing functionalized carbon nanotubes; *Polym Int*; 60, 1629–1637(2011).
- [36] Ramanathan T, Fisher F.T., Ruoff R.S. and Brinson L.C., *Chem Mat*, 17, 1290–1295 (2005).
- [37] Xu J.Q., Bartels J.W., Bohnsack D.A., Tseng T.C., Mackay M.E. and Wooley K.L., *Adv Funct Mater*, 18, 2733–2744(2008).
- [38] Borowski E., Soliman E.M., Kandil U.F., Taha, M.M.R., Interlaminar Fracture Toughness of CFRP Laminates Incorporating Multi-Walled Carbon Nanotubes; *Polymers*, 7(6),1020-1045(2015).
- [39] Soliman E.M., Kandil U.F., Taha, M.M.R; Improved Strength and Toughness of Carbon Woven Fabric Composites with Functionalized MWCNTs; *Materials*, 7,4640-4657(2014).
- [40] Barus S., Zanetti M., Bracco P., Musso S., Chiodoni A., Tagliaferro A., Influence of MWCNT morphology on dispersion and thermal properties of polyethylene nanocomposites, *Polym. Degrad. Stab.*, 95(5), 756-762(2010).
- [41] Leyton R.S., Quijada R., Bastías R., Zamora N., Moya F.O., Palza H.; *Composites Science and Technology*, 184, 107888(2019).
- [42] Scott, G., Mechanisms of Polymer Degradation and Stabilization; Elsevier Applied Science: London, (1990).
- [43] Grassie, N.; Scott, G., Polymer Degradation and Stabilization; Cambridge University Press:Cambridge, England, (1988).
- [44] Hawkins, W. Polymer Degradation and Stabilization; Springer-Verlag: Berlin, (1984).
- [45] Rodrigo L.C., Greus A.R., Imrie C.T., Thermal analysis of high-density polyethylene and low-density polyethylene with enhanced biodegradability, *J. Appl. Polym. Sci.*, 86, 764–772(2002).