MULERSTTATE BUILDERSTTATE BUILDERS MINISTERUL EDUCAȚIEI NAȚIONALE ROMÂNIA

UNIVERSITATEA DE MEDICINĂ, FARMACIE, ȘTIINȚE ȘI TEHNOLOGIE "GEORGE EMIL PALADE" DIN TÂRGU MUREȘ Acta Marisiensis. Seria Technologica Vol. 21 (XXXVIII) no. 1, 2024 ISSN 2668-4217, ISSN-L 2668-4217

Review of the polymeric material composite, optimization for industrial application

Dan Cristian CRACIUN¹, Ildiko PETER²

¹Geroge Emil Palade University of Medicine, Pharmacy, Science, and Technology of Targu Mures Doctoral School Department of Industrial Engineering and Management ²George Emil Palade University of Medicine, Pharmacy, Science, and Technology of Targu Mures Faculty of Engineering and Information Technology Department of Industrial Engineering and Management ¹dan.craciun@umfst.ro ²ildiko.peter@umfst.ro

Abstract

Polyethylene, a widely used polymeric material, has garnered attention for its light weight and some properties. This review focuses on high-density polyethylene (HDPE), a type of PE recognized for its strength, durability, and ease of processing. HDPE is synthesized through low-pressure polymerization of ethylene, resulting in a material that is resistant to acids and alkalis, non-toxic, and cost-effective. It is used in various applications, from everyday products to construction and medical devices. However, HDPE's susceptibility to UV-induced ageing limits its outdoor use. To address this, researchers have explored incorporating titanium dioxide (TiO_2) into HDPE, enhancing its UV resistance and mechanical properties.

The review paper highlights the potential of $HDPE/TiO_2$ composites for outdoor applications, highlighting the need for further research to optimize these materials for long-term stability and performance. The ongoing research aim to create composites that can resist prolonged UV exposure without degradation, making them suitable for a generous range of industrial uses.

Key words: Polyethylene, titanium dioxide, HDPE, degradation, ultraviolet radiation, coating, photo degradation

1. Outline of the topic presented

On the one side, polyethylene (PE) is a material that can be easily shaped and due to its interesting properties, can be used in various industrial applications., On the other side, today's evolution is continuously growing, therefore the investigations does not stop. In this context, the use of PE in some newly developed applications, requires more attention and the own research of the authors of the present manuscript, begin with the careful consideration of the actually reported literature and will continue in the future to enrich them with some own scientific data.

In the following paragraph, the most important aspects related to the data and results obtained by researchers in the field of polymers will be presented, considering the current literature data. Since its discovery in 1933, PE has risen to importance as one of the world's most utilized and acknowledged thermoplastic materials. Its apparent ability to soften and mould into various shapes through repeated heating offers a broad range of applications,

highlighting its versatility across different industries [1]. PE stands as the most efficiently produced synthetic polymer, blending easy processing and economical production with advantageous mechanical characteristics. This stems from the crystalline alignment of elongated hydrocarbon chains, a feature particularly pronounced in high-density polyethylene (HDPE), which contains linear chains without branching, thus ensuring undisturbed crystalline packing [2].

HDPE, one of the five general-purpose plastics, is produced through different procedures, like lowpressure polymerization of ethylene, achieving in parts in the form of granules, like those in figure 1. Its widespread exploitation in different areas area such as lifestyle, construction, and medicine is attributed to its commendable mechanical attributes, resistance to acids and alkalis, non-toxic nature, and other intrinsic advantages, [3] moreover, HDPE possesses a low cost and excellent workability, further enhancing its appeal for various applications [4].

HDPE products incorporate a wide range of pieces, including tubes, plates, profiles, cans, films, and others. Despite the absence of unsaturated bonds in the HDPE molecular chain and their regular arrangement, they are prone to ageing naturally. When exposed to high-energy ultraviolet (UV) rays outdoors. [5-6] Taking into account the challenge of prolonged outdoor usage could significantly broaden the scope of HDPE applications as a general-purpose plastic. Potential uses may include serving as floating bodies for floating power plants, synthetic grass for artificial lawns, and various other innovative applications [7] .However, HDPE does have some limitations, under severe or extreme conditions such as high pressure, low temperatures, and rapid rates of deformation. determine embrittlement, situation which compromising and reducing its use in some of the industrial applications where structural integrity is requested [8].



Fig. 1 Polyethylene in granola shape

2. Short exposition of remarkable data and results from the actual scientific literature

Much research show that in order to successfully combine HDPE with TiO2, special machinery is required, such as injection molding machines, extruders, or heated mixers.

Examples of methods for combining the two compounds can be mentioned from Wang, et.al. [9] who prepared their composite. In the first instance, the wood flour (WF) was dried for 12 hours at 103°C to remove moisture. After that the dried WF was mixed with a HDPE matrix, in a maleic anhydride grafted polyethylene (MAPE), lubricants, and other additives in a high-speed mixer for 8 minutes. Lastly this mixture was afterwards melt-blended and pelletized into wood plastic composites (WPC) pellets using a co-rotating twin-screw extruder. The temperatures in the extruder barrel ranged from 145°C to 170°C, moving from the feeding zone to the die zone, with a fixed screw rotating speed of 100 rpm.

Wang et.al. [10] offers a study about the method of incorporating titanium dioxide particles with highdensity polyethylene. The HDPE powder was blended with three types of TiO₂ (3% by mass) in a XSS-300 torque rheometer. The operating temperature was 150 °C with a speed of 60 rpm, and the mixing time was 10 minutes. The compounds were compressed into sheets with a thickness of 1 mm. UV irradiation was conducted using Q-SUN 1000 xenon lamp test chamber, maintaining an intensity of 0.51 W/m² at 340nm. The panel temperature was kept constant at 65°C, with a distance of 25cm from the light source. The irradiation duration ranged from 0 to 400 hours.

Jing et al. [11] considered and performed within the same preparation method some composites materials described above. The composites underwent trial melting in a torque rheometer at a mixing of 60rpm at 150°C for 10 minutes. Artificial accelerated UV irradiation was conducted in a Q-SUN 1000 xenon lamp test chamber. The irradiation intensity was held at 0.51 W/m² (λ =340 nm), while maintaining a constant air atmosphere at 65°C. The duration of irradiation varied from 0 to 800 hours.

In [9] the authors obtained promising results, observing the microstructure by from Scanning Electron Microscope (SEM) analysis. During the analysis, it comes out that as weathering duration, the small cracks on the surface of the samples increases. However, there was no peeling, and the ageing effect of UV light only occurred on the surface of the composites, which demonstrated that the composites containing CB and TiO₂ had an obvious effect on long-term resistance to UV-induced ageing. Analyzing the aforementioned data, is evidence on the antioxidant's effects and on the role of UV absorption which play a

crucial role in enhancing the UV ageing resistance of HDPE/TiO₂ composites. To further assess the cooling efficiency post-UV exposure, a specially designed apparatus was employed. The experiment was carried out under sunny conditions with a gentle breeze, at a slightly high temperature of 40°C, between midday and 1 p.m. for an hour. The testing site was chosen in Nanjing City, situated at 118° East longitude and 32° North latitude. Prior to UV exposure, the samples showed effective cooling aided by UV absorbers and antioxidants, resulting in a significant reduction of their internal temperature has been observed from 58°C to 44.5°C. Following UV exposure, the samples continued to demonstrate excellent cooling efficacy. with the internal temperature decreasing to 46°C. This fact suggests that the incorporation of UV absorbers and antioxidants not only improves the ageing resistance of HDPE/TiO2 but also preserves their exceptional solar reflectivity and cooling performance [11]

Nasu et al. [12] developed a novel TiO₂-HDPE material. This composite, type material made up of HDPE and silane-coupled TiO₂ particles, exhibits the flexibility of polyethylene and the biocompatibility of TiO2, and mechanical properties like the cortical bone. Here in this study, the objective the bone bonding capacity and biocompatibility of the composite, which demonstrate once again the high importance/competitivity of such polymeric materials. The following preparation method has been performed: HDPE has been melted at about 210°C and mixed with silane-coupled TiO2. particles, with a diameter of around 200nm. The mixed material was pressed under a pressure of 2.5 - 5.8 MPa, and both sides of the material has been exposed to ultraviolet irradiation. The surface of the material has been analyzed through SEM, revealing that the TiO₂ particles have been covered by PE. UV irradiation has been performed for 3600 seconds, and the bioactivity of the material has been evaluated. It comes out that the exposure time was too short. Then, UV irradiation has been carried out for 9 hours, determining an important variation of the mechanical properties the Young's modulus decreased from 10 to 0.9 GPa, and a decrease of the flexural strength has been observed from 65.7 to 13.5 MPa.

The mentioned results are important for some causes, highlighting both the technical advantages and practical applications of compounds formed from HDPE/TiO₂. Composites presents increased resistance to UV-induced ageing due to the antioxidant and UV-absorbing properties of TiO_2 particles. This characteristic is essential for outdoor applications where materials are constantly exposed to solar radiation. The results show that these composites can

maintain their structural aesthetic integrity over the long term, preventing the fast degradation typically seen in unprotected polymeric materials. The efficiency of HDPE/TiO₂ compounds in reflecting solar radiation and maintaining low temperatures is another aspect of benefits. The reduction in heat accumulation can contribute to energy saving for cooling and improve thermal comfort inside the buildings.

Incorporating TiO₂ particles into the HDPE matrix can improve the mechanical properties of the material, providing a combination of flexibility and strength. This is important for applications requiring durability and the ability to withstand external factors.

Given that this material has a low cost and excellent properties for reflecting ultraviolet radiation, interest in this product is quite high. Titanium dioxide (TiO2) is one of the most extensively studied materials also in the field of photocatalysis. In their study, Barzan et al. [13] proposed some approaches for the introduction of TIO2, aiming to design the energy band and improve solar light absorption. The most popular methods involve either the introduction of dopants (metals and nonmetals) or the generation of oxygen vacancies through reheating (degassing at high temperatures under vacuum) or reduction in a hydrogen atmosphere. TiO₂ is a particle capable of reflecting, scattering, and absorbing light below 385 nm and can promote electrons from the valence band to the conduction band, generating electron-hole pairs. The incorporation and good dispersion of TiO₂ in polymers, such as polyethylene, are important for modifying mechanical and thermal properties without losing the film transparency [14] Transparency is achieved because TiO2 is a semiconductor with a bandgap that absorbs short wavelengths [15] However, semiconductor oxide nanoparticles are transparent to visible light, absorbing UV radiation that could otherwise degrade the content when the polymer is used. Additional protection of the content can occur if the semiconductor captures oxygen. While absorption of wavelengths below approximately 350nm protects the polymer from photochemical degradation, it may induce its oxidation. Innovative nanocomposite filaments have been obtained produced using melt extrusion, with HDPE matrix filled with TiO₂ nanoparticles at specific loading concentrations [16]. The experiments yielded the following data: a 28.5% increase in tensile strength for HDPE with a 10% by weight filler loading, and a 77.6% increase in axial strength for HDPE with a 2.5% by weight filler loading. HDPE-based composites with varying quantities and sizes of TiO₂ nanoparticles were studied to determine if these two parameters have any impact on the development of electrical tracking,

both before and after accelerated ageing of the composite. HDPE is one of the most important polymers used in dielectric applications due to its high resistance to dielectric breakdown. On the other TiO₂, is an important metal oxide used in many industrial applications, ranging from pigments to catalysts [17]

One significant drawback of this composite is the interaction caused by TiO_2 , leading to blistering points on the surface of the composite material, which can later develop into cracks along their edges.

The solar spectrum comprises three main components: 5% ultraviolet light, 43% visible light, and 52% near-infrared light. Ultraviolet light, with wavelengths ranging from 300 to 400 nm, is particularly potent, capable of breaking the chemical bonds of most polymers. [18] In practical applications of HDPE, many products have been used outdoor for extended periods, requiring excellent UV resistance. Therefore, enhancing UV resistance is crucial task. The most important approach to improve HDPE ageing resistance involves adding antioxidants or UV absorbers to the HDPE system during the melt processing stage [5-7].

Exposure to ultraviolet (UV) light leads to the degradation of polymer materials, resulting in a loss of their mechanical properties. This degradation occurs due to chain scission or chemical cross-linking, causing alterations in the mechanical characteristics of the polymeric material. Consequently, UV radiation induces photo-degradation of the polymer. Therefore, finding a solution to mitigate this issue is essential. [19].

To improve the ageing properties of HDPE against UV rays, numerous types of combinations have been tried [20] These methods include adding antioxidants and UV absorbers to the HDPE system during melt processing. These additives help to prevent material degradation by absorbing or blocking UV radiation, thereby maintaining mechanical integrity and extending the lifespan of HDPE products used outdoors.

3. Some final remarks

In conclusion, PE is an easy-to-work material, with a relatively low melting temperature between 140 and 200°C, and it finds efficiency in almost all fields of applications, like agriculture, medicine, textile industry, etc. Additionally, this material is recyclable and environmentally friendly, actually very issue during the increases of the industrialization. PE can be split into two main classes based on the density of molecules: low and -density polyethylene. However, any material in a favourable composition presents physical-mechanical, chemical, or spectral properties. Numerous HDPE compounds have been identified and

developed, but some of the research has encountered difficulties awaiting a solution. One of the solutions can be the exploitation of on the development of composite material, able to withstand long-term exposure to ultraviolet radiation without developing cracks or signs of degradation on the external surfaces of created objects. Further research will be performed by the authors of the present manuscript to contribute obtaining concrete results in this direction. Titanium dioxide, among all the compounds presented in numerous scientific studies, exhibits the highest values against radiation, contributing to the increased lifespan of the composite. However, the study and research have to continue in order to develop and to arrive a high integrity and advanced material to be employed in a wide range of applications.

4. References

[1] Ioana M. (2020), *Modification of the physicomechanical properties of polyethylene*, IMJST, vol.5 pp.11

[2] Baur Maximilian, Fei Lin, Tobias O. Morgen, Lukas Odenwald, Stefan Mecking,(2021) Polyethylene material with in-chain ketones from nonalternating catalytic copolymerization, Science, 374,604-607.

[3] Hu W, Liu C, Liu W, Ren X. (2018) *The study* on the stress and photooxidative ageing of polyethylene cable sheath under different processing conditions. Macromol Res.426-437.

[4] Jiang MM, Koyama K. (2015) *Thermal, physico-mechanical, and morphological properties of HDPE graft-copolymerized with polystyrene.* Polym Adv Technol.1285-1293.

[5] Guo J, Yan H, Hu Z, Yang J. (2015) *Chemical* structure changes and correlation analysis of high density polyethylene after natural and xenon ageing. Mater Sci Forum.323-329.

[6] Yang ZB, Mao ZP, Xiang B, Zhang J. (2019) Construction of a binary channel efficient cooling composites with reflective and phase-change properties. Compos Part B Eng.178

[7] Jiang, T., Mao, Z., Qi, Y., Wu, Y., & Zhang, J. (2021). The effect of two different UV absorbers combined with antioxidants on UV resistance of HDPE. Polymers for Advanced Technologies.

[8] Oliveira, A. D. B., Freitas, D. M. G., Araújo, J. P., Cavalcanti, S. N., Câmara, D. S., Agrawal, P., & Mélo, T. J. A. (2019). *HDPE/LLDPE blends: rheological, thermal, and mechanical properties.* Materials Research Innovations, 1–6.

[9] Wang, X., Song, K., & Ou, R. (2017). *Effects* of Carbon Black and Titanium Dioxide on Ultraviolet Weathering of Wood Flour-HDPE/Lumber

Composites Using Multi-phase Co-extrusion Technology. BioResources, 12(3).

[10] Wang, S., Zhang, J., Liu, L., Yang, F., & Zhang, Y. (2015). Evaluation of cooling property of high density polyethylene (HDPE)/titanium dioxide (TiO2) composites after accelerated ultraviolet (UV) irradiation. Solar Energy Materials and Solar Cells, 143, 120–127.

[11] Jiang, T., Wang, S., & Zhang, J. (2019). Enhanced UV resistance of solar cooling high density polyethylene/titanium dioxide composites for long outdoor life via synergy effect of UV absorber and antioxidant. Journal of Vinyl and Additive Technology.

[12] Nasu, T., Fujibayashi, S., Neo, M., & Nakamura, T. (2006). *TiO2-HDPE Composite: Bone Bonding Ability and Biocompatibility. Key Engineering Materials, 309-311*, 415 - 418.

[13] Barzan, C., Groppo, E., Bordiga, S., & Zecchina, A. (2014). *Defect Sites in H2-Reduced TiO2 Convert Ethylene to High Density Polyethylene without Activator. ACS Catalysis, 4,* 986-989.

[14] Llorente-García, B.E., Hernández-López, J.M., Zaldívar-Cadena, A.A., Siligardi, C., & Cedillo-González, E.I. (2020). *First Insights into Photocatalytic Degradation of HDPE and LDPE Microplastics by a Mesoporous N–TiO2 Coating: Effect of Size and Shape of Microplastics. Coatings.*

[15] Tello, Z.-., Barrios, E.-., Calderon, G.-., & Pérez (2019). Chemical modification of titanium dioxide nanoparticles with dicarboxylic acids to mediate the UV degradation in polyethylene films. Polymer Bulletin, 77, 6409 - 6431.

[16]Ariza-Tarazona, M.C., Villarreal-Chiu, J.F., Hernández-López, J.M., Rivera de la Rosa, J., Barbieri, V., Siligardi, C., & Cedillo-González, E.I. (2020). Microplastic pollution reduction by a carbon and nitrogen-doped TiO2: Effect of pH and temperature in the photocatalytic degradation process. Journal of hazardous materials, 395, 122632.

[17] Ladeira, N.E., de M. Furtado, J.G., Visconte, L.L., & Pacheco, E.B. (2017). *Tracking resistance of nanocomposites of HDPE and TiO2 nanoparticles. IEEE Transactions on Dielectrics and Electrical Insulation, 24,* 3515-2521

[18] Ranby B, Rabek JF. *Photodegradation, Photo-oxidation and Photostabilization of Polymers: Principles and Applications.* New York:Wiley

[19] Sahu, A. K., Sudhakar, K., & Sarviya, R. M. (2020). U.V light effect on the mechanical behaviour of HDPE/Carbon black composites. IOP Conference Series: Materials Science and Engineering, 788, 012054. [20] Podzorova, M., Tertyshnaya, Y.V., Karpova, S.G., & Popov, A.A. (2019). Impact of UV treatment on polylactide–polyethylene film properties. IOP Conference Series: Materials Science and Engineering, 525.