

# Influence of UV irradiation on the degradation of composites based on polyethylene

*M. V. Podzorova*<sup>1, 2, 3\*</sup>, *I. A. Varyan*<sup>2, 3</sup>, *N. V. Kiselev*<sup>2, 3</sup>, *Yu. V. Tertyshnaya*<sup>2, 3</sup>, and *A. V. Khramkova*<sup>4</sup>

<sup>1</sup> Bauman Moscow Technical University, ul. Baumanskaya 2-ya, 5/1, 105005 Moscow, Russia

<sup>2</sup> Plekhanov Russian University of Economics, 36 Stremyanny per., 115054 Moscow, Russia

<sup>3</sup> Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygina str., 119991 Moscow, Russia

<sup>4</sup> Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133 Milan, Italy

**Abstract.** The study of photo degradation of polymers is an important task of the present. In particular, understanding the kinetics of these processes helps to improve the properties of polymeric materials. In this article, films based on low-density polyethylene with a content of 10-50 wt.% natural rubber were studied when exposed to ultraviolet radiation. It has been established that the addition of natural rubber to polyethylene promotes the onset of photo degradation of the resulting composite material upon irradiation at a wavelength of 254 nm. At the same time, no changes occur in the structure of 100% polyethylene under similar conditions.

## 1 Introduction

Currently, more than 150 million tons of petroleum-based synthetic polymers are produced annually. Some polymers, such as low density polyethylene (LDPE), are used in a wide variety of fields of science, technology and economy due to their good physical and chemical properties. However, LDPE practically does not decompose after disposal, which leads to the accumulation of this polymer in the environment and disrupts the ecosystem.

The properties of polymers change with time due to various physical, chemical, thermal factors and their combinations [1–3]. In recent years, there has been increased interest in assessing the service life of polymeric materials exposed to environmental factors. This problem is the change in the physical and chemical properties of materials after exposure to factors such as ultraviolet radiation, humidity and temperature. Degradation causes abrupt changes in the structure, which affect the mechanical properties [4,5]. The non-degradable nature of synthetic polymers along with stringent environmental laws and regulations have forced the industry to look for other sustainable and biodegradable polymer materials [6, 7].

Taking into account the various decomposition processes, it is possible to distinguish between photodegradation, thermal-oxidative degradation and biodegradation of polymer waste. Among these processes, photocatalysis stands out, which is characterized as an

---

\* Corresponding author: [mariapdz@mail.ru](mailto:mariapdz@mail.ru)

environmentally friendly process and is able to decompose organic pollutants and then convert them into carbon dioxide, water and mineral acids, is one of the promising decomposition processes, since this process has a significant potential for the decomposition of plastic waste. An important aspect of plastic decomposition using photocatalysis is the formation of two components - hydroxyl and superoxide radicals [8]. These two species are powerful oxidizing agents that can initiate the process of plastic degradation, leading to the degradation of the polymer structure of the plastic [9].

The main reactions that occur during the photooxidodegradation of polyethylene are well studied, see, for example, references [10–12]. The main degradation mechanism is the chain splitting reaction in the amorphous phase [13, 14], where oxygen easily diffuses. Photodegradation of polyethylene results in random chain cleavage and photooxidation, which leads to secondary crystallization and the formation of various degradation products such as carboxylic acids, ketones and aldehydes [15, 16].

At the same time, the main factors causing polymer chain breakage under biodegradation conditions are microorganisms, enzymes and water. In hydrophobic polymers, which include, for example, polyolefins, polyesters, polysiloxanes, it is possible to form an ordered structure stabilized by hydrogen bonds of water molecules [17-20].

Since polyethylene is one of the most used polymers, it is extremely important to study the possibility of giving it the properties of accelerated degradation in the natural environment. One of the options for creating degradable polyethylene can be the addition of a biodegradable polymer. In this case, rubber can be used as the second component of the mixture to improve the degradable properties of the polymeric material. Natural rubber (NR), epoxidized natural rubber and nitrile rubber (NBR) offer a unique combination of strength, flexibility, biocompatibility and biodegradability [21-24].

As noted in [25], an important property required for the production of a heat shrink film is the crystallization of the polymer during stretching. It is crystallization that controls the shrinkage of the finished product (film). The outstanding properties of unvulcanized natural rubber also include deformation-induced crystallization during the stretching process. The authors propose to use the composition of LDPE/NR as a shrink film [26].

*The aim of this work* is to study the effect of ultraviolet radiation on polymeric materials based on polyethylene with natural rubber and polylactide.

## 2 Methodology and materials of the experiment

*The object of the study* were mixtures based on low-density polyethylene and natural rubber (NR, brand SVR-3L, Vietnam). The content of NR in the mixtures was 10, 20, 30, 40, 50 wt.%. All the mixtures were prepared using Plasticorder PLD-651 (Brabender, Germany) plastic extruder in an argon atmosphere at the temperature of  $(140 \pm 2)$  °C. Film samples were obtained on a press at a temperature of  $(140 \pm 2)$  °C on a cellophane substrate, followed by quenching in water at  $(20 \pm 2)$  °C. As a result, round-shaped film samples with a diameter of 7 cm and a thickness of  $(120 \pm 10)$  μm were obtained. Mixtures of LDPE/PLA (PLA - Nature works 4032D, USA) were obtained by the same way. Mixing and pressing temperature -  $(180 \pm 2)$  °C.

*Methods of structural analysis.* The study of the structure of the material was carried out on an optical microscope Olympus BX3M-PSLED at magnification of 50x and 200x.

*DSC analysis* was performed using a DSC 214 Polyma (Netzsch, Germany) at a heating rate of 10 deg/min and a sample weight of  $(10 \pm 0.1)$  mg. Melting heat of an ideal polyethylene crystal  $\Delta H_m^* = 293$  J/g [27].

*TGA analysis.* The thermal characteristics were measured in an argon atmosphere using a TGA/DSC 3+ thermogravimetric analyzer (Mettler Toledo, Switzerland). All samples were heated from 25 to 700 °C at a heating rate of 20 °C/min.

*IR analysis.* The infrared spectra of the samples were recorded on a Lumos Bruker FTIR spectrometer (Germany) at  $T = (23 \pm 2)^\circ\text{C}$  in the wavenumber range  $4000 \leq \nu \leq 600 \text{ cm}^{-1}$  in reflected light by the method of multiple frustrated total internal reflection.

*UV radiation.* The resistance of samples to photodegradation was studied using a VL-6.LC ultraviolet radiation source from Viber Lourmat (France). The radiation wavelength was 254 nm for 250 hours (LDPE/NR) and 150 hours (LDPE/PLA).

### 3 The results of experiments and discussion

Polyolefins are high molecular weight hydrophobic polymers that do not degrade under the influence of abiotic and biotic factors. UV irradiation of polyethylene for 16 days prior to incubation in soil for 10 years has been shown to release  $< 0.5\%$  carbon by mass compared to unirradiated polyethylene which produced  $< 0.2\%$   $\text{CO}_2$  over the same period [28].

Photodegradation involves the natural ability of most polymers to gradually react with atmospheric oxygen in the presence of light. The photodegradation mechanism involves the absorption of ultraviolet light, which then leads to the formation of free radicals. Then the autoxidation process takes place, which ultimately leads to the degradation of the polymer. It is believed that the instability of polyolefins is observed due to the presence of impurities (carbonyl and hydroperoxide groups) that are formed during the manufacture or processing of polyolefin products.

The addition of a filler to the polymer matrix leads to significant changes in the morphology of the composite material and the macromolecular mobility of the boundary layers, which in the future may affect the degradation of the material as a whole. It was shown in [29] that with an increase in the NR content in the PE matrix, a more uniform scattering of domains occurs with a decrease in their size.

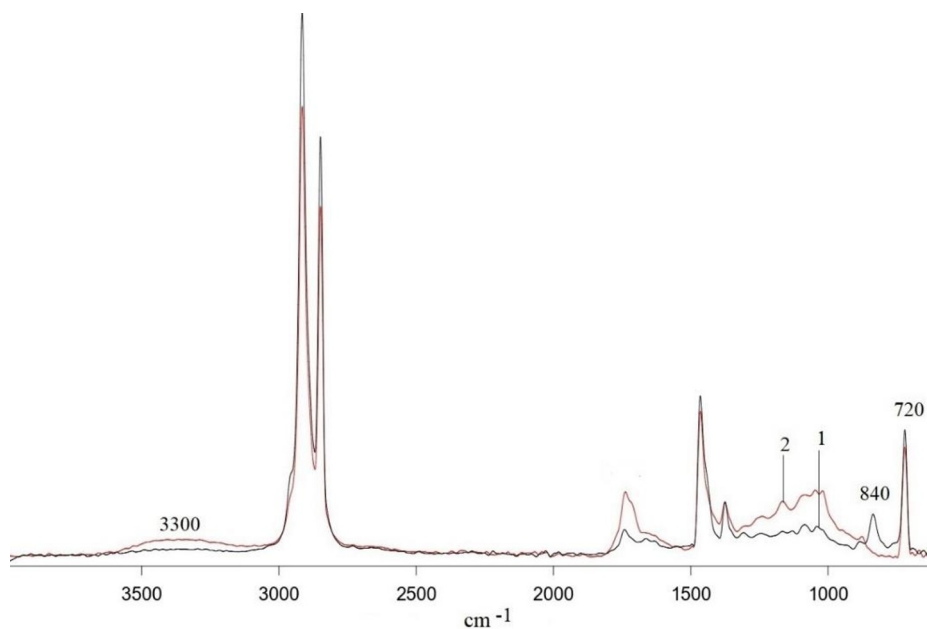
As a result of the study of mixtures of LDPE/NR exposure to UV irradiation with a wavelength of 254 nm for 250 hours, it was found that there is a change in the properties of the compositions. The melting temperature of LDPE in mixtures decreases by 1.5-2  $^\circ\text{C}$ , while the degree of crystallinity of LDPE increases by almost 4-8 %, which may be due to the process of polyethylene oxidation, a change in the crystal structure and the degradation of the amorphous part due to the presence of NR in mixtures (Table 1). The characteristics of pure LDPE did not change significantly, which indicates the resistance of this polymer to UV radiation.

In this work, polyethylene and its composites before and after different exposure times to ultraviolet radiation were analyzed using the IR spectroscopy method, which is one of the main spectral methods for studying the chemical structure. Figures 1 and 2 show the IR spectra of LDPE/NR compositions containing 30 and 50 wt.% NR, before and after UV irradiation ( $\lambda = 254 \text{ nm}$ , 250 hours). It was found that changes occur in the structure of both polymers. In the IR spectra, it is possible to distinguish regions related to the vibrations of the vinyl group ( $-\text{C}=\text{C}$ ), this is the range from  $1000 \text{ cm}^{-1}$  to  $900 \text{ cm}^{-1}$ , the peaks of the carbonyl group ( $-\text{C}=\text{O}$ ) in the range from  $1800 \text{ cm}^{-1}$  to  $1500 \text{ cm}^{-1}$  and peaks of the hydroxyl group ( $-\text{OH}$ ) in the range from  $3600 \text{ cm}^{-1}$  to  $3100 \text{ cm}^{-1}$ . The region  $1660\text{--}1640 \text{ cm}^{-1}$  refers to bending vibrations of N–H and C–N amide groups. One of the structural bands of natural rubber is  $840 \text{ cm}^{-1}$ , which refers to the C–H-out-of-plane bending vibration of the  $\text{C}(\text{CH}_3)=\text{CH}$  group. The decrease in this band after irradiation indicates the degradation of the NR.

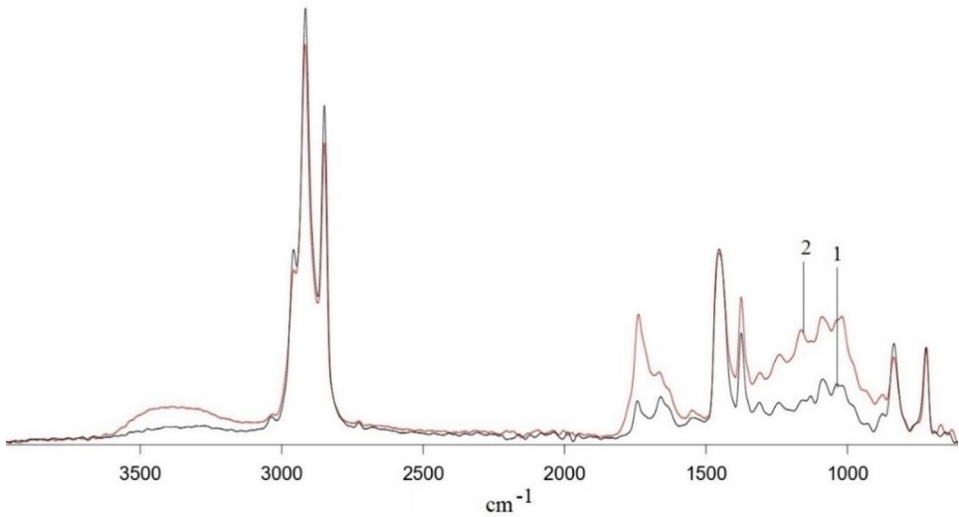
**Table 1.** Thermophysical characteristics of LDPE/NR compositions before and after exposure to UV radiation ( $\lambda = 254 \text{ nm}$ ) for 250 hours.

Composition of LDPE/NR,	Tm, $^\circ\text{C}$ $\pm 0,1 \text{ }^\circ\text{C}$	$\chi$ , % $\pm 0,5\%$	Tm, $^\circ\text{C}$ $\pm 0,1 \text{ }^\circ\text{C}$	$\chi$ , % $\pm 0,5\%$
-------------------------	--	---------------------------	--	---------------------------

wt %			After 250h	
1	2	3	4	5
100/0	108,0	25	107,5	27
90/10	106,8	20	105,2	28
80/20	106,4	22	105,4	29
70/30	105,7	21	104,7	24
60/40	105,4	23	104,2	26
50/50	105,2	15	103,2	19

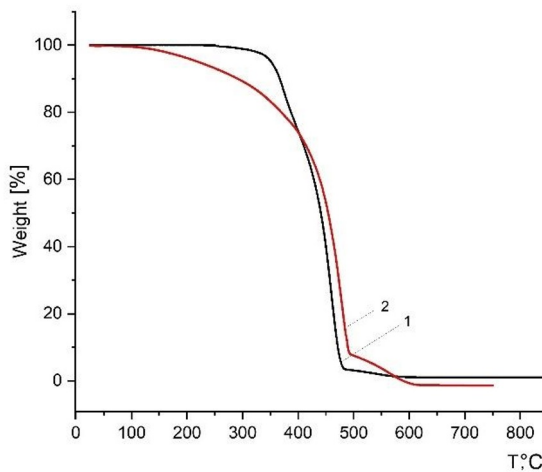


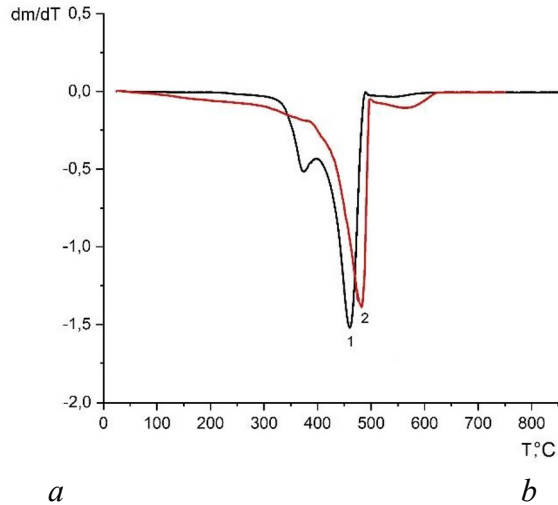
**Fig. 1.** IR spectra of 70LDPE/30NR film before (1) and after (2) exposure to 250 hours of UV radiation ( $\lambda = 254$  nm).



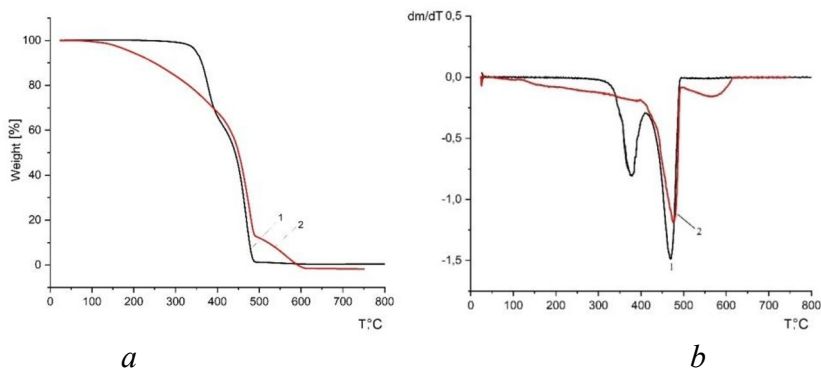
**Fig. 2.** IR spectra of 50LDPE/50NR film before (1) and after (2) exposure to 250 hours of UV radiation ( $\lambda = 254$  nm).

The impact of UV radiation is also reflected in the thermal stability of the compositions. As an example, the TGA and DTG curves of the composition with 30 wt.% NR in the mixture are shown (Fig. 3, 4). According to the results of the experiment, after exposure to UV radiation, the process of weight loss is accelerated. Figure 4b clearly shows two peaks at about 355 °C and 460 °C in the original sample, which correspond to  $T_{max}$  of the degradation of NR and LDPE, respectively. It should be noted that exposure to UV radiation changes the NR peak, which practically disappears, while the LDPE peak shifts to 470 °C, which may be due to the degradation of the amorphous phase and an increase in the proportion of crystalline.





**Fig. 3.** TGA (a) and DTG (b) of 70LDPE/30NR film before (1) and after (2) exposure to 250 hours of UV radiation.



**Fig. 4.** TGA (a) and DTG (b) of 50LDPE/50NR film before (1) and after (2) exposure to 250 hours of UV radiation.

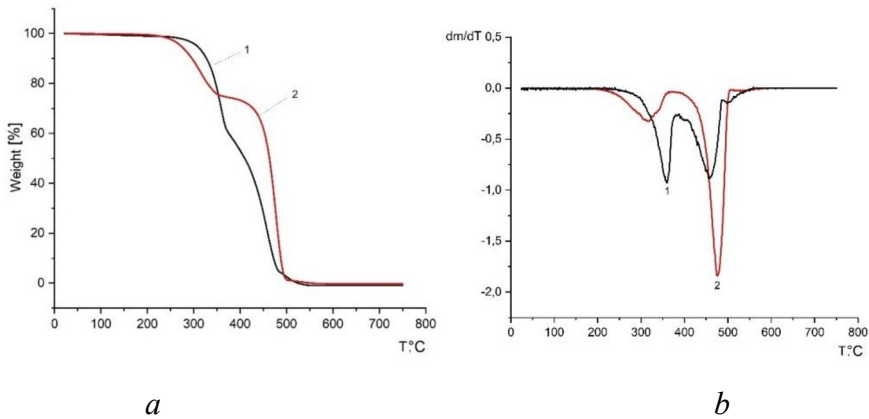
For LDPE, as in the case of LDPE/NR samples,  $T_{max}$  increases by almost 15 °C. At the same time, a shift in the degradation peak of LDPE indicates the degradation of the amorphous part of the polymer. Despite the fact that, according to TGA data, LDPE has a higher degradation temperature, photooxidation begins in it.

PLA is a potential candidate for wide application in various fields of industry. LDPE/PLA are promising due to the susceptibility of PLA to accelerated disintegration under the influence of aggressive environmental factors. In the articles [30-32], the authors report on the exposure of PLA to UV irradiation. The Norrish II mechanism was the most possible degradation route [33].

The method DSC showed that the melting point of PLA decreases by 20-24 ° C, the degree of crystallinity – by 15-22%. Changes in thermal properties are also recorded by the TGA method (Fig. 5).

The degradation temperature of the PLA decreases by 50° C, which indicates the degradation of both the amorphous and crystalline parts of the PLA. As for LDPE/NR

samples,  $T_{max}$  of LDPE increases by almost  $15^{\circ}\text{C}$ . At the same time, the displacement of the LDPE degradation peak indicates the degradation of the amorphous part of the polymer.



**Fig. 5.** TGA (a) and DTG (b) of 70LDPE/30NR film before (1) and after (2) exposure to 150 hours of UV radiation.

## 4 Conclusions

In this study, the process of photodegradation of mixed LDPE/NR and LDPE/PLA compositions is considered. It has been found that exposure of NR to UV radiation can accelerate the degradation of LDPE. At the initial stage, the degradation of the NR matrix and PLA matrix occurs, and then this entails the degradation of the composites. These data are confirmed by both IR spectroscopy: a change in the characteristic bands of the mixture components is noted, and DSC: changes in the thermophysical characteristics are observed. For example, in LDPE/NR compositions, an increase in the degree of crystallinity occurs due to more active degradation of NR. Due to the degradation PLA, there is a significant decrease in the melting temperature and the degree of crystallinity, which leads to embrittlement of the entire material. Based on the results of the study, it can be concluded that UV irradiation in LDPE/NR samples first destroys the biodegradable component of NR, and then the LDPE matrix.

## References

1. J. R. White, Polymer ageing: physics, chemistry or engineering? Time to reflect *Comptes Rendus Chimie*, **9**, 1396-1408 (2006) DOI: 10.1016/J.CRCI.2006.07.008
2. A. Fairbrother, H. C. Hsueh, J. H. Kim, D. Jacobs, L. Perry, D. Goodwin, C. White, S. Watson, L. P. Sung, Temperature and light intensity effects on photodegradation of high-density polyethylene *Polymer Degradation and Stability*, **165**, 153-160 (2019) DOI: 10.1016/J.POLYMDEGRADSTAB.2019.05.002
3. Y. U. V. Tertyshnaya, N. S. Levina, A. A. Popov, M. N. Moskovskii, A. Y. Izmailov, Hydrolytic Destruction of Agrofiber Made of Natural Polymers *Fibre Chemistry*, **51**, 117-120 (2019) DOI: 10.1007/s10692-019-10053-0
4. J. Avossa, R. Paolesse, C. di Natale, E. Zampetti, G. Bertoni, F. de Cesare, G. Scarascia-Mugnozza, A. Macagnano, Electrospinning of Polystyrene/Polyhydroxybutyrate Nanofibers Doped with Porphyrin and Graphene for Chemiresistor Gas Sensors *Nanomaterials*, **9**, 280 (2019) DOI: 10.3390/nano9020280

5. R. Tabassum, R. Kant, Recent trends in surface plasmon resonance based fiber–optic gas sensors utilizing metal oxides and carbon nanomaterials as functional entities *Sensors and Actuators B-chemical*, **310**, 127813 (2020) DOI: 10.1016/j.snb.2020.127813
6. R. Muthuraj, M. Misra, A. K. Mohanty, Studies on mechanical, thermal, and morphological characteristics of biocomposites from biodegradable polymer blends and natural fibers *Biocomposites: Design and Mechanical Performance*, 93-140 (2015) DOI: 10.1016/B978-1-78242-373-7.00014-7
7. S. M. Bhasney, P. Bhagabati, A. Kumar, V. Katiyar, Morphology and crystalline characteristics of polylactic acid [PLA], linear low density polyethylene [LLDPE]/microcrystalline cellulose [MCC] fiber composite *Composites Science and Technology*, **171**, 54-61 (2019) DOI: 10.1016/J.COMPSCITECH.2018.11.028
8. V. P. Ranjan, S. Goel, Recyclability of polypropylene after exposure to four different environmental conditions *Resources Conservation and Recycling*, **169**, 105494 (2021) DOI: 10.1016/J.RESCONREC.2021.105494
9. F. Schmidt, Y. S. Zimmermann, G. A. dos Reis Benatto, B. A. Kolvenbach, A. Schäffer, F. C. Krebs, E. D. van Hullebusch, M. Lenz, Biodeterioration Affecting Efficiency and Lifetime of Plastic-Based Photovoltaics *Joule* **4**, 2088-2100 (2020) DOI: 10.1016/J.JOULE.2020.08.015
10. B. Fayolle, E. Richaud, X. Colin, J. Verdu, Review: Degradation-induced embrittlement in semi-crystalline polymers having their amorphous phase in rubbery state *Journal of Materials Science*, **43**, 6999-7012 (2008) DOI: 10.1007/s10853-008-3005-3
11. S. A. Jabarín, E. A. Lofgren, Photooxidative effects on properties and structure of high-density polyethylene *Journal of Applied Polymer Science*, **53**, 411-423 (1994) DOI:10.1002/APP.1994.070530404
12. P. K. Roy, P. Surekha, C. Rajagopal, V. Choudhary, Degradation behavior of linear low-density polyethylene films containing prooxidants under accelerated test conditions *Journal of Applied Polymer Science*, **108**, 2726-2733 (2008) DOI: 10.1002/APP.27889
13. P. K. Roy, P. Surekha, R. Raman, C. Rajagopal, Investigating the role of metal oxidation state on the degradation behaviour of LDPE *Polymer Degradation and Stability*, **94**, 1033-1039 (2009) doi: 10.1016/j.polymdegradstab.2009.04.025
14. T. Ojeda, A. Freitas, K. Birck, E. Dalmolin, R. Jacques, F. Bento, F. Camargo, Degradability of linear polyolefins under natural weathering *Polymer Degradation and Stability*, **96**, 703-707 (2011) doi: 10.1016/j.polymdegradstab.2010.12.004
15. M. Gardette, A. Perthue, J. L. Gardette, T. Janecska, E. Földes, B. Pukánszky, S. Therias, Photo- and thermal-oxidation of polyethylene: Comparison of mechanisms and influence of unsaturation content *Polymer Degradation and Stability*, **98**, 2383-2390 (2013) doi: 10.1016/j.polymdegradstab.2013.07.017
16. J. F. Heacock, F. B. Mallory, F. P. Gay, Photodegradation of polyethylene film *Journal of Polymer Science Part A Polymer Chemistry*, **6**, 2921-2934 (1968) DOI: 10.1002/POL.1968.150061019
17. Y. V. Tertysnaya, S. G. Karpova, M. V. Podzorova, A. V. Khvatov, M. N. Moskovskiy, Thermal Properties and Dynamic Characteristics of Electrospun Polylactide, Natural Rubber Fibers during Disintegration in Soil Polymers, **14**, 1058 (2022) DOI: 10.3390/polym14051058



18. Y. V. Tertyshnaya, M. V. Podzorova, Degradation of Polylactide–Polyethylene Blends in Aqueous Media Russian Journal of Applied Chemistry, **94**, 639-946 (2021) DOI: 10.1134/S1070427221050128
19. S. M. Bhasney, R. Patwa, A. Kumar, V. Katiyar, Plasticizing effect of coconut oil on morphological, mechanical, thermal, rheological, barrier, and optical properties of poly(lactic acid): A promising candidate for food packaging Journal of Applied Polymer Science, **134**, 45390 (2017) DOI: 10.1002/APP.45390
20. R. Avolio, R. Castaldo, M. Avella, M. Cocca, G. Gentile, S. Fiori, M. E. Errico, PLA-based plasticized nanocomposites: Effect of polymer/plasticizer/filler interactions on the time evolution of properties Composites Part B Engineering, **152**, 267-274 (2018) doi: 10.1016/j.compositesb.2018.07.011
21. K. Pongtanayut, C. Thongpin, O. Santawitee, The Effect of Rubber on Morphology, Thermal Properties and Mechanical Properties of PLA/NR and PLA/ENR Blends Energy Procedia, **34**, 888-897 (2013) doi: 10.1016/j.egypro.2013.06.826
22. C. Xu, D. Yuan, L. Fu, Y. Chen, Physical blend of PLA/NR with co-continuous phase structure: Preparation, rheology property, mechanical properties and morphology Polymer Testing, **37**, 94-101 (2014) doi: 10.1016/j.polymertesting.2014.05.005
23. T. Talbamrung, C. Kasemsook, W. Sangtean, S. Wachirahuttapong, C. Thongpin, Effect of Peroxide and Organoclay on Thermal and Mechanical Properties of PLA in PLA/NBR Melted Blend Energy Procedia, **89**, 274-281 (2016) doi:10.1016/j.egypro.2016.05.035
24. S. Mahapram, S. Poompradub, Preparation of natural rubber (NR) latex/low density polyethylene (LDPE) blown film and its properties Polymer Testing, **30**, 716-725 (2011) doi: 10.1016/j.polymertesting.2011.06.006
25. M. Tsuji, T. Shimizu, S. Kohjiya, TEM Studies on Thin Films of Natural Rubber and Polychloroprene Crystallized under Molecular Orientation II. Highly Prestretched Thin Films Polymer Journal, **32**, 505-512 (2000) doi: 10.1295/polymj.32.505
26. N. K. Kalita, N. A. Damare, D. Hazarika, P. Bhagabati, A. Kalamdhad, V. Katiyar, Biodegradation and characterization study of compostable PLA bioplastic containing algae biomass as potential degradation accelerator Environmental Challenges, **3**, 100067 (2021) doi: 10.1016/j.envc.2021.100067
27. M. V. Podzorova, Y. V. Tertyshnaya, Degradation of Polylactide—Polyethylene Binary Blends in Soil Russian Journal of Applied Chemistry, **92**, 767–774 (2019) doi: 10.1134/s1070427219060065
28. J. R. Haines, M. Alexander, Microbial Degradation of High-Molecular-Weight Alkanes Applied Microbiology, **28(6)**, 1084-1085 (1974) doi: 10.1128/am.28.6.1084-1085.1974
29. E. Mastalygina, I. Varyan, N. Kolesnikova, M. I. C. Gonzalez, A. Popov, Effect of Natural Rubber in Polyethylene Composites on Morphology, Mechanical Properties and Biodegradability Polymers, **12**, 437 (2020) DOI: 10.3390/polym12020437
30. E. Olewnik-Kruszkowska, I. Koter, J. Skopińska-Wisniewska, J. Richert, Degradation of polylactide composites under UV irradiation at 254nm Journal of Photochemistry and Photobiology A, **311**, 144-153 (2015) doi: 10.1016/j.jphotochem.2015.06.029
31. A. A. Marek, V. Verney, Photochemical reactivity of PLA at the vicinity of glass transition temperature. The photo-rheology method European Polymer Journal, **81**, 239-246 (2016) doi: 10.1016/j.eurpolymj.2016.06.016

32. Y. V. Tertyshnaya, M. V. Podzorova, M. N. Moskovskiy, Impact of Water and UV Irradiation on Non-Woven Poly lactide/Natural Rubber Fiber Polymers, **13**, 461 (2021) doi: 10.3390/polym13030461
33. S. Lv, X. Liu, J. Gu, Y. Jiang, H. Tan, Y. Zhang, Effect of glycerol introduced into PLA based composites on the UV weathering behavior Construction and Building Materials, **144**, 525-531 (2017) doi: 10.1016/j.conbuildmat.2017.03.209