Thermal properties of polyethylene compositions with micro- and nanocellulose

A N Perova¹, S V Usachev², E V Koverzanova², A V Khvatov¹, S M Lomakin¹

¹ N M Emanuel Institute of Biochemical Physics, Russian Academy of Science, Moscow 119334, Russia
² N N Semenov Institute of Chemical Physics, Russian Academy of Science, Moscow 199334, Russia

E-mail: aleksandra.perova1994@mail.ru

Abstract. The effect of micro- and nanocellulose addition on the thermal properties of polyethylene compositions has been studied by means of thermogravimetric analysis and pyrolysis-gas chromatography-mass spectrometry. The main temperature characteristics of the thermo- and thermo-oxidative degradation of the compositions are determined. The influence of micro- and nanocellulose additives on change of the distribution of hydrocarbon pyrolysis products of composite materials was established.

1. Introduction

Cellulose is the most common natural biopolymer with a low density, high specific strength and specific elastic modulus [1-4]. Various forms of cellulose can be considered as promising fillers for thermoplastic and thermostetting polymers [5-6] due to the possibility of creating materials with improved physical and mechanical characteristics due to the reinforcement of the polymer matrix. The resulting materials can be widely used in medicine, textile industry, construction, etc.

Despite the advantages of such materials, their properties are limited by the characteristics of cellulose fillers, such as: relatively low interfacial adhesion, low thermal stability, and hydrophilicity [7-8]. In the process of preparing polyolefin composites containing cellulose, problems arise in their thermodynamic incompatibility, which makes it very difficult to achieve uniform distribution of cellulose, especially nanocellulose (NC) in the polymer matrix. To solve these problems, methods of physical [9-10] and chemical [11-12] cellulose modification are used, as well as the use of functionalized polymers [13], which allows to increase the compatibility of the polar cellulose filler and non-polar polymer matrix.

To increase the degree of distribution of nanocellulose (NC) in polymer composites, various methods are proposed based on the combined use of solution and melt technology in their preparation. So in [13] the problems of increasing the dispersion of crystalline NC in the hydrophobic matrix of polypropylene (PP) were solved by a preliminary step of preparing a suspension of NC at 130 °C in toluene, followed by the addition of PP powder until it was completely dissolved. The resulting suspension of the PP/NC composite was dried to obtain a solid powder of the PP/NC composition, which was then extruded and molded under pressure.

The main goal of the present work was an assessment of the effect of micro- and nanocellulose on the thermal properties of polyethylene (PE) compositions.
2. Experimental

2.1. Materials
For the synthesis of compositions, high-density polyethylene HDPE 273-83 (Stavrolen, LLC, Russia), low-density polyethylene LDPE 15803-020 (Ufaorgsintez, open society, Russia), microcrystalline cellulose (Lachema, Czech Republic) and nanocellulose gel (0.5 %), obtained by the method described in [14].

Compositions HDPE 273-83 with microcrystalline cellulose (MC) were obtained by mixing the components in a two-rotor laboratory mixer with a chamber volume of 25 cm³ (N N Semenov Institute of Chemical Physics, RAS) at a temperature of 170 °C and a rotor speed of 30 rpm for 5 minutes.

Compositions based on LDPE 15803-020 and nanocellulose (NC) were prepared as follows. LDPE 15803-020 was dissolved by heating in o-xylene to 115-120 °C, after which an aqueous solution (gel) of NC was added with vigorous stirring. Heating and stirring were carried out until the azeotropic mixture water-o-xylene was completely withdrawn. When the boiling point of o-xylene (144-145 °C) was reached, stirring was stopped. The resulting clear solution was evaporated to form a solid film.

2.2. Thermogravimetric analysis (TGA)
TGA of PE, MC, NC, PE/MC and PE/NC composites was made by Netzsch TG 209 F1 thermal balance at the heating rate of 20 °C/min in inert atmosphere of Ar and the samples weight of about 5±0.5 mg.

2.3. Pyrolysis
Pyrolysis of sample compositions was carried out in a flow pyrolytic cell with a heating zone of 50 mm. A tube with a diameter of 3 mm with the test sample was placed in a cell preheated to 500±2 °C. Argon was purged for 15 minutes through a tube at a rate of 15 ml/min. The pyrolysis products were condensed in 1.5 ml n-hexane cooled to 4 °C.

2.4. Gas chromatography-mass spectrometry (GC-MS)
GC-MS measurements were performed on a gas chromatograph Trace-1310 and Single Quadrupole MS ISQ Detector. The pyrolysis products were injected into the GC capillary quartz column 15 m × 320 μm i.d. and 0.25 μm film (TG-SQC, Thermo Scientific Phase) under the temperature-programmed conditions in the range of 40 – 290 °C with gradient 15 °C/min. MS-spectra of degradation components were identified and interpreted by matching the results with NIST Mass Spectral library and literary data [15─16].

The yields of all degradation products were standardized by relative peak area of individual product (RPAi) according to equation

\[ RPA_i = \frac{P_Ai}{\sum P_Ai} \times 100\% \]

PAi - peak area of individual product, \(\sum P_Ai\) – sum of peak areas of all individual product.

Relative peak area for hydrocarbon fraction (RPAf) presents a sum of RPAi for corresponded fraction.

3. Results and discussion

3.1. TGA of PE/MC and PE/NC compositions
The results of TGA of PE/MC and PE/NC compositions are showed in Figure 1 and Table 1. The studies showed that with an increase in the concentration of MC (Figure 1a) in the composition in argon, the decomposition onset temperature decreases compared to the initial sample, and thermal degradation proceeds in two stages, which is associated with the decomposition of the cellulose additive. The decomposition temperature of PE (the second stage of thermal decomposition of the compositions in Table 1) is practically independent of the content of MC, which indicates the absence
of the influence of MC on the thermal decomposition of PE (Figure 1a, Table 1). You can also see the absence of the influence of NC additives in a concentration of 0.5 to 5% for thermal degradation of PE (Figure 1c and Table 1).

Figure 1. a - TG curves of PE/MC composites heated in Ar flow (1 - MC, 2 - PE, 3 - PE/MC - 5%, 4 - PE/MC - 20%, 5 - PE/MC - 50%), b - TG-curves of PE/MC composites heated in air flow (1 - MC, 2 - PE, 3 - PE/MC - 5%, 4 - PE/MC - 20%, 5 - PE/MC - 50%), c - TG curves of PE/NC composites heated in Ar flow (1 - NC, 2 - PE, 3 - PE/MC - 0.5%, 4 - PE/MC – 3%, 5 - PE/MC - 5%), d - TG-curves of PE/NC composites heated in air flow (1 - NC, 2 - PE, 3 - PE/MC - 0.5%, 4 - PE/MC – 3%, 5 - PE/MC - 5%).

Under the conditions of thermo oxidative degradation (Figure 1b, d), a tendency is observed for the temperature of the onset of reactions similar to that observed in an inert medium. The appearance of the third stage of decomposition with the introduction of the MC filler in the composition with PE is associated with the burnout of the carbonized cellulose residue.

A distinctive feature of the influence of MC and NC fillers on the thermal-oxidative degradation of compositions with PE is the increase in the temperature of the maximum decomposition rate at the second stage of thermooxidative degradation (Table 1, Figure 1b, d). In our opinion, this effect of PE stabilization is due to inhibition of the radical chain process of composition destruction due to the recombination of macroradicals of PE and cellulose coke, leading to chain termination.
Table 1. Key TGA features of PE, PE/MC and PE/NC composites

| PE matrix (brand) | Filler | The filler content, % | $T_d^1$, °C Ar/Air | $T_m^2$, °C Ar/Air | Stage 1 | Stage 2 | Stage 3 |
|-------------------|--------|-----------------------|-------------------|-------------------|---------|---------|---------|
|                   |        |                       |                   |                   |         |         |         |
| LDPE 273-83       | MC     | 0                     | 420 / 285         | - / 323           | 488 / 424 | - / -   |         |
|                   |        | 5                     | 340 / 280         | 363 / 342         | 490 / 439 | - / 481 | - / -   |
|                   |        | 20                    | 300 / 280         | 360 / 346         | 490 / 438 | - / 487 | - / -   |
|                   |        | 50                    | 270 / 257         | 353 / 346         | 488 / 446 | - / 490 | - / -   |
|                   |        | 100                   | 285 / 263         | 370 / 344         | - / -     | - / -   | - / 482 |
| HDPE 15803-020    | NC     | 0.5                   | 407 / 315         | - / -             | 483 / 415 | - / -   | - / -   |
|                   |        | 3                     | 415 / 312         | - / -             | 484 / 455 | - / -   | - / -   |
|                   |        | 5                     | 405 / 308         | - / -             | 483 / 453 | - / -   | - / -   |
|                   |        | 100                   | 245 / 235         | 312 / 316         | - / -     | - / -   | - / 492 |

1. decomposition onset temperature, °C.
2. temperature of the maximum decomposition rate, °C.

3.2. Pyrolytic chromatography-mass spectrometry of PE, PE/MC and PE/NC compositions

In Figure 2 shows chromatograms of volatile products of pyrolysis of HDPE 273-83 and compositions of HDPE 273-83 containing 5, 20 and 50 % MC, and in Figure 3 - LDPE 15803-020 and composition LDPE 15803-020 containing 5 % NC. The main products of pyrolysis consist of unsaturated (alkenes) and saturated (alkanes) hydrocarbons of various structures, as well as dienes. In addition, the chromatograms of the HDPE 273-83/MC compositions revealed the products of the pyrolysis of cellulose additives: a - furfural, b - 5-methyl-2-furfural, and c - levoglucosenone (Figure 2).

![Chromatograms of hexane solutions of pyrolysis products](image)

**Figure 2.** Chromatograms of hexane solutions of pyrolysis products of PE (1), PE/MC - 5 % (2), PE/MC - 20 % (3), PE/MC - 50 % (4) compositions, a - furfural, b - 5-methyl-2-furfural, and c - levoglucosenone
Figure 3. Chromatograms of hexane solutions of pyrolysis products of PE (1), PE/NC - 5 % (2)

Table 2 presents data reflecting the distribution of hydrocarbon products of the pyrolysis of PE and its compositions with MC and SC at different concentrations of cellulose fillers. From the data provided in Table 2 one can easily see that with the rise of concentration of MC and NC the content of lighter gaseous products of C8-C17 pyrolysis in PE/MC and PE/NC compositions increases as compared with unfilled PE.

**Table 2.** The distribution by molecular weight of hydrocarbon pyrolysis products of PE and PE compositions with different concentration of MC and NC.

| PE matrix (brand) | Filler | The filler content, % | Content of components in the sample, % |
|------------------|--------|------------------------|---------------------------------------|
|                  |        |                        | C₈-C₁₇   | C₁₈-C₃₄   |
| LDPE 273-83      | MC     | 0                      | 48.25    | 51.75     |
|                  |        | 5                      | 56.20    | 43.80     |
|                  |        | 20                     | 78.58    | 21.42     |
|                  |        | 50                     | 82.25    | 17.75     |
| HDPE 15803-020   | NC     | 0                      | 62.34    | 37.66     |
|                  |        | 5                      | 62.70    | 37.30     |

In works [17–18] on the study of the joint pyrolysis of PE compositions and cellulose-containing derivatives at a temperature of 700 °C, it was found that the products of thermal degradation of PE compositions containing up to 50 % cellulose there was a significant increase in the amount of low molecular weight aliphatic hydrocarbons (C₅-C₁₅), compared with the original PE. The authors explained this fact by the acceleration of hydrogen abstraction reaction in polyethylene macromolecules by the radical-acceptor products of cellulose pyrolysis (carbonaceous char residue).

In Figure 3 one can note the characteristic products of cellulose pyrolysis: furfural, 5-methyl-2-furfural, and levoglucosenone, which we found on chromatograms of hexane solutions of products of PE / MC compositions. According to the mechanism of cellulose pyrolysis, along with volatile
degradation products, the main product of aromatization and condensation is formed - carbonaceous coke. Thus the shift in the distribution of hydrocarbon pyrolysis products observed in our experiments towards the formation of lighter gaseous C_8-C_17 products for PE compositions with MC and SC is due to an increase in the rate of initiation of the radical chain process of PE degradation by the coke residue of cellulose additives at temperatures above 400 °C.

4. Conclusions
Studies of TGA and pyrolytic chromatography-mass spectrometry of the PE/MC and PE/NC compositions showed the effect of cellulose additives at the stage of thermal and thermal-oxidative degradation of polyethylene. This is explained by the radical acceptor properties of cellulose coke, which affect the elementary stages of initiation and termination during the destruction of PE compositions.

The work was carried out within the framework of budget financing on the theme of state assignment No. of state registration 01201253305.

References
[1] Elsabbagh A, Steuernagel L and Ziegmann G 2009 Processing and modelling of the mechanical behaviour of natural fiber thermoplastic composite: flax/polypropylene Polym. Compos. 30(4) 510–519
[2] Bledzki A K, Reihmane S and Gassan J 1996 Properties and modification methods for vegetable fibers for natural fiber composites J. Appl. Polym. Sci. 59(8) 1329–1336
[3] Hornsby P R, Hinrichsen E and Tarverdi K 1997 Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibres: Part II analysis of composite microstructure and mechanical properties J. Mater. Sci. 32(4) 1009–1015
[4] Khalil H P S A, Bhat A H and Yusra A F I 2012 Green composites from sustainable cellulose nanofibrils: A review. Carbohydr. Polym. 87 963–979
[5] Herrera-Franco P and Aguilar-Vega M 1997 Effect of fiber treatment on the mechanical properties of LDPE – cellulose fiber composites Appl. Polym. Sci. 65(1) 197–207
[6] Sdrobis A, Darie R N, Totolin, Cazacu G and Vasile C 2012 Low density polyethylene composites containing cellulose pulp fibers Composites: Part B 43(4) 1873–1880
[7] Saheb D N, Jog J P 1999 Natural fiber polymer composites: a review Advan. Polym. Tech. 18(4) 351–363
[8] Georgopoulos S T, Tarantili P A, Avgerinos E, Andreopoulos A G and Koukios E G 2005 Thermoplastic polymers reinforced with fibrous agricultural residues Polym. Degrad. Stab. 90(2) 303–312
[9] Low I M, McGrath M, Lawrence D, Schmidt P, Lane J, Latella B A and Sim K S 2007 Mechanical and fracture properties of cellulose-fibre-reinforced epoxy laminates Composites: Part A. 38(2) 963–974
[10] Alamri H, Low I M 2012). Mechanical properties and water absorption behavior of recycled cellulose fibre reinforced epoxy composites. Polym. Test. 31(5),620–628.
[11] Khalil A, Bhat I U H, Jawaid M, Zaidon A, Hermawan D and Hadi Y S 2012 Bamboo fibre reinforced biocomposites: a review Mater. Des. 42(2) 353–368
[12] Mohamed H G, Mostafa A E, Kazuya O and Toru F 2010 Effect of microfibrillated cellulose on mechanical properties of plain-woven CFRP reinforced epoxy Compos. Struct. 92(5) 1999–2006
[13] Gwon J G, Cho H D, Lee D, Choi D H, Lee S, Wu Q and Lee S Y 2018 Physicochemical and mechanical properties of polypropylene-cellulose nanocrystal nanocomposites: effects of manufacturing process and chemical grafting BioResources 13(1) 1619–1636
[14] Voskoboynikov I V, Konstantinova S A, Korotkov A N, Mikhailov A I and Nikolsky S N 2010
Preparation of hydrogels of nanocrystalline cellulose from plant raw materials Forestry Bulletin 6 151–154

[15] Poutsma M L 2003 Reexamination of the pyrolysis of polyethylene: data needs, freeradical mechanistic considerations, and thermochemical kinetic simulation of initial productforming parhways Macromolecules 36 8931–8957

[16] Sojak L, Kubinec R, Jurdakova H, Hajekova and Bajus M 2006 GC-MS of polyethylene and polypropylene thermal cracking products Petroleum & Coal 48(2) 1–14

[17] Xue Y, Kelkar A and Bai X 2016 Catalytic co-pyrolysis of biomass and polyethylene in a tandem micropyrolyzer Fuel 166 227–236

[18] Matsuzawa Y, Ayabe M and Nishino J 2001 Acceleration of cellulose co-pyrolysis with polymer Polym. Degrad. Stab. 71(3) 435–444