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SINGLE-STAGE AND SIMPLE FABRICATION OF POLYETHYLENE FILMS DECORATED WITH HALLOYSITE NANOTUBES

Background. Environmental pollution with plastic waste is a global problem that requires searching for effective and safe ways to dispose or process secondary raw materials. The use of photocatalysts for polymer degradation is a modern approach. Combining photocatalysts with support material to improve stability, activity, and lifetime is an important area of research.

Objective. The aim of the work was to develop a technique for applying nanomaterials to the surface of a polyethylene film by partially dissolving the upper layer of the polymer in a heated nanomaterial suspension, namely, aluminosilicate halloysite nanotubes in a solvent. Cyclohexane was used as a solvent.

Methods. Thermogravimetric, optical, and dynamic mechanical analyses of synthesised samples were carried out, and their properties were compared with reference samples of pure polyethylene and treated without the addition of nanomaterial.

Results. A method of decorating PE film with halloysite nanotubes has been developed. The introduction of 2.83 % by mass under the condition of immersing the film in a suspension of HNTs in cyclohexane (3 % by mass) at a temperature of 50 °C for 120 seconds was achieved. The decrease of the contact angle of the sample to 77.11° indicates the inclusion of hydrophilic HNTs into the surface layer of PE. Optical analysis confirmed the uniform distribution of particles on the surface of the film. The synthesized samples show a decrease in mechanical properties such as elasticity and tensile strength due to the destructive effect of the solvent on the polymer.

Conclusions. Different conditions of application of HNTs on the surface of PE films using cyclohexane were tested. A method allows to achieve the introduction of a maximum of 2.83 % by mass of HNT. This method confirmed the possibility of attaching nanomaterials, namely HNTs, to the surface of the film by partially dissolving the surface layer of the polymer. Unlike our previous study [3], where the solvent casting method was used to introduce the catalyst into the PE film, the above approach does not require complete dissolution of the polymer and heating of the material to high temperatures and can be applied to the processing of industrially produced PE films. The addition of functional materials can be useful for modifying the properties of films, in particular PE. Studying the peculiarities of adding a photocatalyst to a polymer film at ambient temperature and the technology of industrial production of a PE film capable of decomposition can be the next stage of research.

Keywords: polymer, halloysite, nanomaterial, thermogravimetry, chemical technology

Introduction

The wide use of plastics, the difficulties of their recycling, and the long degradation time in ambient conditions give rise of environmental pollution on a planetary scale. Understanding this problem, the European Commission adopted the EU Plan, in which all plastic packaging will be recyclable by 2030 [1]. The biggest challenge is household waste,

as a mixture of different types of contaminated plastics. One of the approaches used for processing household plastic is mechanical recycling. There are two types of mechanical recycling: Primary recycling (processing exclusively uncontaminated plastic of a single type into a product of equal quality) and Secondary recycling. A latter is often demanding on materials since preliminary sorting by type and rejection of contaminated plastic or washing is

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necessary. Thus, recycled material costs are often higher than pristine plastic, and the quality of the processed material decreases with each cycle. As an alternative, thermo-chemical recycling – is less demanding and often acceptable for heterogeneous raw materials. The main idea is to split the polymer into individual monomers to produce a high-quality secondary product. Quaternary recycling is used for highly contaminated packaging, namely, waste incineration for energy recovery. The most environmentally friendly way for waste utilization is biological. Plastics can be degraded with the help of bacteria, fungi and enzymes. The disadvantage of biorecycling is its extremely long duration. Using landfills for waste disposal is one of the common methods, but it leads to soil and water contamination and occupies large areas.

Solid phase photocatalysis is a promising research topic for the removal of pollutants from the environment. Some commonly used photocatalysts for acceleration of degradation are TiO_2 , ZnO , ZrO_2 , SnO_2 , CoO , In_2O_3 , ZrO_2 , Cu_2O NiO etc. The introduction of 0.1 % of TiO_2 in LDPE film leads to enhanced degradation up to 18 % mass loss after UV exposure during 300 h [2]. This work is focused on the degradation of PE packaging through photocatalytic processes where oxides of Ti/Mn display the most promising activity [3]. The mechanical mixture of TiO_2 and MnO_2 in a ratio of 1:1 added to the HDPE film in an amount of 1 % led to an increase in the rate of degradation of the polymer. After 90 h of UV irradiation composite film lost 21.2 % of the mass, while the pure polymer lost only 0.5 %. The nature of its properties explained the choice of manganese dioxide. The choice of manganese dioxide was explained by its properties as a semiconductor widely used in catalysis, organic synthesis, and energy storage. Its distinctive feature is a narrow bandgap of around 1–3 eV, which allows it to be an active photocatalyst even in daylight [4]. To achieve higher efficiency of photocatalysts, the possibility of introducing such a support as halloysite nanotubes in a catalytic system should be studied.

Halloysite (HNT) is a natural aluminosilicate of the kaolin group with Al : Si in the ratio 1:1, having the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, where n can vary from 0 to 4. The average size depends on the origin and ranges between 40 and 70 nm in diameter and 200–1500 nm in length [5, 6]. Different methods for introducing the nanoparticles in the polymer matrix are reported. For instance, in

situ polymerization, solvent casting method, extruder blending, and deposition by layer [7].

The chemical compositions and the opposite charge of the inner and outer surfaces open up wide possibilities in the development of HNT-based composite materials. Namely, decorating the outer surface of nanotubes with positively charged molecules or nanoparticles and loading the inner cavity with negatively charged molecules. The cavity can be used as a container for loading active substances (drugs, proteins, surfactants, corrosion inhibitors, catalysts) and their subsequent controlled release. Moreover, some inorganic salts may also be loaded into the tube cavity [8]. Modifying the outer surface of nanotubes can affect the stability of colloidal solutions, improve the filler distribution in polymer matrices [9], and develop surface area of catalysts, preventing aggregation. Moreover, adding HNT to the polymer leads to the improvement of the mechanical properties of films, influencing the flammability [10], and crystallinity of materials [11].

Problem statement

In our previous work, the solvent-casting method was used for introducing the catalyst into the PE film [3]. This technique has shown high efficiency. But at the same time, it includes using toxic solvents at high temperatures during a long time (100 °C for 45 minutes). Therefore, this study aimed to find alternative methods for adding nanomaterials to the polymer film interface.

Methodology. PE film decorating technique

PE is resistant to most solvents at room temperature. Only some liquids are capable of dissolving polyethylene when heated. Cyclohexane (CHX) was chosen as one used widely in similar works as the most suitable for PE dissolving at relatively low temperatures [12]. Cyclohexane was heated to 50 °C and 60 °C then 3 mass % of HNT was added. Mechanical and ultrasound stirring was applied to achieve a uniform distribution of particles. Rectangular PE film samples of 12 cm² were immersed in suspension for various time intervals (60 sec. and 120 sec.) at 50 and 60 °C (Table 1). Sample 0 was prepared without halloysite at the same conditions for comparison. After, the film was washed with distilled water and dried at room temperature.

Table 1. Film preparation conditions.

Sample name	HNT / mass %	Temperature / °C	Immersion time / sec
0	0	50	60
1	3	50	60
2	3	50	120
3	3	60	60

Methods

The efficiency of introducing nanoparticles into the film, as well as HNT's influence on PE film properties, was examined by the following methods: the wettability was measured using OCA 20 Data Physics Instruments equipped with a high-resolution CCD camera; the contact angle (θ) of water in the air was measured by the sessile drop method.

Dynamic mechanical measurements were conducted using the DMA Q800 (TA Instruments). Tensile tests were performed with a stress ramp of $1 \text{ MPa}\cdot\text{min}^{-1}$ at $25 \text{ }^\circ\text{C}$.

Thermogravimetric analysis (Q5000 IR, TA Instruments) under nitrogen flow with heating ramp $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from 25 to $600 \text{ }^\circ\text{C}$ was performed to evaluate the efficiency of HNT's introduction in the film and thermal stability of treated samples.

Optical images were taken with Optika polarizing microscope to study the uniformity of nanomaterial deposition on the surface.

Results and Discussion

The TG curve of pure halloysite nanotubes has one mass loss of $14.95 \text{ mass } \%$ [13] is attributed to the removal of the interlayer water molecules from the HNT structure. On the other hand, Sample 0–3 showed a significant mass reduction of about $90\text{--}100 \%$ from 400 to $520 \text{ }^\circ\text{C}$ as a consequence of the PE thermal degradation.

Moreover, thermogravimetric data provided the mass fraction of HNT in composite films. Sample II, immersed in HNT suspension in cyclohexane at $50 \text{ }^\circ\text{C}$ for 120 seconds, showed the most considerable residual mass among all samples (Table. 1). The calculated HNT content was equal to $2.83 \text{ mass } \%$ corrected on water loss. Sample III immersed at $60 \text{ }^\circ\text{C}$ for 60 sec, showed a slightly lower HNT content of 2.74% . PE degradation temperature (T_d) was calculated from the maximum of the DTG peaks. It can be pointed out that T_d for Sample II is shifted towards lower temperatures 37° compared with pure PE, while for Sample III the main degradation peak

is shifted towards higher temperature for 14° compared with pure PE.

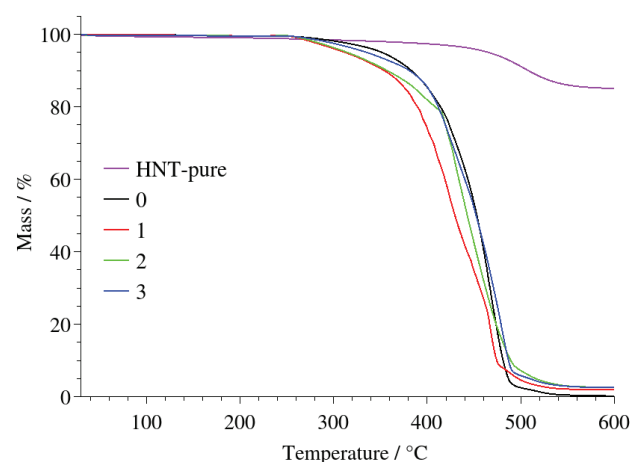


Fig. 1. Thermogravimetric curves of treated PE composite samples

At the same time, Sample 2 showed the highest hydrophilicity with contact angle 77.11° when Sample 0 demonstrates contact angle of 99.24° (Fig. 2). It can be explained by the presence of hydrophilic HNTs on the film's surface. Which is in good agreement with TGA analysis. Sample 3, in turn, remains hydrophobic despite the almost equal content of nanotubes. Possibly due to the higher treatment temperature, nanotubes were included into a deeper layer of a film.

Dynamic mechanical analysis (Fig. 3) showed that samples are elastic since the strain grows linearly with stress. After reaching the yielding point – deformation becomes irreversible. As a result of mechanical tests, it can be concluded that the duration of treatment is of key importance. Processed for the longest time of 120 sec Sample II, has the lowest mechanical characteristics. An increase in elasticity can be noted for samples treated for 60 sec. (Sample 1 and 3) in a Halloysite suspension, while the strength characteristics remained almost constant compared to reference Sample 0, prepared without HNT's (Table 3).

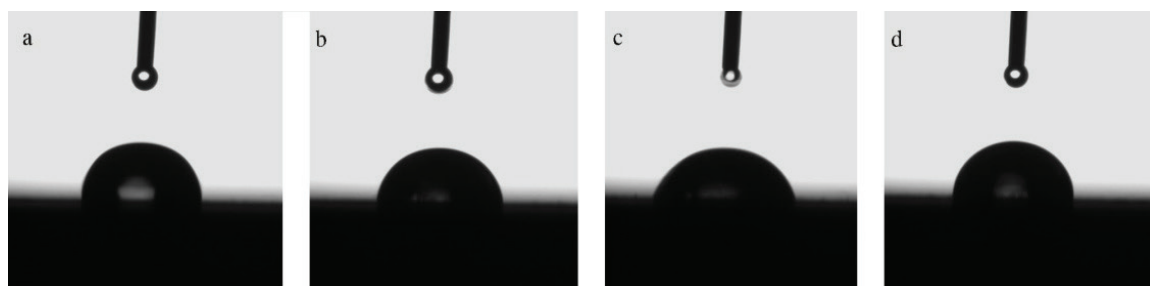


Fig. 2. Images of droplets just after their deposition onto the surface of (a) Sample 0, (b) Sample 1, (c) Sample 2, (d) Sample 3

Table 2. Thermogravimetric and wetting properties of treated samples

Sample name	RM600, %	Contact angle, °
0	0.18	99.24 ± 0.76
1	1.93	85.21 ± 8,81
2	2.59	77.11 ± 4,71
3	2.51	89.18 ± 4,03

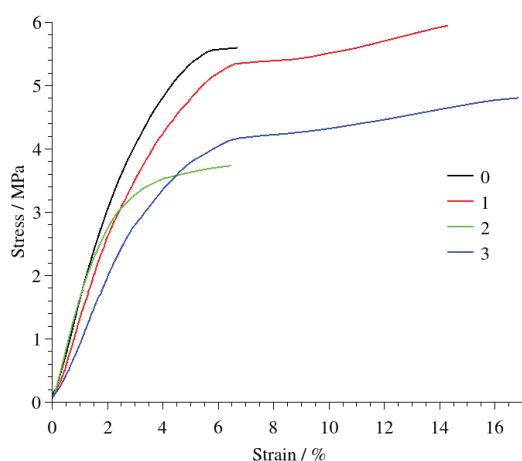


Fig. 3. Stress vs. strain curves of treated samples

It is worth notifying the values of Elastic Modulus, also known as Young's modulus, as a property of materials that measures their stiffness or resistance to elastic deformation for the synthesized samples, are higher than those of pristine PE. The reinforcing effect of HNT in polymers is often explained as a result of agglomerates of nanoparticles and the formation of the interface region between matrix/nanoparticles, which restricts the mobility and deformability of PE [14, 15].

Based on the analysis of optical images, we can assert that treatment of films at a temperature of 50 °C allows us to obtain a uniform deposition of nanomaterial on the surface while raising the temperature to 60 °C leads to the formation of areas with aggregated particles (Fig. 4).

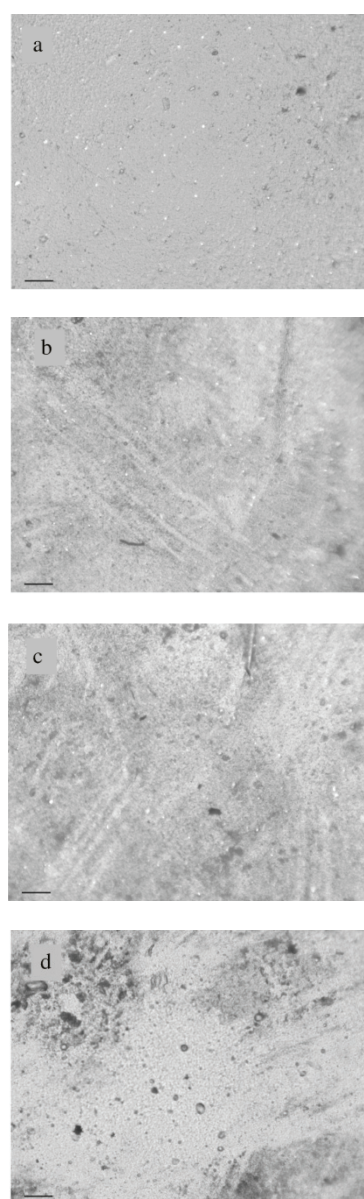


Fig. 4. Optical images of PE films treated in HNT/cyclohexane suspension under different conditions: (a) Sample 0, (b) Sample 1, (c) Sample 2, (d) Sample 3. The scale bar is equal to 0.1 mm

Table 3. Tensile strength properties of films

Sample name	Elongation at break / %	Stress at break point / MPa	Elastic modulus / MPa	Yield point / %
PE non-treated	>150	>12	80.4	11.9
0	6.68	5.60	168.9	3.48
1	14.27	5.64	135.2	5.69
2	6.45	3.74	164.8	2.44
3	16.82	4.81	103.3	5.39

Conclusions

Different conditions of application of HNTs on the surface of PE films using cyclohexane were tested. A method allows to achieve the introduction of a maximum of 2.83 wt. % of HNT. This method confirmed the possibility of attaching nanomaterials, namely HNTs, to the surface of the film by partially dissolving the surface layer of the polymer. Unlike our previous study [3], where the solvent casting method was used to introduce the catalyst into the

PE film, the above approach does not require complete dissolution of the polymer and heating of the material to high temperatures and can be applied to the processing of industrially produced PE films.

The addition of functional materials can be useful for modifying the properties of films, in particular PE. Studying the peculiarities of adding a photocatalyst to a polymer film at ambient temperature and the technology of industrial production of a PE film capable of decomposition can be the next stage of research.

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ОДНОСТАДІЙНЕ ТА ПРОСТЕ ДЕКОРУВАННЯ ПОЛІЕТИЛЕНОВИХ ПЛІВОК ГАЛУАЗИТНИМИ НАНОТРУБКАМИ

Проблематика. Забруднення навколишнього середовища полімерними відходами є глобальною проблемою, що вимагає пошуку ефективних та безпечних способів утилізації або переробки вторинної сировини. Використання фотокаталізаторів для деградації полімеру є сучасним підходом. Сполучення фотокаталізаторів з матеріалом підкладки для підвищення стабільності, активності та тривалості роботи є важливим напрямом досліджень.

Мета дослідження. Метою роботи була розробка методу нанесення наноматеріалів на поверхню поліетиленової (ПЕ) плівки за допомогою часткового розчинення верхнього шару полімеру в нагрітій суспензії наноматеріалу, а саме алюмосилікатних нанотрубок галуазиту (ГНТ) у розчиннику. В якості розчинника використовувався циклогексан.

Методика реалізації. Проведено термогравіметричний, оптичний аналіз та вивчені механічні властивості синтезованих зразків, порівняно їх властивості з референтними зразками чистого та обробленого ПЕ без додавання ГНТ.

Результати дослідження. Розроблено метод декорування ПЕ плівки нанотрубками ГНТ. Досягнуто введення 2,83 мас. % за умови занурення плівки в суспензію ГНТ у циклогексані (3 мас. %) за температури 50 °C упродовж 120 сек. Зниження кута зразка до 77,11° свідчить про включення гідрофільних ГНТ у поверхневий шар ПЕ. Оптичний аналіз підтвердив рівномірний розподіл частинок на поверхні плівки. Зафіксовано зниження механічних властивостей (еластичність та міцність на розрив), що може бути пов'язано із деструктивною дією розчинника на полімер.

Висновки. Протестовано різні умови нанесення нанотрубок ГНТ на поверхню ПЕ плівок з використанням циклогексану. Розроблено метод, що дозволяє досягти введення максимум 2,83 мас. % ГНТ. Цей метод підтвердив можливість прикріплення наноматеріалів, а саме ГНТ, до поверхні плівки за допомогою часткового розчинення поверхневого шару полімеру. На відміну від нашого попереднього дослідження [3], де для введення каталізатора в ПЕ плівку використовувався метод лиття з розчинника, вищезазначений підхід не вимагає повного розчинення полімеру та нагрівання матеріалу до високих температур та може бути застосований для обробки промислово виготовлених ПЕ плівок. Додавання функціональних матеріалів може бути корисним для модифікації властивостей плівок, зокрема ПЕ. Вивчення особливостей додавання фотокаталізатора до полімерної плівки за температури навколишнього середовища та технології промислового виготовлення здатної до розкладання ПЕ плівки може стати наступним етапом досліджень.

Ключові слова: полімер, галуазитні нанотрубки, наноматеріал, термогравіметрія, хімічна технологія.

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