Zeszyty Naukowe SGSP 2019, Nr 71/3/2019

Anna Dmochowska, PhD
Lt. Col. Małgorzata Majder-Łopatka, PhD
Lt. Col. Zdzisław Salamonowicz, PhD
Faculty of Fire Safety Engineering
The Main School of Fire Service

Is it Possible to Identify a Polymer Easily?

Abstract

Plastics are raw materials that play a very important role in our lives. We can find them in medical devices, cell phones, clothes, cars, furniture, cutlery, plates, toys, bottles etc. Their diversity and quantity mean that we have no awareness of which substances we use. The aim of the research was to develop a scheme allowing the simple identification of the most commonly used synthetic polymers. Hazards occurring during their use and burning under uncontrolled conditions were also determined.

Keywords: tests for the identification of plastics

Czy można w prosty sposób zidentyfikować polimer?

Abstrakt

Tworzywa sztuczne to surowce odgrywające bardzo istotną rolę w naszym życiu. Możemy je znaleźć w wyrobach medycznych, telefonach komórkowych, ubraniach, samochodach, meblach, sztućcach, talerzach, zabawkach, butelkach itp. Ich różnorodność i ilość sprawia, że nie mamy świadomości z jakich substancji korzystamy. Celem badań było opracowanie schematu pozwalającego na prostą identyfikację najczęściej stosowanych polimerów syntetycznych. Określono także zagrożenia występujące podczas ich użytkowania i spalania w niekontrolowanych warunkach.

Słowa kluczowe: testy na identyfikację tworzyw sztucznych, rodzaje i właściwości tworzyw sztucznych

Introduction

The most commonly used plastics are: PVC-polyvinyl chloride, PET - polyteraphtalane ethylene, PE - polyethylene, PS – polystyrene and PU – polyurethane. These polymers represent about 75% of the European demand for all plastics and are the largest group of plastics deposited on landfills. Polymers, in spite of many advantages, also have defects that can often pose a threat to people and the environment around them [3, 8]. That is why it is important to be aware of what materials we use and what hazards they may cause. The big plastic problem turned out to be plastic packages of various products which constitute about 30% of the total amount of polymers produced [10, 11].

Termodegradation of polymers usually occurs at a temperature exceeding the flow temperature in the amphoric polymers or the melting point in crystalline polymers. During these processes, quite significant amounts of small-molecule polymer breakdown products are released. These substances depend on the chemical structure of the material and can be: carbon monoxide, carbon dioxide, water, hydrogen chloride, hydrogen cyanide, hydrocarbons such as propylene, methane, butadiene, propane, acetylene, benzene, ethylene, ethane. Toxic products of thermal decomposition of polymers also include: phenols, dioxins, phosgene, amines, hydrogen chloride, aldehydes, ammonia [4, 5]. Disadvantages of plastics are low heat resistance and low temperature of decomposition compared to other materials. These undesirable features of polymers cause that they create a high fire hazard. Thermal characteristics of polymers determine heat resistance and thermostability. Thermal resistance is the maximum temperature of the polymer in which the material retains its mechanical properties. Thermostability is the temperature at which the chemical destruction begins in the polymer [9, 15].

In table 1 presents an examples of the temperature of ignition and melting of the most commonly used polymers.

Tab. 1. The temperatures of ignition and melting of plastics

Polymer	Ignition temperature [°C]	Melting temperature [°C]
Poliester	432–488	220–268
Polyethylene ld	349	107–124
Polyethylene hd	349	122–137

Polypropylene	570	158–168
Polystyrene	488–496	100–120
Polyurethane	416	85–121
Polychloric vinyle	435–557	75–110

Source: study based on [15]

For plastics, a general three-stage combustion mechanism is assumed. In the first stage, taking place at a temperature between 100°C ÷ 250°C, the supplied energy is consumed to remove hydrogen halides or water. In the second stage, taking place in the temperature range 250°C ÷ 500°C, the supplied energy leads to the break of the main polymer chains bonds (degradation or depolymerization) as a result of which flammable monomers or other compounds are formed. It is also possible to create aromatic condensed rings that remain stable within these temperatures. In the third stage, taking place at a temperature exceeding 500°C, the aromatic compounds formed in the earlier stage are subject to further condensation. A charred layer is formed, which is characterized by insulating properties and is flame retardant under ordinary atmospheric conditions. Initially, the layer has a thick liquid consistency and the gaseous combustion products that are released cause foaming. As a consequence, this step leads to the formation of a fire-resistant foamed coating [12, 16]. The formation of a charring layer during the combustion of a polymeric material has a significant effect on the energy release only in the case of samples with a high thickness. Plastics in the form of thin elements burn quickly and intensively basically regardless of the material they are made of. Nowadays, materials made on the basis of polymers have to meet many of requirements. In this way, their useful properties are determined, as well as the flammable properties and fire characteristics. A fire feature is a numerical value that is a function of the system parameters in which it was designated. Fire features are also: Heat Release Rate – HRR; Smoke Extinction Area – SEA; toxicity of gaseous combustion products; Char Yield – CY; ignitability of the material [6, 17].

The conducted research has shown that the most important feature is HRR, because this parameter has a major impact on the rate of fire spreading and the time in which human life can still be saved. It has been proven that the two-fold increase in the toxic potential of the material and its flammability did not significantly affect the survival time of the victims. On the other hand, a two-fold increase in HRR has shortened this time more than three times. In addition, the rate of heat release also affects the temperature of the fire, which directly affects the speed of its development. The occurrence of a fire is always characterized by the emission of smoke. It makes it difficult to carry out rescue and firefighting operations and limits visibility, which results in an increase in the number of victims. Poisonous substances that arise from the combustion of polymer materials penetrate the human body with all possible ways: absorption through the skin, respiratory tract, gastrointestinal tract. The most dangerous and most common product of burning plastics is carbon monoxide. During the combustion of polymer materials in an increased concentration there is also carbon dioxide and other products of combustion depending on the type of polymers burned [1, 15]. These may be gases such as: phosgene, hydrogen chloride, sulfur oxides, hydrogen cyanide and others. The parameter describing the flammability of a given material is the oxygen index. It determines the lowest oxygen content in the nitrogen-oxygen mixture, expressed as a percentage by volume, at which the combustion process is possible. The lower value of the oxygen index translates into higher flammability of the material. Plastics with an oxygen index < 21% are classified as flammable [2, 13].

Tab. 2. Values of the oxygen index of selected plastics

Polymer	Oxygen index (% O_2)
Polyethylene	17,4
Polypropylene	17,4
Polystyrene	18,3
Polycarbonate	26,0
Silicone rubber	30,0
Polychloride vinylin	45,0
Polytetrafluoroethylene	95,0

Source: study based on [15]

Thus, plastics from the fire point of view are safer to use, the lower the value of heat release rate (HRR) and smoke formation rate (SEA) and the higher oxygen index (OI) and the degree of charring after combustion (CY) [5].

Research methodology and test stand

The research aimed at determining the polymer being the main component of the tested plastic included: organoleptic observations, roasting of the material in a glass tube, testing the material with an open flame, behavior of the material against organic solvents and water, calculation of the specific gravity of the material, identification of plastics and marking pH of pyrolysis gases. In addition, the smell of the generated fumes, the appearance of the flame and its characteristics and the ability of the material to support the combustion process were determined. Figure 1 shows the schematic of the laboratory stand.

Fig. 1 Research equipment
Source: own study

Organoleptic observations

The external appearance and certain characteristics are often very strongly related to a particular plastic or a group of materials to which a given polymer belongs. On the basis of organoleptic observations, we can largely narrow the identification of a given polymeric material to a relatively small amount. The most important features of plastics that facilitate their identification include: color; transparency; translucency (few plastics); shape of the material, for example by extrusion, it is possible to form only a few polymers and from thermosetting molds we will not get large, bulky moldings. Some plastics can be identified unambiguously. An example of such a polymer may be celluloid, which rubbed with the hand or clothing exudes a specific camphor smell only for it. On the other hand, polystyrene thrown onto a solid surface will be characterized by a humming glass-metallic sound while other materials give a deaf sound. Polypropylene and polystyrene give the illusion of paraffin.

Tab. 3. Identification of materials based on appearance and properties

Form, appearance and properties of the material	**Probable material or group of materials**
Transparent, colorless, colored material	Polystyrene, polyvinyl chloride, polyethylene (only very thin foils)
Translucent material, opaque completely	Polystyrene, polyvinyl chloride, polyethylene (only very thin foils)
Plastic films	Polyethylene, polyvinyl chloride. Less often polystyrene
Fibers	Polyesters (PET), polyurethanes
Stiff foam	Cross-linked polyurethanes
Flexible foams	Foamed poly (vinyl chloride), polyurethanes, polystyrene (snow white)
Chemical resistant kits	Polyester resins. Less often polyurethane resins
Soft profiles, tubes, lines	Softened poly (vinyl chloride), polyethylene, polypropylene
Rigid profiles, long pipes	Unplasticized poly (vinyl chloride). They can not be all thermosetting and chemosecure plastics as well as very plastic materials

Sewage fittings	Unplasticized poly (vinyl chloride), polypropylene
Laminates reinforced with fiberglass	Epoxy-glass laminates, polyester-glass laminates
Colorless and transparent plates	Polymethyl methacrylate

Source: own study

Roasting in a glass tube

During these tests a test tube was used, which limited air access to the tested material and allowed for comfortable observation and testing of gases, vapors and fumes. The tube was filled with the fragmented plastic in the height from 1 cm to 2 cm. Then it was placed in the pliers and inserted into the flame of the gas burner. At the same time, reactions inside the test tube were observed. During this test, the smell and the reaction of the thermal decomposition products formed were also registered.

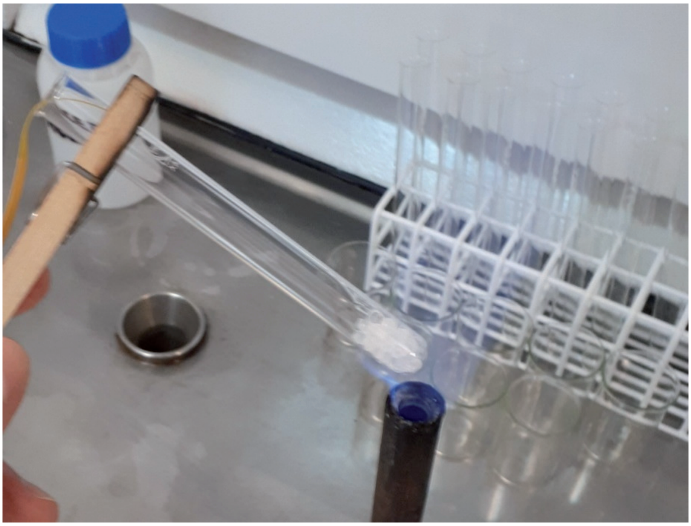

Fig. 2. Roasting polyethylene in a glass tube
Source: own study based on [7]

In tab. 4, the results of roasting polymers in a glass tube are provided

Tab. 4 Roasting polyethylene in a glass tube

Polymer	Observations noted during roasting polymer in a glass tube
Poly (ethylene terephthalate)	It melts and then breaks down. It produces white fumes during roasting.
Polypropylene	It melts very easily and loses turbidity.
Polystyrene	It melts and evaporates and turns yellow during decomposition.
Polyethylene	It melts very easily and loses turbidity.
Polyvinyl chloride)	Decomposes to form a dark brown residue.
Polyurethane	It melts and then breaks down.

Source: own study

Examination using an open flame

The polymer sample was collected with tweezers and placed in the burner flame. It was observed what happened to it during direct contact with the flame, then the sample was removed from the flame. It was checked whether the polymer extinguishes after moving away from the flame, whether it supports the combustion process or the flame is luminous or causes smoke. The shape and color of the flame was observed and whether it melts, drips or pulls in the form of threads, whether it forms blisters or delaminates. The smell after extinguishing was also examined.

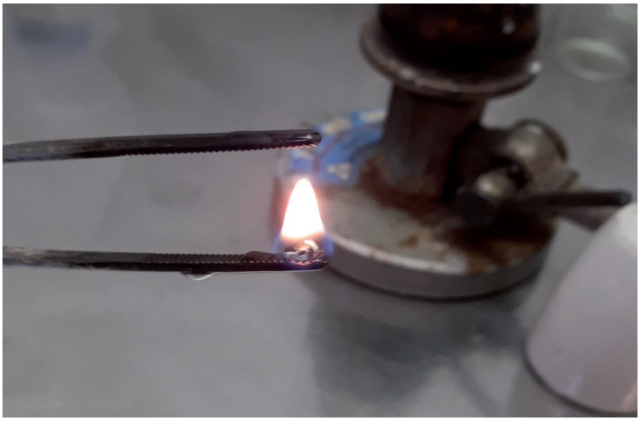

Fig. 3. Flame analysis of polyethylene

Source: own study based on [7]

Tab. 4. Polymer testing using an open flame

Polymer	Observations recorded during testing using an open flame
Poly (ethylene terephthalate)	Maintains the combustion process. The material softens, melts and then drips. Flame and slightly burning flame.
Polypropylene	Maintains the combustion process. The material melts and drips with drops. Flame, yellow flame with blue core.
Polystyrene	Maintains the combustion process. The material softens. Flame yellow-orange, strongly moistening.
Polyethylene	Maintains the combustion process. The material melts and drips with drops. Flame, yellow flame with blue core.
Polyvinyl chloride	It does not support the combustion process. He burns in a flame. The material softens and then decomposes to form a brown or black residue. Flame yellow, sparkling with a green rim. Produces white fumes.
Polyurethane	Maintains the combustion process. A bluish flame with a yellow edge. The material drips and threads are drawn.

Source: own study

Behavior towards organic solvents and in water

A feature that facilitates the identification of a given material is its solubility in water and organic solvents. During the test, a small amount of the sample of the particulate material was poured in a defined solvent and the following changes were observed, i.e. swelling, gelation, dissolution. This test was performed cold and after heating the sample in the flame of the burner.

In tab. 5 present polymers behave in organic solvents.

Tab. 5. Behavior of materials in organic solvents and in water

Polymer	Observations during the study of the behavior of the material in organic solvents and in water
Poly (ethylene terephthalate)	Dissolves in: phenol, strong acids and bases. It is hydrolyzed in boiling water.
Polypropylene	It dissolves in boiling toluene. After cooling, it precipitates.
Polystyrene	Dissolves in: benzene, acetone, styrene, toluene.
Polyethylene	It dissolves in boiling toluene.
Polyvinyl chloride)	Dissolves in: cyclohexane, tetrahydrofuran.
Polyurethane	It dissolves in dimethylformamide. Besides, almost insoluble

Source: own study

Calculation of loose plastic material density

The density of a material is the ratio of the weight of a given substance to its volume or as the weight of a unit of the volume of material without the use of voids, determined in g/cm^3. During the test, a measuring cylinder with 2 cm^3 water was weighed, made up 1 cm of ground plastics in and weighed again to obtain the weight of the sample. The next step was to determine the specific weight from the formula:

$$\gamma = \frac{P}{V_2 - V_1} \tag{1}$$

where:
V_1 – water volume, [cm^3];
V_2 – volume of water with sample, [cm^3];
P – sample mass, [g].

In table 6 compiled the densities of selected polymers.

Tab. 6. Comparison of polymers density

Polymer	Density [g/cm³]
Poly (ethylene terephthalate)	1.38–1.41
Polypropylene	0.89–0.91
Polystyrene	1.04–1.08
Polyethylene	0.91–1.00
Polychloride vinyl	1.19–1.41
Polyurethane	1.20–1.26

Source: own study

Identification marks of plastics

Plastic products are often marked with a polymer symbol from which they were created. This allows you to predict what hazards can be encountered during their use or combustion.

Table 7 shows the symbols of some of the most commonly used polymers determined according to the international standard.

Tab. 7. Symbols of polymers according to ISO

Polymer	Symbol of a polimer
Polyamide	PA
Plybutylene	PB
Polycarbonate	PC
Polychlorotrifluoroethylene	PCTFE

Polymer	Symbol of a polimer
Low density polyethylene	PE-LD
High density polyethylene	PE-HD
Polyethylene terephthalate	PET
Polyethylene ethoxylate	PMMA
Polyformaldehyde (polyoxymethylene)	POM
Polypropylene	PP
Polystyrene	PS
High impact polystyrene	PS-HI
Polyurethane	PUR
Polychloride vinyl	PVC
Plasticized polyvinyl chloride	PVC-P

Source: own study based on PN-EN ISO 1043: 2011-1

Determination of the pH of pyrolysis gases

Also the pH of gases generated as a result of thermal decomposition of plastics is their characteristic feature. During the gas test, a lightly moistened strip of universal paper was applied to the outlet of the polymer-containing tube. The pH of the strip was determined by the reaction of pyrolysis gases: blue – gases are alkaline; red – gases are acidic; it will not change color – gases are inert. Table 8 shows the reaction and odor of pyrolytic gases, while fig. 4 shows the course of the test.

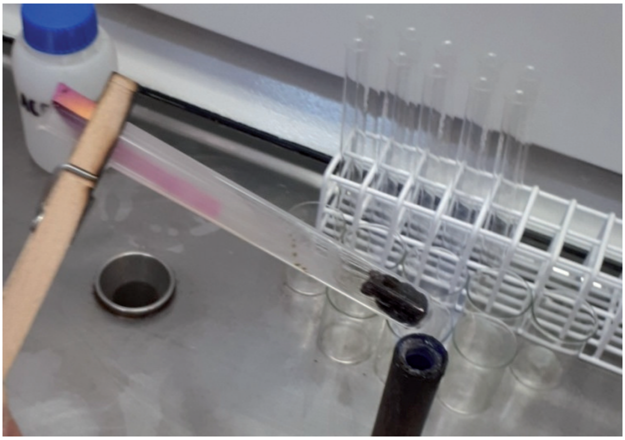

Fig. 4. Read the pH of pyrolytic polychloride vinyl gases
Source: own study based on [7]

Tab. 8. pH and smell of pyrolysis gases

Polymer	PH and smell of pyrolysis gases
Poly (ethylene terephthalate)	Slightly acid. The smell is sweet, aromatic, biting.
Polypropylene	Inert. The smell is weak, burned paraffin.
Polystyrene	Inert. Sweet-floral fragrance, hyacinths, styrenes.
Polyethylene	Inert. The smell is weak, burned paraffin.
Polychloride vinyl	Strongly acidic. The aroma is, biting, tart, such as hydrochloric acid.
Polyurethane	Alkaline. Odor characteristic, unpleasant.

Source: own study

List of received results

Table 9 presents the summed up results of all performed tests. It illustrates the behavior of selected polymers during individual tests. By performing all of the above activities systematically, it is possible to identify the material relatively easily.

Tab. 9 . List of research results

Polymer	Roasting the polymer in a glass tube	Behavior of polymer in a flame	The appearance of the flame	Behavior of the polymer in organic solvents and in water	Density [g/cm^3]	pH of gases	Smell of pyrolytic gases
PET	It melts and then breaks down. It produces white fumes during roasting	Softens, melts and drips	Maintains the combustion process. Flame luminous and slightly smoke	Dissolves in: phenol, strong acids and bases. It is hydrolyzed in boiling water	1.38–1.41	Slightly sour	Sweet, aromatic, biting
PP	It melts very easily and loses turbidity	It melts and drips with drops	Maintains the combustion process. Flame yellow with blue core	It dissolves in boiling toluene. After cooling, it precipitates	0.89–0.91	Inert	Weak, roasted paraffin
PS	It melts then	It melts and soften	Maintains the combustion process. Flame yellow-orange, strongly smoke	It dissolves in benzene, acetone, styrene, toluene	1.04–1.08	Inert	Sweet-floral, hyacinths, styren
PE	It evaporates and turns yellow during decomposition	It melts and drips with drops	Maintains the combustion process. Flame yellow with blue core	It dissolves in boiling toluene	0.91–1.00	Inert	Weak, roasted paraffin
PVC	It melts very easily and loses turbidity	Softens and then decomposes to form a residue of black	It does not support the combustion process. He burns in a flame. Flame yellow, sparkling with a green rim. Produces white smoke	It dissolves in cyclohexane and tetrahydrofuran	1.19–1.41	Strongly sour	Sharp, biting, tart, such as hydrochloric acid
PU	Decomposes to form a residue	Drops and threads are created	Maintains the combustion process. A bluish flame with a yellow edge	It dissolves in dimethylformamide. Besides, almost insoluble	1.20–1.26	Basic	Characteristic, unpleasant

Source: own study

Summary and conclusions

Plastics can be classified as materials whose importance will grow. Properly used, they will reconcile the needs of people with environmental problems. In 2017, the Polish industry used approx 3.5 million tons of plastics. This tendency is of increasing nature, more and more objects with which we come into contact will be made of various polymers. The analysis of simple identification methods has shown that using them can determine the type of polymer. The following conclusions were made on the basis of the conducted research:

1. The identification of polymers should start with the search for appropriate markings on their surface.
2. Polyethylene and polypropylene, in contrast to other polymers tested, have a density lower than water. If we throw the sample into the water and find that it is not sinking, we can almost be sure that we are dealing with PE or PP.
3. A similar relationship can be used for polystyrene. Mixing 140 g of table salt and 860 g of water together gives a solution with a density of 1.1 g/cm^3. PS having a density of about 1.07 g/cm^3, unlike other polymers, should float on the surface.
4. Polyolefins (PE, PP) differ only slightly in density, so it is difficult to clearly determine the type of material. They can be distinguished during dissolution in boiling toluene. After cooling, the polypropylene will precipitate and polyethylene will still be dissolved.
5. The identification of plastics based on the smell of pyrolysis gases may be unreliable due to the difficulty in describing them. During this test, it is worth performing a trial test with a sample of a known material.
6. Research on the behavior of the material in organic solvents and in water in some cases, it is quite long-lasting and cumbersome. This method should be used if other samples do not provide an unambiguous answer.
7. When identifying polymers in the event of not obtaining the expected results, the only solution may be to carry out additional chemical tests requiring the use of specialized equipment and a high level of knowledge of chemical issues.
8. In order to limit losses resulting from fires involving plastics, it is necessary to aim at reducing the rate of heat release in polymers. This parameter has a major impact on the rate at which the fire spreads and time in which it is possible to save human life.

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