

Features of Some Polymer Building Materials Behavior at Heating

Alexey Vasilchenko^{1,a*}, Olexandr Danilin^{1,b}, Tatiana Lutsenko^{1,c},
Artem Ruban^{1,d} and Dmytro Nestorenko^{2,e}

¹National University of Civil Defence of Ukraine, 94, Chernishevskya st., Kharkov, Ukraine, 61023

²Slovak University of Technology in Bratislava, Slovakia

^aavas2006@ukr.net, ^bdanilin7887@gmail.com, ^clutsenkota13@gmail.com,
^druban_artem1979@ukr.net, ^edmytronestorenko@ukr.net

Keywords: polymer building materials, thermal degradation, heat resistance, pyrolysis

Abstract. The problems of reducing combustibility and increasing fire resistance of some polymer building materials are considered. And the toxicity of the gaseous products of their thermal degradation was evaluated both individually and in various combinations with each other. The features of thermal degradation and the loss of mechanical properties under the influence of a flame of polymer building materials were studied. The following samples were used: water pipes based on polyethylene; Tarkett linoleum, Ondex roofing products, Rolvaplast PVC profile panels; structural panels of the company "Polygal"; facing tile based on phenol-formaldehyde oligomers. The processes occurring during pyrolysis and combustion are considered, the results of a study of the combustibility and mechanical properties of polymer building materials based on polyethylene, polyvinyl chloride, polycarbonate, phenol-formaldehyde and epoxy oligomers under the influence of a flame are presented. For the studied building polymer materials, the products of pyrolysis and combustion were studied; their ignition and self-ignition temperatures, and also the flame propagation velocity were measured. The data on the toxicity of the products of their combustion, both individually and under combined action, are summarized. Also, for the studied polymer building materials, the losses of heat resistance, toughness, and flexural strength under the influence of a flame were studied. Thermogravimetric analysis of Rolvaplast PVC panels and Poligal polycarbonate panels allowed us to determine the maximum temperatures and activation energies of the polymer decomposition process. It was concluded that if the material is recognized as non-combustible or slow-burning, it will not always be fire resistant, since its strength and thermal properties can sharply decrease already in the first seconds of flame exposure.

1. Introduction

The development of new technologies in construction is currently impossible without the use of polymer materials. One of the valuable properties of many plastics is their low bulk density and high strength. They are a valuable material for interior and exterior decoration of buildings as combine the best performance qualities of wood, non-ferrous metals and ceramics. Polymer materials are used for the manufacture of sealants, heat and sound insulation, rolled and facing materials, as well as structural products, in which, in addition to strength, it is necessary to ensure high corrosion resistance [1, 2]. In addition, polymer materials are used in flame retardant coatings for metal, wooden structures and other products [3].

However, plastics have a number of significant drawbacks that limit their scope in construction. This is a low heat resistance, a decrease in strength when exposed to elevated temperatures, creep when exposed to constant loads. Also, most polymeric materials have low fire resistance and are combustible [4, 5].

Therefore, the problem of reducing combustibility and increasing fire resistance is always relevant for such materials. One of the most important problems is the assessment of the toxicity of gaseous products of thermal degradation of polymeric materials, both individually and in various combinations with each other.

The range of products based on polymeric materials that are used in the construction of buildings and finishing works is very large. Therefore, there was a need to clarify and, if possible, summarize their fire hazard characteristics. It is especially interesting from this point of view to consider products based on the most common polymers: polyethylene (PE), polycarbonate (PC), polyvinyl chloride (PVC), phenol-formaldehyde (PF).

In this work, we studied the features of thermal degradation, as well as the loss of mechanical properties when exposed to the flame of such building polymer materials as: water pipes based on PE; Tarkett linoleum, Ondex roofing products, Rolvaplast profile panels based on PVC; Polygal PC-based structural panels, facing tile based on phenol-formaldehyde oligomers (PFO).

2. Features of the Reactions of Thermal Decomposition of Polymers

The mechanism of gaseous products formation from thermal degradation of polymers to ignition is extremely complex. Thermal destruction can go according to three schemes [4, 6]:

- 1) the molecules are depolymerized almost completely with the formation of monomers;
- 2) chains of macromolecules are randomly split in various places;
- 3) chain splitting is such that, along with a large number of monomers, there are large macromolecules, but with a lower degree of polymerization.

In most cases, the thermal degradation of polymers proceeds as a radical chain process with stages of initiation, growth, and chain termination or as an ion-molecular process.

Thermal degradation of polyethylene is usually accompanied by a break in the main chain [4, 7]:



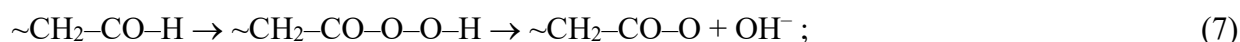
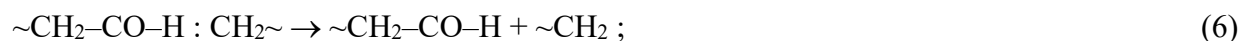
In the presence of atmospheric oxygen, peroxide radicals are formed. They contribute to the further destruction of the polymer and reduce the possibility of restoring the original structure of PE due to the recombination of radicals:



Due to the migration of free valency, the oxidation process quickly captures the entire volume of the material. The decomposition of hydroperoxides leads to the additional formation of free radicals. In this case, the oxidation rate increases, and the process becomes autocatalytic in nature:



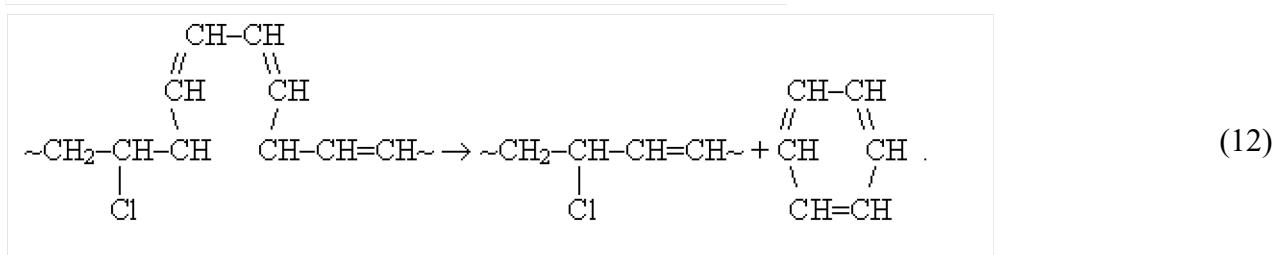
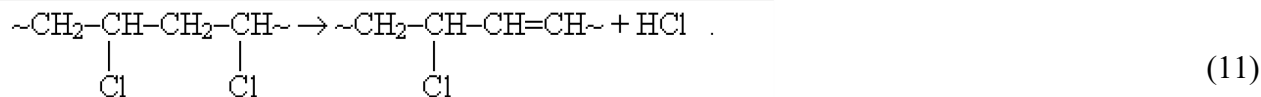
Oxidation of polymers at a sufficiently high temperature is accompanied by a rapid decrease in their molecular weight. The chain breaking occurs due to the decay of the middle alkoxy radicals formed during the decomposition of hydroperoxide groups:



The process of burning PE is directly accompanied by the release of low molecular weight hydrocarbons, which in turn decompose into CO₂ (with an excess of oxygen), CO (with a lack of oxygen) and H₂O.



The decomposition of polyvinyl chloride begins at a temperature of 150 °C and occurs with the release of hydrogen chloride. Intermolecular cyclization reaction leads to a violation of the conjugation of the polyene sequence [4, 8]. The resulting cyclodiene fragments are unstable, while the benzene molecule is split off.



Otherwise, the processes of pyrolysis and combustion of polyvinyl chloride are similar to the corresponding processes of polyethylene.

During the destruction of polymers based on phenol-formaldehyde oligomers (PFO), water, formaldehyde, and low molecular weight hydrocarbons are released at the initial stage ($t = 300$ °C). In the range of 250-600 °C, thermal isomerization occurs due to the formation of free radicals of various compositions, including the products of the destruction of benzene rings, which initiate further destruction or attach to the polymer. The decomposition products in this range are benzene and phenol ($\text{MPC } 5 \text{ mg}\cdot\text{m}^{-3}$) [4, 9].

When burning plastics with insufficient aeration, toxic gases can form: carbon monoxide ($\text{MPC } 20 \text{ mg}\cdot\text{m}^{-3}$), hydrogen chloride ($\text{MPC } 5 \text{ mg}\cdot\text{m}^{-3}$), formaldehyde ($\text{MPC } 1 \text{ mg}\cdot\text{m}^{-3}$). Most plastics also contain a certain amount of toxic metal compounds (lead, tin, zinc, cadmium, barium), which are part of fillers, stabilizers, pigments, dyes. At $t = 700$ °C, most of these metals go into a gaseous state [4, 5].

As mentioned above, the general toxicity of several substances released during pyrolysis and combustion can be much stronger than the toxicity of each of these substances separately, and the resulting concentration is higher than the maximum permissible. Analysis of the thermo-oxidative degradation and combustion of polymers shows that the final products of the combustion of materials from PE, PC, and plastic based on PFO are CO , CO_2 , H_2O (depending on the combustion conditions). These substances do not interact with each other and do not cause an amplifying toxic effect on the human body. The intermediate products of the pyrolysis of PE, PC, and PFO can be various saturated and unsaturated hydrocarbons, the rate of decomposition of which into CO_2 and H_2O is so high that they cannot cause toxic poisoning in humans. An exception is PVC thermal decomposition products. In the early stages, hydrogen chloride and a small amount of free chlorine are released. Chlorine released during PVC degradation can combine with CO – the product of the pyrolysis of PE, PC, and PFO, resulting in the formation of a very toxic substance – phosgene ($\text{MPC } 0.03 \text{ mg}\cdot\text{m}^{-3}$) [4, 5, 7-10].

Thus, consideration of the nature of the thermal decomposition reactions of polymers used in polymer building materials allows us to give a preliminary recommendation on their joint use. The combination of PVC-based materials with materials based on PE, PC, and PFO should be limited, because highly toxic substances can form during their joint thermal degradation.

3. Experimental Study of Thermal Effects on Polymer Building Materials

The study of polymer building materials combustibility and their loss of mechanical properties when exposed to a flame was studied on samples: water pipes, facing tiles, Polygal structural panels, Tarkett linoleum, Ondex roofing products, Rolvaplast profile panels. The control identification of polymer samples by the pH of the pyrolysis products, the Lieberman-Storch method [11], and the study of their behavior in a flame made it possible to confirm that polymer samples belong to four groups: polyethylene, polyvinyl chloride, polycarbonate, and paper-laminate based on phenol-formaldehyde oligomer [12, 13]. The research results are given in Table 1.

The sanitary-chemical analysis of the facing tile based on the PFO by colorimetry method showed a residual formaldehyde content in the polymer of $3.6 \text{ mg}\cdot\text{l}^{-1}$, which corresponds to acceptable standards.

Table 1. Identification of polymers

Name of samples	Flame behavior	Flame character	Nature of burning	Smell of decomposition products	Polymer
Water pipes	Burn in the burner flame and after removal from the flame	Blue with yellow top	The flame smokes, the melt drips	Burning paraffin	Polyethylene (PE)
Tarkett linoleum. Rolvaplast profile panels. Ondex roofing products.	Burning. When removed from the flame, the burner goes out	Green with a blue top	Gray white smoke	Pungent odor of hydrogen chloride	Polyvinyl chloride (PVC)
Polygal PC-based structural panels	Burning. When removed from the flame, it fades	Yellow, luminous	A bit of soot	Phenol	Polycarbonate (PC)
Facing tiles	It burns with difficulty, gradually goes out	Yellow with blue edge	Cracks when burning	Phenol and formaldehyde	Phenol-formaldehyde (PF)

The combustibility of product samples from the studied polymer materials was evaluated according to the standard method on a device of the type "Ceramic pipe" [14]. By the sum of the indicators (flue gas temperature $t < 450 \text{ }^\circ\text{C}$, damage degrees along the length $\Delta l > 85 \%$ and mass $\Delta m < 50 \%$, self-burning time $30 \text{ s} < \tau < 300 \text{ s}$), most samples of the studied polymer materials can be attributed to group G3 of medium combustibility. Only the performance of the facing tile allows it to be assigned to group G2 of moderate combustibility (flue gas temperature $t < 235 \text{ }^\circ\text{C}$, damage degree along the length $\Delta l < 85 \%$ and mass $\Delta m < 50 \%$, self-burning time $\tau < 30 \text{ s}$).

When evaluating the combustibility of plastics, the method of determining the flame propagation rate by a horizontally fixed sample was used.

For the studied polymer building materials, the products of pyrolysis and combustion were studied, their ignition and self-ignition temperatures, and also the flame propagation velocity were measured. The obtained data on the studied materials are given in Table 2.

Comparing the data obtained, we can conclude that the most combustible of the materials studied are PC panels and PE pipes. PVC linoleum and facing tiles based on PFO occupy an intermediate position in combustibility. The roofing products made of PVC turned out to be the most resistant to burning.

In this work, the polymer building materials losses of heat resistance, impact toughness, and flexural strength under the influence of a flame were studied. Studies were conducted for samples suitable for the test conditions.

For tests on heat resistance according to the Vic method, Ondex roofing and Rolvaplant panels made of PVC were selected. From Fig. 1 shows that the heat resistance of samples that were in the flame for 3...6 s, drops sharply by 20 %.

Table 2. Products of pyrolysis and combustion of polymers

Product name, polymer	Ignition temperature, t_i [°C]	Self-ignition temperature, t_{si} [°C]	Flame spreading speed, v [mm/min]	Pyrolysis products	Combustion products
Water pipes based on PE	341	349	90	Paraffins, olefins, cycloaliphatic hydrocarbons	CO, CO ₂
Tarkett linoleum (PVC) Rolvaplant profile panels (PVC)	391	454	30 - 40	Aromatic hydrocarbons, hydrogen chloride	HCl, CO, CO ₂ , COCl ₂
Polygal PC-based structural panels	522	550	81	Phenol	CO, CO ₂ ,
Facing tile (PFO)	300	430	24	Phenol and formaldehyde	CO, CO ₂ , CH ₂ O

To determine the impact toughness on a device of the Dinstat type, Ondex roofing (PVC), Polygal structural panel (PC), and laminated paper plastic based on PFO were taken. From Fig. 2 shows that the most durable was the Ondex roofing material. However, when exposed to a flame for 3...6 s, the impact toughness of all test materials are reduced by 45-50 %.

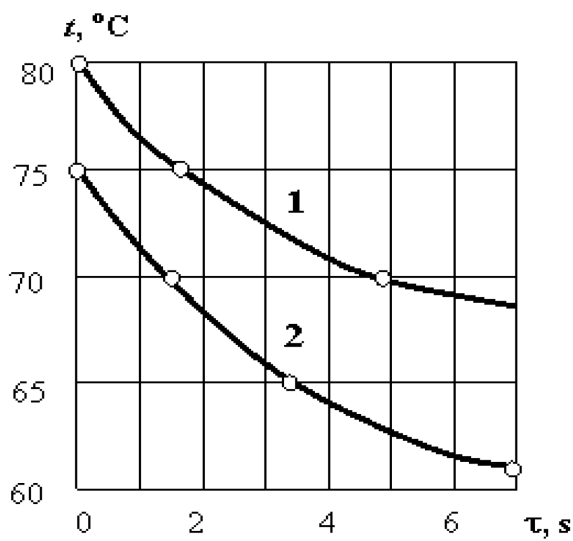


Fig. 1. Dependence of heat resistance of PVC on exposure time of flame: 1 – Ondex roof; 2 – Rolvaplant panels

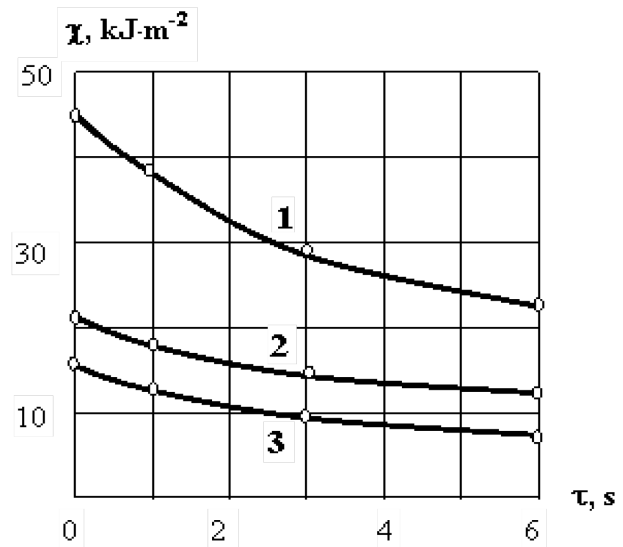


Fig. 2. Dependence of impact toughness on exposure time of flame: 1 – PVC-based plastics; 2 – PFO-based plastics; 3 – PC-based plastics

When determining the bending strength on the Dinstat device, only a sample of the facing tile was chosen. Analyzing Fig. 3, we can say that the sample after 6 s of flame exposure loses its flexural strength by 40 %.

Thermogravimetric analysis of Rolvaplast PVC panels and Poligal PC panels (see Fig. 4) made it possible to determine the maximum decomposition temperatures of these polymers: $t_{PVC} = 250\text{ }^{\circ}\text{C}$, $t_{PC} = 430\text{ }^{\circ}\text{C}$.

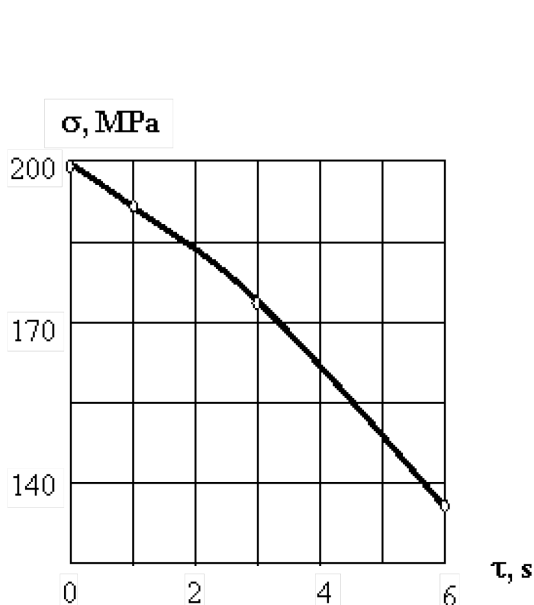


Fig. 3. Dependence of breaking stress during bending of samples of facing tiles based on PFO on time of exposure to flame

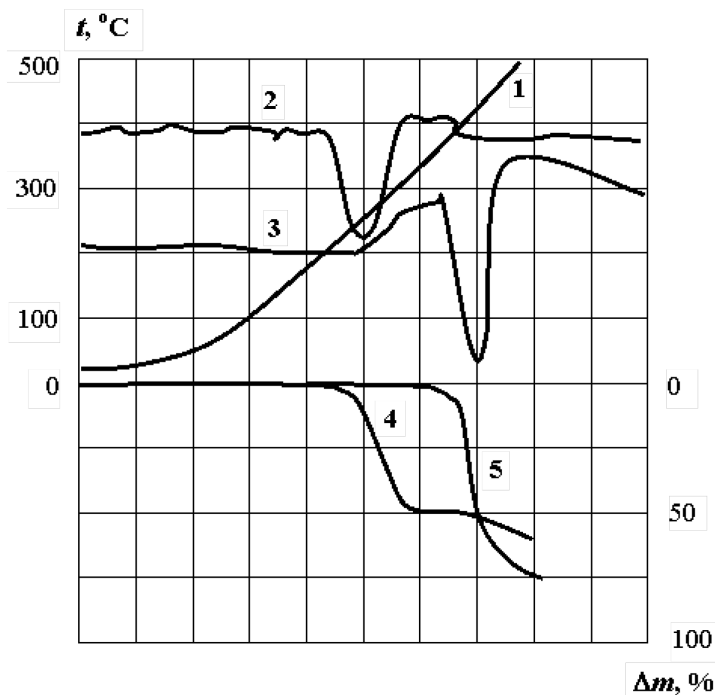


Fig. 4. Thermogram of heating: 1 - temperature curve of heating; 2 - differential curve of weight loss of a sample of a Rolvaplast PVC panel; 3 - differential curve of weight loss of a sample of the Poligal PC panel; 4 - weight loss curve of a sample of a Rolvaplast PVC panel; 5 - curve of weight loss of a sample of the Poligal PC panel

Based on the thermogram, the activation energy of the decomposition process was also calculated: $E_{PVC} = 130\text{ kJ}\cdot\text{mol}^{-1}$, $E_{PK} = 43\text{ kJ}\cdot\text{mol}^{-1}$. The activation energy of PVC-based panels is higher than PC-based panels, i.e. it takes more energy to start decomposing PVC than decomposing a PC. This confirms the previously obtained results that the Rolplast panels belong to the class of slow-burning materials, and the Poligal panels are combustible.

4. Conclusion

Summarizing the results on the combustibility and fire resistance of polymer materials, we can conclude that if the material is recognized as non-combustible or slow-burning, it will not always be fire resistant. This was confirmed by comparing the test results. So the materials of the "Ondex" roof (PVC) and facing tiles based on PFO are slow-burning, but not fire-resistant, since their strength and thermophysical properties sharply decrease in the first seconds of exposure to a flame. PC-based panels are both combustible and not fireproof, although the value of heat resistance for this material is the highest ($t = 150\text{ }^{\circ}\text{C}$). The evaluation of fire resistance by tests for heat resistance, impact toughness and breaking stress during bending showed that the samples, in general, reduce their performance by 20-45 % within 3-6 seconds of exposure to flame.

There is some gap between the requirements for the combustibility of materials and the fire resistance of products made from these materials. A material may be considered non-combustible, and a product made of this material may not be fire resistant due to a sharp decrease in performance.

Therefore, when assessing the operational capabilities of a material, in addition to evaluating its combustibility, it is necessary to know about a change in the strength, thermophysical, and other properties of the material during heating and combustion in order to be able to assess the safety of its operation in emergency situations.

Consideration of the nature of the thermal decomposition reactions of polymer building materials, it can also be noted that a combination of PVC-based materials with materials based on PE, PC, and PFO from the point of view of fire safety is undesirable because that during their joint thermal destruction highly toxic substances can form.

Thus, from the point of view of the convenience of designing finishing work in buildings and monitoring their fire safety, it would be useful to classify polymers according to some general criterion, which would take into account the simultaneous manifestation of several of the most dangerous factors.

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