INTRODUCTION

A modern person’s life cannot be imagined without plastic products which are used in all areas, from industry to everyday life. According to American scientists, humankind has produced 8.3 billion tons of plastic throughout history; half of those have been manufactured over the past 13 years [Geyer, 2017]. Most plastic products are used for a short period of time before they end up in a bin – those are plastic containers, bags and packaging. This leads to the formation of a large amount of plastic waste. Of all the plastics that end up in a bin, less than 9% are recycled, 12% are burnt, and another 79% are in the landfills [https://mistosite.org.ua]. Under the influence of external factors, the partial destruction of polymers takes place, and plastic waste disintegrates into small particles. As a result, a new environmental problem has arisen – microplastic pollution. Microplastics are found all over the world. The global migration of microplastics is caused by living beings, from the smallest soil organisms to oceanic giants. Microplastics can be found in the sea, in freshwater environment such as rivers and lakes, in the atmosphere and in food. Having tested tea, Canadian scientists have found that some premium brand tea bags can leave billions of microscopic plastic particles in the cup [Madeline, 2018; Fotopoulou, 2016]. The only way to save the environment from plastic waste pollution is to utilize it safely. The main method of recycling plastic waste in Ukraine is its reuse as raw material [Denysenko, 2014; Rhodes, 2018]. However, under the influence of mechanical and thermal factors while recycling, polymer chains are broken, which worsens the performance characteristics of the products. According to this scheme, the multiplicity of waste recycling is limited, and in the end, products made from recycled plastic become unsuitable for reuse. Eventually, they end up in landfills or burn in recycling plants.
Safe plastic utilization is the completion of the life cycle in the form of natural source elements. Polymers, which are widely used for the manufacture of plastic products, are obtained from oil feedstock, the life cycle of which begins with the biomass of primary producers. The synthesis of those biomass producers is based on the absorption of water and carbon dioxide. Therefore, the safest method of recycling plastic waste is its final decomposition under the influence of destructor organisms. Biodegradable plastics have been used in the plastics processing industry. Nevertheless, their widespread use has its limitations due to the instability of such products when exposed to external factors [Masyuk, 2021; Levytskyi, 2021].

Therefore, the search for new ways to solve the problem of environmental pollution with plastic waste will remain relevant in the future. Taking its amount into account, the search is urgent so as to prevent an environmental crisis and new threats to human safety.

The aim of our study is to develop the fundamental principles for the utilization of household plastic waste in the technologies for the production of slow-release mineral fertilizers with the final degradation of the polymer under the influence of soil environment.

MATERIALS AND METHODS

For our research, polymers that are part of household waste were used: polyethylene terephthalate and polystyrene. Polyethylene terephthalate (PET) accounts for 25% and polystyrene (PS) for 6% of the total volume of polymer waste [Yashchuk, 2011]. Polyethylene terephthalate and polystyrene are mainly used in the production of containers and packaging for beverages and food. These products are disposable and end up in waste in a short time. Ethyl acetate was used to make film-forming solutions based on polyethylene terephthalate waste, and carbon tetrachloride was used for polystyrene. The choice of the solvent was based on the solubility of the polymer and the safety of the technological processes. In addition to the polymer, we added hydrolysis lignin to the film-forming solutions, which is a by-product of wood processing in paper and pulp industry, the residue of the production process – wood hydrolysis. Hydrolysis lignin acts as an initiator for the biological decomposition of the polymer. This method is based on determining the mass loss of samples and is widely used in degradation tests, although it serves as indirect evidence of the process. The third method is the change in mechanical properties. The change in mechanical properties is determined by a tensile test.
strength test. A decrease in the breaking force of the sample indicates the destruction process. The fourth method is changes in mechanical properties and molecular weight. To determine the change in molecular weight, we used the medium-viscosity molecular weight. Its determination is experimentally the simplest and is based on the dependence of the viscosity of polymer solutions on their molecular weights. This dependence is also affected by the shape of the polymer molecules. Depending on their shape, the viscometric method can determine the approximate or number average or weight average molecular weight. For many linear polymers, the average viscometric molecular weight is close to the weight average. The viscometric method was used to determine the viscosity of polymer solutions.

RESULTS AND DISCUSSIONS

The successful use of household plastic waste as secondary raw material is possible only if they are sorted at the stage of waste generation and separate collection. At the legislative level, the rules for waste management and the introduction of separate collection of household waste are enshrined in the Law of Ukraine “On Waste” adopted by the Verkhovna Rada on March 5, 1998 [Vidomosti Verkhovnoi Rady Ukrainy].

In order to introduce the separate collection of household waste in accordance with Article 35-1 of the Law of Ukraine “On Waste” by the order of the Ministry of Regional Development, Construction and Housing and Communal Services of Ukraine dated August 1, 2011 under No. 133, the “Methodology for the separate collection of household waste” was approved and registered in the Ministry of Justice on October 10, 2011 under No. 1157/19895 [Nakaz Ministerstva regionalnoho rozvytku, budivnytstva ta zhyttio-komunalnoho hospodarstva Ukrainy]. The methodology determines that the separate collection of household waste is the collection of household waste based on individual components, including the sorting of household waste for its further processing and utilization. Legislative requirements for separate collection are implemented using the example of the collecting of polyethylene terephthalate waste directly from household consumers at communal adjoining sites. Other plastic waste is gathered by specialized enterprises with the help of recycling reception centres. Primary processing of plastic waste is carried out at these enterprises. It consists of the removal of heavy external dirt, sorting, separation, washing in special baths using alkaline solutions and detergents. At the final stage, the material is shredded into the commodity fraction, passes through a secondary air separation system and is packed for sale as secondary raw material [https://galpet.com.ua, https://vtor-resursy.com.ua, https://ecolos.com.ua, https://nowaste.com.ua].

After primary processing, plastic waste can be used in the production of slow-release encapsulated mineral fertilizers. For this purpose, a shell consisting of polymeric basis and certain composites is applied to the surface of synthetic mineral fertilizer granules. Coating (encapsulation) is carried out by spraying a liquid film-forming composition into a layer of granular fertilizers using a nozzle. Therefore, it is necessary to obtain a film-forming composition in a liquid aggregation state. The polymers used in our studies are insoluble in water. Thus, organic solvents were used. Polystyrene and polyethylene terephthalate are characterized by different properties of their solubility. Various technological methods were used to obtain solutions of these polymers.

Polystyrene dissolves in aromatic and chlorinated aliphatic hydrocarbons such as toluene, acetone, benzene, dichloroethane, ethyl acetate, carbon tetrachloride.

Taking into account the solubility of the polymer and the safety of technological processes to obtain a film-forming composition based on polystyrene, we chose carbon tetrachloride which is low toxic, non-flammable and incombustible solvent. The solubility of polystyrene in carbon tetrachloride was determined experimentally. Under conditions of carbon tetrachloride temperature of 18 °C and constant stirring for 20 minutes, the solution was saturated at the concentration of 18 g of polymer per 100 ml of solvent. On the basis of such a solution, a polymer dispersion for fertilizer encapsulation was obtained with the following ratio of components, wt%: carbon tetrachloride: 90.7–96.0; recycled polystyrene: 3.1–7.6; hydrolysisin lignin: 0.9–1.7.

PET dissolves only at a temperature of 40–150 °C in phenols and their alkyl- and chlorine-substituted compounds, aniline, benzyl alcohol, chloroform, pyridine, dichloroacetatic and chlorosulfonic acids, cyclohexanone, etc. The use of these substances is not advisable in terms of their aggressiveness and high toxicity. In order to improve the
solubility of PET waste, it was chemically modified. The reactor was loaded with PET waste in the form of flakes, which underwent primary processing at a specialized enterprise, and diethyleneglycol in a PET:DEG molar ratio of 1:0.5. The contents of the reactor were heated to a temperature of 220 °K. Two hours later after reaching the required temperature, ethylene glycol was distilled off from the reactor at a residual pressure of 20 kPa. The total duration of the process was 3.5 hours. Modified PET is characterized by a maximum solubility in ethyl acetate 13 g of polymer per 100 ml of solvent. On the basis of that solution, a polymer dispersion for fertilizer encapsulation was obtained with the following ratio of components, wt%: ethyacetate: 90.0–95.0; modified polyethylene terephthalate: 5.0–10.0. During encapsulation with this film former, to prevent particles from sticking together, the fertilizer layer was periodically dusted with a solid powder mixture of starch and natural zeolite in the ratio of components, wt %: 50:50. The amount of the mixture to the weight of the film was 0.5–1 wt% [Nagursky O.A. 2020a].

The next step in the handling of plastic waste is the encapsulation of mineral fertilizers using the obtained film-forming composition. Encapsulation is the technological process of placing a particle of one substance into a shell of another substance that is inert to the former one. Encapsulation includes the isolation of particles of the encapsulated substance from the environment and from each other without regulating the structure, size and shape of the capsule constituent elements – a core and a shell. The main purpose of fertilizer encapsulation is to create slow-release plant nutrition products. The most appropriate of the wide variety of encapsulation methods is the coating of fertilizer granules in an apparatus with active hydrodynamics (fluidized state). The implementation of the encapsulation process in the fluidized bed apparatus allows to obtain a uniform coating of fertilizer particles and to achieve the maximum intensity of heat and mass transfer processes in the material layer [Gumnitsky, 2012]. The main technological parameters of encapsulation of dispersed materials by this method are air velocity, air temperature, the intensity of the film-forming solution flow to the material layer and the time of the process. Air velocity determines the hydrodynamic mode of the apparatus operation. It means that the material layer is in a state of stable fluidization. The air velocity value is determined by the system of criterial dependencies [Nahurskyi O.A. 2012b]:

\[
Re_{cr} = \frac{\nu_{cr} d}{\nu_c}
\]

\[
Re_{cr} = \frac{Ar}{1400 + 5.22\sqrt{Ar}}
\]

\[
Ar = \frac{d^3 \rho_p g}{\nu_c^2 \rho_c}
\]

where: \(\nu_{cr}\) is the air velocity at which the material layer passes into the fluidized state, m/s; \(d\) is the diameter of the particle, m; \(\nu_c\) is the air density under process conditions, m³/s; \(\rho_c\) is the air density under process conditions, kg/m³; \(\rho_p\) is the density of the particle material, kg/m³.

In order to ensure the regime of stable fluidization, the operating air velocity was greater than the minimum by the value of the fluidization coefficient \(k_f\) which was taken to be equal to 2.

The temperature regime of encapsulation is determined by the physicochemical characteristics of the materials. The limiting factors which have a direct impact on the intensity of the encapsulation process are the boiling point of the solvent and the thermal stability of the materials. Boiling of the solvent will lead to a sharp deterioration in the coating quality. In the case of encapsulation of thermally unstable substances, the limiting temperature is determined by the preservation of the material properties. Heating of ANP fertilizer above 70 °C leads to thermal decomposition. Carbon tetrachloride has a boiling point of 76.7 °C and ethyl acetate has a boiling point of 77.11 °C. Accordingly, the air temperature at the inlet of the apparatus was accepted as 70 °C.

The air flow velocity in the apparatus and its temperature has a decisive influence on the intensity of heat exchange and mass transfer processes of the encapsulation. They characterize the interaction in the system solid phase (mineral fertilizer granules) – liquid (film-forming composition) – air. Thermal energy is spent both on heating the layer of mineral fertilizers to the operating temperature and on the evaporation of the solvent from the granule surface where the functional shell is formed. The solvent evaporation rate \(W\) (kg/s) determines the intensity of the film-forming solution flow to the material layer. It can be determined by the dependence [Nagursky, O. 2015c]:

\[
W = \frac{\rho_{c, f} V_{f, c} \Delta H_{c, f}}{\rho_s \Delta H_{s, f}}
\]
\[ W = \beta F(C_{sat} - C) \]  
(2)

where: \( \beta \) is the mass transfer coefficient of the solvent vapour from the particle surface to the air, m/s; 
\( C_{sat} \) and \( C \) – concentration of solvent vapour in the air in the state of saturation and operating respectively, kg/m³; 
\( F \) is the mass transfer surface area, m².

The determination of the kinetic parameters of heat and mass transfer required to calculate the evaporation rate of the solvent was carried out on the basis of experimental studies presented in the relevant publications [Nagursky, O. 2015d].

Solution consumption \( P \) (kg/s) with the concentration \( C_p \) (kg of film former/kg of solvent) was found using the dependence:

\[ P = W(1 + C_p) \]  
(3)

The coating duration of the surface of the particles is determined by the required thickness of the shell \( \delta \) (m) on the surface of the granules, or the weight of the shell as a percentage of the weight of the fertilizer. For the materials used in our studies, the following values of the main technological parameters of encapsulation of 1 kg of ANP fertilizer were obtained per 1% of the coating mass to the mass of fertilizers (Table 1).

The encapsulation quality according to the selected technological parameters was controlled for the nature of the curve of the nutrient release (Fig. 1) and visually for appearance (Fig. 2).

Both the smooth kinetic curves of the nutrient release and the appearance of the shells indicate a uniform coating of mineral fertilizer granules.

The final stage of plastic waste management, according to the proposed technology, is their biological degradation under the influence of soil environmental factors. At the first stage, polymer destruction was studied by determining the change in molecular weight. Based on the planned experiments, we built a statistical model of polystyrene biodegradation in peat-podzolic soil, which can be used to calculate the degree of polystyrene biodegradation depending on the content of natural polysaccharide \( G \) and soil moisture \( W \):

\[ y = 0.34G + 0.6W - 3.5 \]  
(4)

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<th>Table 1. Main technological parameters of encapsulation of granular ANP fertilizer with a film-forming solution based on plastic waste</th>
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<td>Film former type</td>
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<td>Ethyl acetate-PET-lignin-zeolite</td>
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<td>Carbon tetrachloride-polystyrene-lignin</td>
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![Figure 1. Kinetics of the release of mineral nutrition elements from granules with an encapsulated shell of polystyrene-lignin ANP fertilizer with different coating values, % mass](image1)

![Figure 2. Appearance of the encapsulated granular ANP fertilizer with a polystyrene-lignin shell](image2)
Using this model, we carried out computer optimization of experimental data and obtained an approximate estimate of the degree of degradation in half a year (Fig. 3).

The results of these studies have shown the possibility of avoiding soil re-contamination and complete degradation of polystyrene in the soil environment until the next use of encapsulated fertilizers. In addition to the possibility of complete degradation of the polymer, the safety of intermediate degradation products is important for the soil environment. For this, we carried out the studies using bioindicators under conditions of cyclic use of encapsulated mineral fertilizers. Simultaneously, visual observation of changes in the plastic appearance and their mechanical properties was applied. The obtained results have shown the safety of the use of encapsulated mineral fertilizers for the soil environment and the complete degradation of the residues of the polymer base of the shell [Nagurskyy, O. 2022].

CONCLUSIONS

Our studies on the handling of household plastic waste of polyethylene terephthalate and polystyrene have demonstrated the technological possibility of using them in the form of secondary material resources to create environmentally friendly encapsulated mineral fertilizers. The possibility of implementing all stages of the safe utilization of these wastes with the final biodegradation without harmful effects on the soil environment has been shown.

The proposed method for processing household plastic waste, according to which plastic is collected and sorted, mechanically and thermally processed with the creation of film-forming composition used for the encapsulation of mineral fertilizers for plant nutrition with the release of environmentally friendly substances, is a method of plastic safe utilization.

REFERENCES


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