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Effect of Heat Treatment on the Supramolecular Structure of Copolymers Based on Poly(propylene glycol fumarate phthalate) with Acrylic Acid

Previous studies investigating the thermal decomposition of p-PGFPh:AA copolymers in an inert atmosphere have provided only a general understanding of the changes that occur during thermolysis. Comprehensive studies are required to gain a better understanding of these processes [1]. The most comprehensive information on the influence of various factors on both the kinetics and the supramolecular structure of the resulting products can be obtained by combining the method of thermal analysis with IR, mass spectrometry, and scanning electron microscopy. The compounds studied have two different compositions, namely p-PGFPh:AA 6.77:93.23 mol % and p-PGFPh:AA 86.67:13.33 mol %. These compounds were then subjected to a thermolysis process, which resulted in the emission of gases and a decrease in sample weight. The degradation process can be divided into three stages: 1) Depolymerization of the main chain; 2) Depolymerization of the side chain; 3) Final decomposition. These processes occur sequentially at different temperature ranges. According to TG- and DTG studies, complete decomposition of p-PGFPh:AA copolymers occurred at $T_{\text{term}} = 340\text{--}350\text{ }^{\circ}\text{C}$. In this temperature range, a slight loss of sample mass (less than 10 wt %) was observed along with a slight gas evolution. The main gaseous products from the transformation of the studied samples were CO and CO₂. This was supported by IR-CO (2000–2200 cm⁻¹) and CO₂ (2310–2370 cm⁻¹) as well as mass spectrometric observations. The final products resulting from the thermolysis of p-PGFPh:AA copolymers were examined under an electron microscope. The results showed a similar morphological pattern of mesostructures with sizes ranging from 0.3–1.5 μm, which were observed depending on the porous structure of the initial polymer material. Based on the experimental data, it can be concluded that the p-PGFPh:AA copolymers (in proportions of 6.77:93.23 mol % and 86.67:13.33 mol %) have a relatively high degree of resistance to heating and do not undergo any changes in chemical composition, particle size and shape. In conclusion, the results clearly indicate that the selection of conditions for pyrolysis plays a crucial role in increasing the thermal stability of polymeric materials. This method allows for purposeful changes in the structure and properties of polymers.

Keywords: acrylic acid, poly(propylene glycol fumarate phthalate), polymer, micrographs, morphology, electron microscope, thermogravimetric analysis, supramolecular structure.

Introduction

In terms of production and consumption, the polymer materials industry has grown to enormous proportions, where extending the lifespan of such materials is equivalent to increasing their production from an economic standpoint [2]. It should be noted that it is important to stabilize polymer materials as raw material resources are being depleted each year. Predicting the service life of polymers is a crucial aspect of stabilization. Incorrect determination of the operating time of polymer materials can lead to unexpected premature failure of parts made of polymers and, as a consequence, to the failure of complex technical devices, which is unacceptable (technological factor). Reduced polymer service life leads to economic loss due to underutilization [3–5].

One way to improve the fire resistance of polymers is to add fire retardants as appropriate additives to ensure a safe environment [6–8].

A key concern is the degradation and stabilization of polymers. This involves both ecological and environmental protection issues. From an environmental point of view, it is becoming relevant to address problems related to recycling waste polymers and minimizing the amount of incinerated polymer waste [9–13].

A promising approach is to create polymers with a precisely defined lifespan. These polymers should be utilized while needed and decompose once they are no longer required.

The problem of stabilizing the properties of polymer products is diverse due to the variety of tasks involved. Solving this problem requires a good understanding of the scientific principles of stabilization, as well as knowledge of the mechanisms of polymer degradation and kinetic patterns [10–16].

A significant amount of research is currently being conducted into the ageing process of polymers, resulting in the development of effective measures for comprehensive protection against all types of degradation. The ageing of polymers is characterized by irreversible changes in the polymer chain, which ultimately lead to a loss of the performance characteristics of the polymer product. The aging of polymers is mainly determined by their structure, the stability of their bonds, and the type of side groups. At most, the macromolecular chains in our body tend to break down, resulting in the formation of many low molecular weight fractions. This process leads to a decrease in the average molecular weight and an expansion of molecular weight distribution [16-17].

The reactivity of the molecular chain causes polymer aging. The rate and direction of aging depend on the molecular and supramolecular structure. The supramolecular structure (morphology) is determined by the way the chains are arranged (packing) into spatially distinct elements in a solid (block) polymer, as well as the size, shape and relative arrangement of these elements. Indeed, the chemical properties of polymers are influenced by various factors such as the length and stereoisomerism of the chains, the way in which the macromolecules are stacked, and their crystallization [18–21].

The supramolecular structure of the polymer is not perfect. It contains correctly packed macromolecules in both crystalline and amorphous regions, but there are also many defects and disturbances of order. These features have significant consequences for the aging of solid polymers [22-23].

Firstly, structural and physical heterogeneity results in the non-uniform distribution of reagents and additives within the polymer system. Secondly, structural microheterogeneity leads to a broad distribution of regions exhibiting disparate frequencies of molecular motion within the polymer. This results in a wide range of kinetic constants and activation energies for elementary reactions. All this makes polymers more susceptible to aging [24–26].

Polymeric materials based on unsaturated polyester resins are widely used in various industries and in our daily lives due to their good mechanical properties, strength, biocompatibility, viscoelastic nature, and the ability to take any shape during processing. Extensive research has been carried out to develop methods for producing unsaturated polyester resins [27-28], including one of the main sources of raw materials — poly(propylene glycol fumarate phthalate), which is used to produce the proposed copolymer (which can be used as hydrogels in the processing of vegetable crops). It is worth noting that the production technology for this raw material has been fully developed [28-29].

The use of moisture sorbents in agriculture for growing crops has led to an increase in the use of hydrogels. However, the long-term use of artificial soil made from hydrogels can lead to their aging and degradation, which can result in reduced crop yields. At present, we do not fully understand the substances that cause the polymer gels added to natural soils and the structures that form the basis of artificial soils to degrade under the influence of various environmental factors. It is vital to identify these factors, including seasonal and daily fluctuations in temperature, in order to prevent the degradation process and maintain high crop yields. We are among the first in the world to emphasize the need to address these issues.

Solving these problems is impossible without studying the supramolecular structure (morphology) of polymer materials using electron microscopy as a function of annealing temperature (it is also important to note that heat treatment affects the morphology of the polymer!). The results obtained make it possible to reveal the mechanism of destruction of a real polymer and try to control it in the desired direction.

The objective of the research is to investigate the supramolecular structure formation mechanisms of copolymers of poly(propylene glycol fumarate phthalate) and acrylic acid, before and after being subjected to heat treatment.

Experimental

Copolymers based on poly(propylene glycol fumarate phthalate) [29] with acrylic acid (Sigma-Aldrich, Germany) at different initial ratios of 6.77:93.23 mol % and 86.67:13.33 mol % were selected as objects of study [27, 30].

Poly(propylene glycol fumarate phthalate) is a chemical compound produced by a polycondensation reaction of propylene glycol, phthalic anhydride, and fumaric acid. The reaction takes place at a temperature of

180 °C and is carried out using a standard procedure [30]. An aluminum chloride catalyst is used in a nitrogen stream to prevent unwanted gelatinization processes. The reaction time is 16 hours.

Copolymers were produced by mixing comonomers in dioxane at 60 °C in glass ampoules. The combination of comonomers ranged from 0.02–0.8 mol fractions with a total monomer concentration of 1 mol/l and $[PB] = 1.0 \cdot 10^{-2}$ mol/l. The copolymers were extracted from the solution by precipitation with hexane followed by re-precipitation with a toluene solution. The samples were then dried under vacuum at 40–45 °C. The PB initiator was recrystallized from benzene several times and stored at –10 °C. The solvents, namely dioxane and ethanol were dried and purified according to known methods.

The study of the microstructure and quantitative analysis of the elemental composition of the surface layer of copolymers were carried out using a JEOL JSM-5910 electron microscope (Jeol Company, Japan). The samples were scanned at varying magnifications ($\times 500$, $\times 1500$, $\times 3000$, $\times 10000$).

The copolymer's surface morphology was studied with the help of an NT-206 atomic force microscope (AFM) (manufactured by MTM in Minsk, Republic of Belarus) in a static scanning mode. A CSC 12/15 silicon cantilever was used for the same. The experimental data were analyzed and visualized using the SurfaceXplorer software (developed by Microtestmachines, an additional liability company) and nanoImages (Scientific Research Center for Preservation of the National Academy of Sciences of Belarus SSI).

The kinetics of the thermal destruction process was studied by thermal analysis with the registration of TGA-DSC-IR curves on a Netzsch Jupiter STA 449 F3 (Germany) combined with a QMS 403 Aeolos Quadro mass spectrometer (NETZSCH-Gerätebau GmbH, Germany) for better accuracy. The sample weighed 30 mg in the form of ground powder. TG curves of the samples were recorded in the range from 50 to 800 °C with heating rates of 5, 7.5, 10.0, 12.5 °C/min in a nitrogen atmosphere.

The experimental data obtained were processed using the licensed software “Origin Pro 8.1”.

Results and Discussion

It is known that network polymers, i.e. PGFPh:AA copolymers, are particles with uncontrolled parameters of molecular weight and morphology [31]. In this work, the dimensional characteristics of the p-PGFPh:AA copolymer were assessed by electron microscopy and the morphological characteristics of p-PGFPh:AA polymer particles were studied.

Many polymeric materials have relatively high thermal stability; they decompose under the influence of high temperatures in a nitrogen atmosphere [32]. Thermal analysis was conducted on the p-PGFPh:AA copolymer (6.77:93.23 mol %) using thermal analysis to record TGA-DSC-IR curves on a Netzsch Jupiter STA 449 F3 instrument combined with a QMS 403 Aeolos Quadro mass spectrometer (Fig. 1). A detailed description of the degradation mechanism of p-PGFPh:AA copolymers of different initial ratios has been given in the referenced work [32].

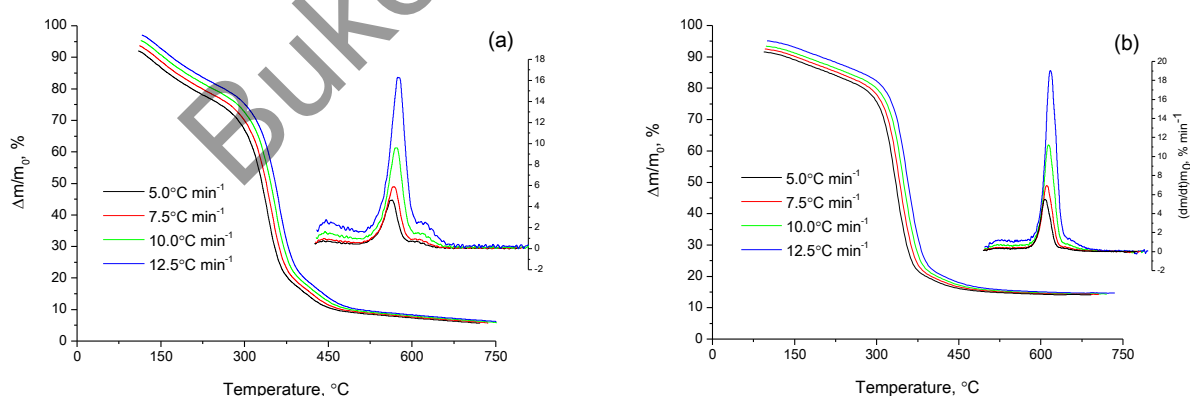


Figure 1. Thermograms of p-PGFPh:AA copolymers at the initial ratios $M_1:M_2$, mol %: (a) — 6.77:93.23 mol %; (b) — 86.67:13.33 mol % in a nitrogen atmosphere

During the annealing process of p-PGFPh:AA copolymers, morphological changes occur along with changes in its chemical composition. The copolymer is a polymer chain of unsaturated polyester resin, which undergoes thermal decomposition in the absence of oxygen. This process can result in the destruction of the copolymer at the ester bond, and the release of carbon dioxide during thermal destruction. Analysis of gaseous products resulting from the thermal decomposition of p-PGFPh:AA copolymers ($T_{\max} = 340\text{--}350$ °C)

indicates the formation of toxic gases, including carbon monoxide (CO) and carbon dioxide (CO₂). Based on TG/DSC-MS analysis, it was found that increasing the proportion of acrylate units in the p-PGFPh:AA copolymer (6.77:93.23 mol %) resulted in a 50 % reduction in the formation of toxic gaseous products such as carbon monoxide (CO) and carbon dioxide (CO₂) (Fig. 2).

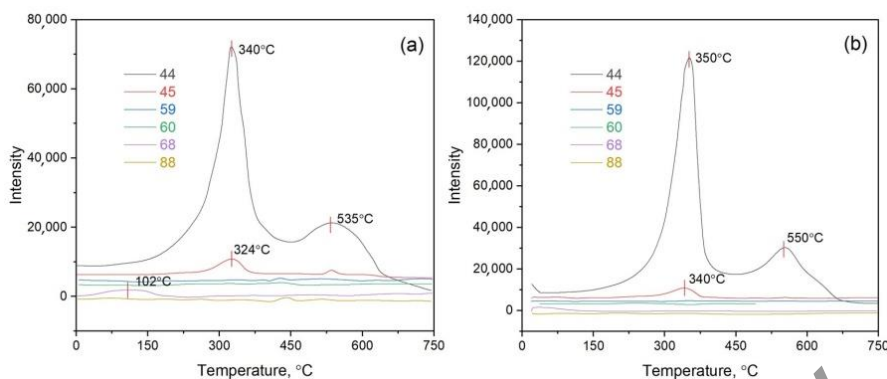


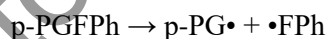
Figure 2. Chromatogram of the pyrolysis products of p-PGFPh:AA copolymers at the initial ratios $M_1:M_2$, mol %: (a) — 6.77:93.23 mol % and (b) — 86.67:13.33 mol %

In these mass spectra in Figure 2, the most intense peaks correspond to a molecular ion with a mass of 44 amu. The results of a search against the NIST mass spectrum database indicate that this peak corresponds to carbon dioxide (CO₂). The release of a small amount of CO₂ also occurs at ~538 °C for p-PGFPh:AA copolymers (6.77:93.23 mol %) and ~550 °C for p-PGFPh:AA copolymers (86.67:13.33). When comparing the thermograms of the samples, it can be concluded that p-PGFPh:AA copolymers are thermally stable [1]. During annealing, p-PGFPh:AA copolymers become black in color which can be attributed to the formation of carbon.

The reaction mechanism of the thermal degradation of the copolymer of poly(propylene glycol fumarate phthalate) with acrylic acid can be presented as follows [1]:

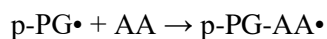
1. Initiation:

Decomposition of p-PGFPh under the influence of high temperatures and the formation of active radicals:



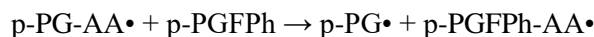
2. Reaction of p-PGFPh radicals with acrylic acid:

p-PG•/•FPh radicals can react with acrylic acid (AA) via an addition reaction to form an adduct:



3. Continued breaking of chemical bonds:

The p-PG-AA• adduct can react further with other radicals or p-PGFPh molecules, breaking bonds and forming new radicals:



4. Formation of destruction products:

The process of breaking down a p-PGFPh:AA copolymer can result in the formation of degradation products such as acrylic acid (AA) monomers, p-PGFPh monomers, and other fragmented compounds. These fragments can further degrade to smaller organic compounds such as acids, aldehydes, CO, CO₂, and other products. The thermal degradation of the copolymer leads to the cleavage of bonds within the macromolecule, resulting in the formation of reaction fragments and degradation products.

In some cases, certain volatile polymer products can be identified by a strong infrared absorption peak. This peak is usually associated with gas phase components of the pyrolysis products, which are mainly CO₂ (2310 cm⁻¹) and CO (2000 cm⁻¹). The results of IR spectrometric analysis confirm this conclusion (Fig. 3).

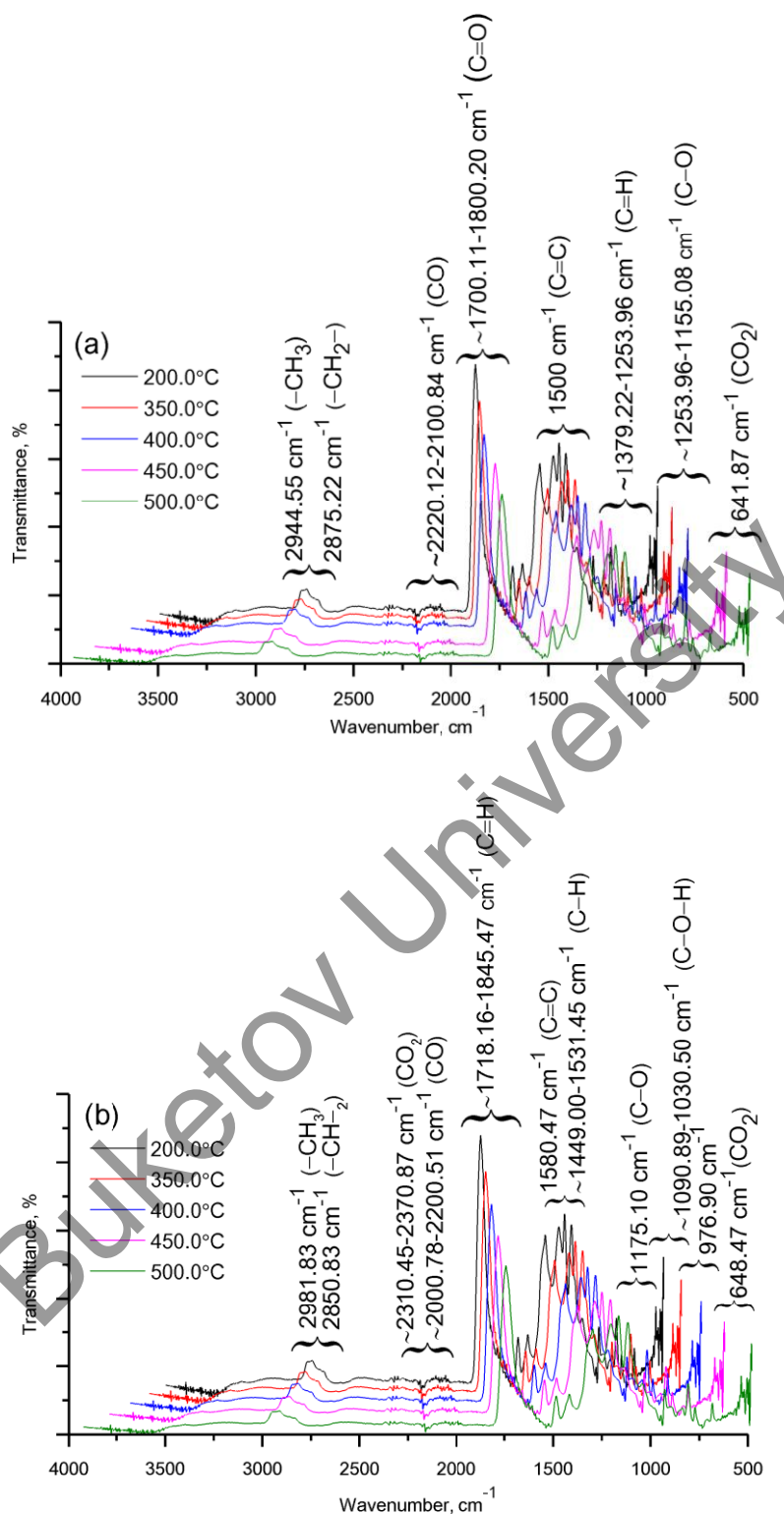


Figure 3. IR spectra of p-PGFPh:AA decomposition products at ratios M₁:M₂, mol %: (a) — 6.77:93.23 and (b) — 86.67:13.33 recorded at temperatures between 200 and 500 °C

In order to determine the potential of p-PGFPh:AA copolymers as binder substances, it is important to understand how they change under high temperatures at different ratios (6.77:93.23 mol % and 86.67:13.33 mol %). To achieve this, it is necessary to study the evolution of the polymer morphology during heat treatment in a nitrogen atmosphere. Annealing can cause phase transformations, recrystallization, and changes in the morphology and characteristics of polymers. It is known that the mobility of polymer molecu-

lar chains increases with temperature. The morphology of polymers is influenced by chain mobility and recrystallization.

After being exposed to a temperature of 150 °C, the surface of p-PGFPh:AA copolymers (initially mixed in the ratio of 6.77:93.23 mol %) showed slight deformation with darkening as shown in Figure 4, *a*. When annealed at 200 °C, the surface appeared wavy with local formation of bumps and grooves. Charring of the material caused a significant darkening and turned it to a brown color as shown in Figure 4, *b*. The change in the surface topography of the copolymers becomes more pronounced as the temperature is increased to 350 °C: local formations appear in the form of mounds and pits, i.e. the surface becomes rough (Fig. 4, *c*). Annealing at 400 °C does not lead to any significant change in the morphology of the copolymer surface; it is only characterized by a greater darkening of the p-PGFPh:AA copolymer (Fig. 4, *d*). The copolymer annealed at 450 °C is characterized by a certain smoothing of the surface relief of the copolymers, but with an obvious blackening and a metallic sheen (Fig. 4, *e*). Membrane samples become hard and brittle. After annealing at 500 °C, the brittle copolymer begins to deteriorate and crumble, which indicates almost complete decomposition of the polymer (Fig. 4, *f*).



a — 150 °C; *b* — 200 °C; *c* — 350 °C; *d* — 400 °C; *e* — 450 °C; *f* — 500 °C

Figure 4. Annealed copolymers p-PGFPh:AA at the initial ratios of 6.77:93.23 mol %

The change in film morphology was analyzed by scanning electron microscopy (Fig. 5). Micrographs of the synthesized poly(propylene glycol fumarate phthalate) with acrylic acid are shown in Figure 5 *a, b*. A study of the surface morphology of the resulting p-p-PGFPh:AA copolymer (at the initial ratio of 6.77:93.23 mol %) showed that the latter is a rather complex structural and morphological organization. Photographs of the sample show a characteristic openwork structure with a high proportion of smaller pores (Fig. 5, *a* and *b*).

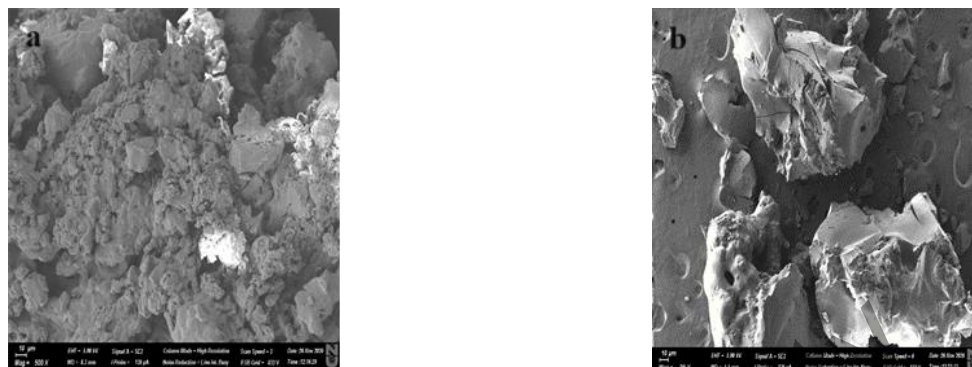


Figure 5. Scanned electron micrographs of the p-PGFPh:AA copolymer at the initial ratios of 6.77:93.23 mol % at magnification: $\times 3000$

This is also evidenced by the data on the state of the surface prior to temperature modification obtained using an atomic force microscope (Fig. 6).

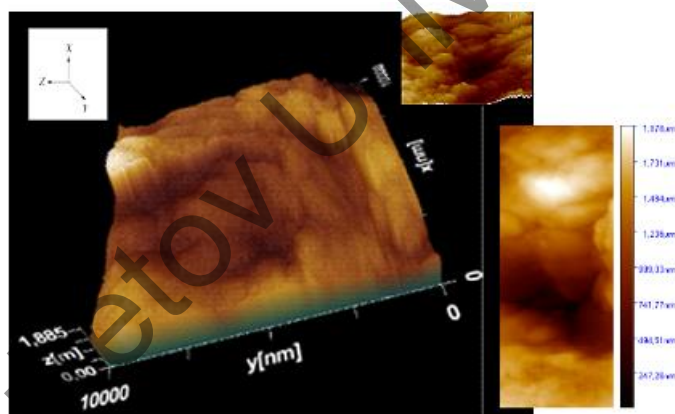
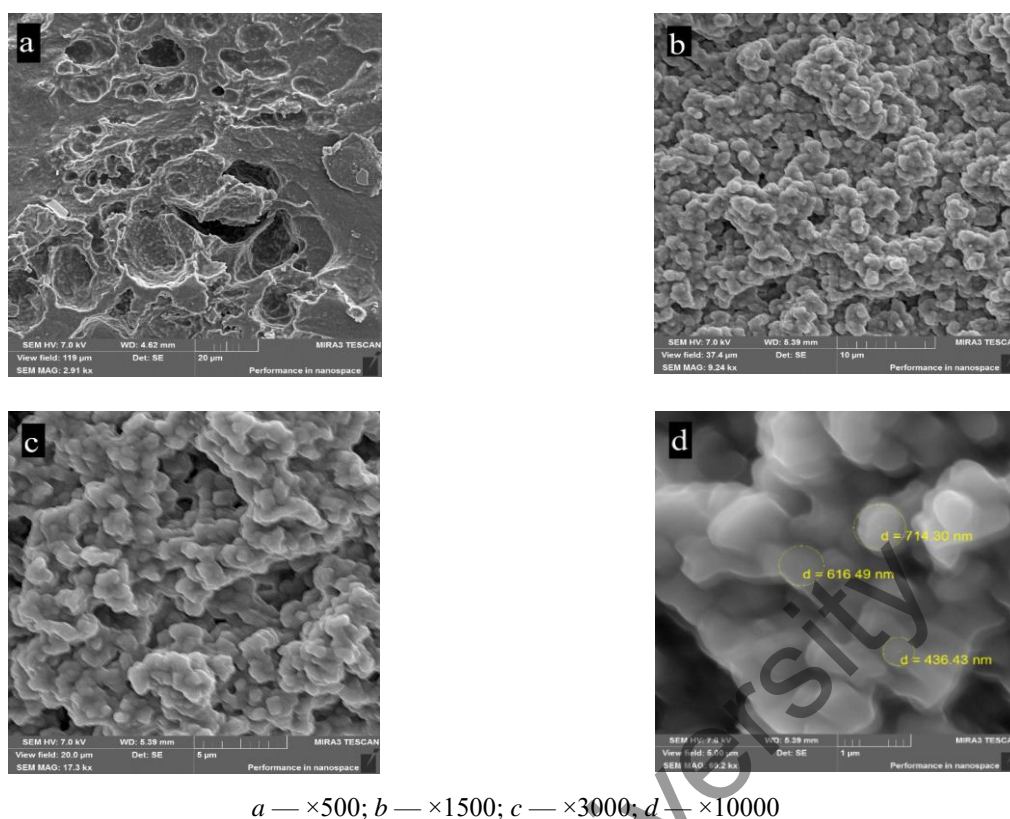


Figure 6. 3D visualization of the surface relief of the p-PGFPh:AA copolymer at the initial ratio of 6.77:93.23 mol % with backlit height

Analysis of the 3D image (Fig. 6) of the p-PGFPh:AA copolymer film (6.77:93.23 mol %) showed that the surface of this copolymer is not flat and has irregularities. A morphometric study of dimensional parameters requires consideration of the shape, radius of curvature, length, width, and height. The studied p-PGFPh:AA copolymer has a length of 105.39 ± 9.86 nm, width of 110.49 ± 11.69 nm, and height of 20.58 ± 3.56 nm. The use of the root-mean-square roughness parameter (R_q is the deviation of the profile points from its center line) and subsequent analysis of the degree of development of the relief show that the surface of the copolymer under study is heterogeneous in texture (R_q values are about 8.69 ± 0.5 nm (Fig. 6)). Analysis of the above three-dimensional image of the surface of the p-PGFPh:AA copolymer (6.77:93.23 mol %) indicates that the analyzed surface of the sample is not flat and that there are irregularities of various sizes on its surface.

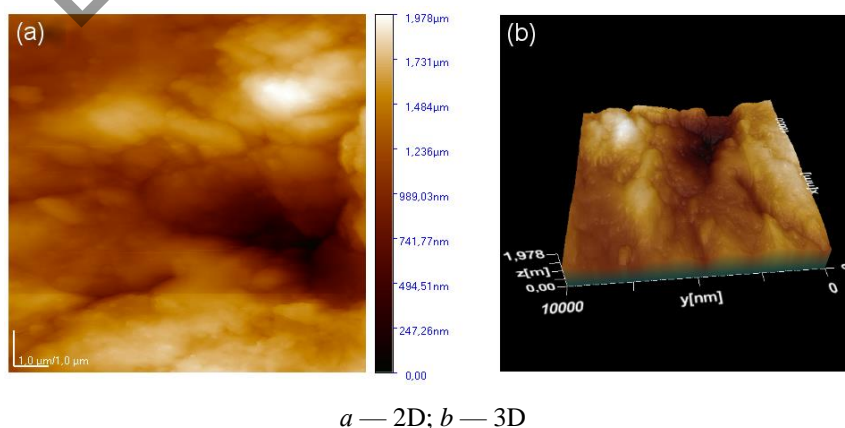
Annealing the copolymers at 290 °C leads to deformation of the polymers (Fig. 7). Figure 7 (*a*) shows that p-PGFPh:AA particles have different shapes and sizes, ranging from several tens to hundreds of microns.



a — $\times 500$; *b* — $\times 1500$; *c* — $\times 3000$; *d* — $\times 10000$

Figure 7. Micrograph of the morphology of the p-PGFPh:AA copolymer at the initial ratio of 6.77:93.23 mol % after heat treatment at 290 °C with successive magnification

Figure 7(a) shows that the surface of the sample appears heterogeneous and has different textures with many microscopic bumps and pores (~ 20 nm). The convex part of the p-PGFPh:AA copolymer at the initial ratio of 6.77:93.23 mol % after heat treatment consists of sintered (shrunken) particles (Fig. 7, a). Upon further magnification (Fig. 7, b), it is clear that the sintered part consists of smaller compacted parts (Fig. 7, c), the surface of which is within the range of 400–700 nm on further magnification (Fig. 7, d). Analysis of the micrographs shows that the structural components are strikingly similar, differing only in size. The SEM images suggest the presence of microphases within the copolymer structure, which could be attributed to thermal treatment at 290 °C. The copolymer surface as illustrated in Figure 7 (b) and (c) appears to have an inconsistent, irregular structure, comprising a mixture of globules and pores of various shapes and sizes, with agglomerates of undefined shapes ranging from 10 to 65 μm . This may be due to changes in the crystal structure or chemical reactions within the copolymer.

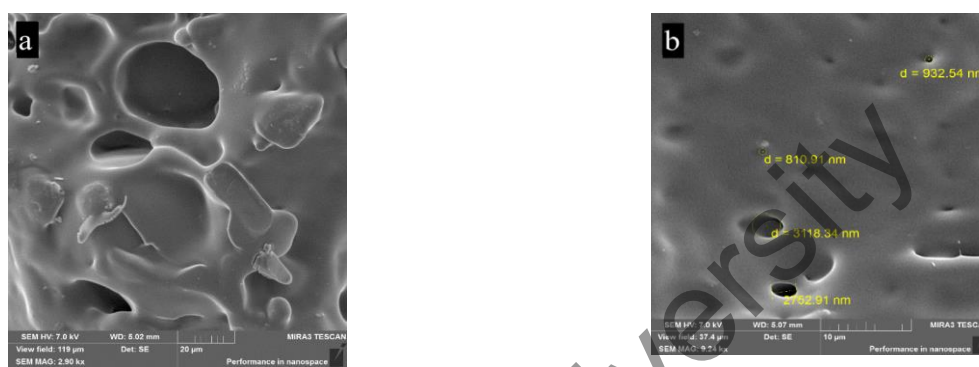


a — 2D; *b* — 3D

Figure 8. Images of the topography of the surface of the p-PGFPh:AA copolymer (6.77:93.23 mol %) after heat treatment at 290 °C

Figures 8 (a) and (b) show the p-PGFPh:AA copolymer with the characteristic topography (6.77:93.23 mol %) obtained using AFM: the surface is covered with spike-like protrusions, the width of which is 110.4 ± 8.1 nm, the length is 25.1 ± 2.7 nm, the average quadratic surface roughness R_q is 8.3 ± 0.8 nm. The high flexibility (in comparison with the p-PGFPh:AA copolymer before firing) can be considered as one of the possible reasons for a slight increase in the surface roughness of this sample.

Next, micrographs of samples of the copolymer composition (6.77:93.23 mol %) were obtained after heat treatment at 440 °C (Fig. 9). The micrographs show the surface of a copolymer of poly(propylene glycol fumarate phthalate) with acrylic acid after heat treatment at 440 °C. The surface of the sample appears greatly altered compared to the untreated sample (Fig. 9). Many small convex and depressed formations can be observed. These structures have dimensions within ~ 1.5 μm (Fig. 9, a). The surface of the sample also appears to be relatively smooth, but with small features at the micro level. The presence of acrylic acid in the copolymer can influence its morphology and structure (Fig. 9, b).



a — $\times 500$; b — $\times 1500$

Figure 9. Micrograph of the morphology of the p-PGFPh:AA copolymer at the initial ratio of 6.77:93.23 mol % after heat treatment at 440 °C with successive magnification

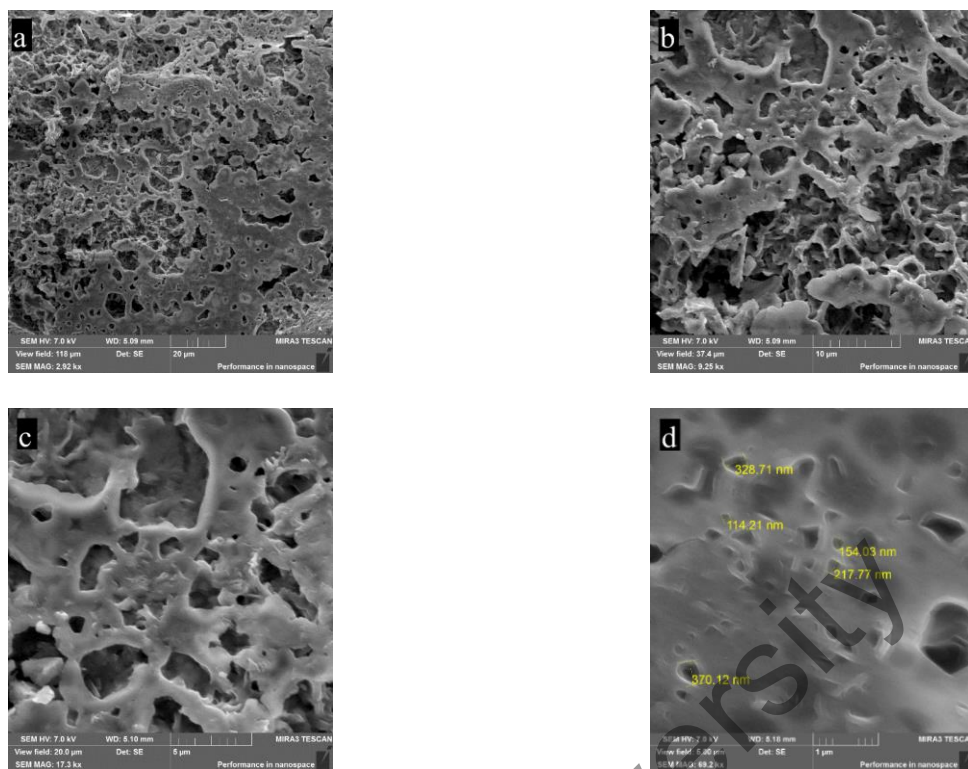
As shown above, the process of sintering and, accordingly, the structure formation of the p-PGFPh:AA copolymer during heat treatment is not a spontaneous process. Based on this, the effect of unsaturated polyester resin on the structure of the p-PGFPh:AA copolymer during heat treatment was investigated. Microscopic studies were carried out on the p-PGFPh:AA copolymer, where the content of poly(propylene glycol fumarate phthalate) in the copolymer was 86.67 mol %.

Figure 10 shows that significant changes in the morphology of the copolymer p-PGFPh:AA (86.67:13.33 mol %) were observed after heat treatment up to 240 °C. The copolymer film has an undefined architecture with a knobby surface, Figure 10 (a) and (d).

These changes may be related to melting processes, structural reorganization, or possible chemical reactions. Differences in the size and shape of structures may indicate heterogeneity in the sample after processing.

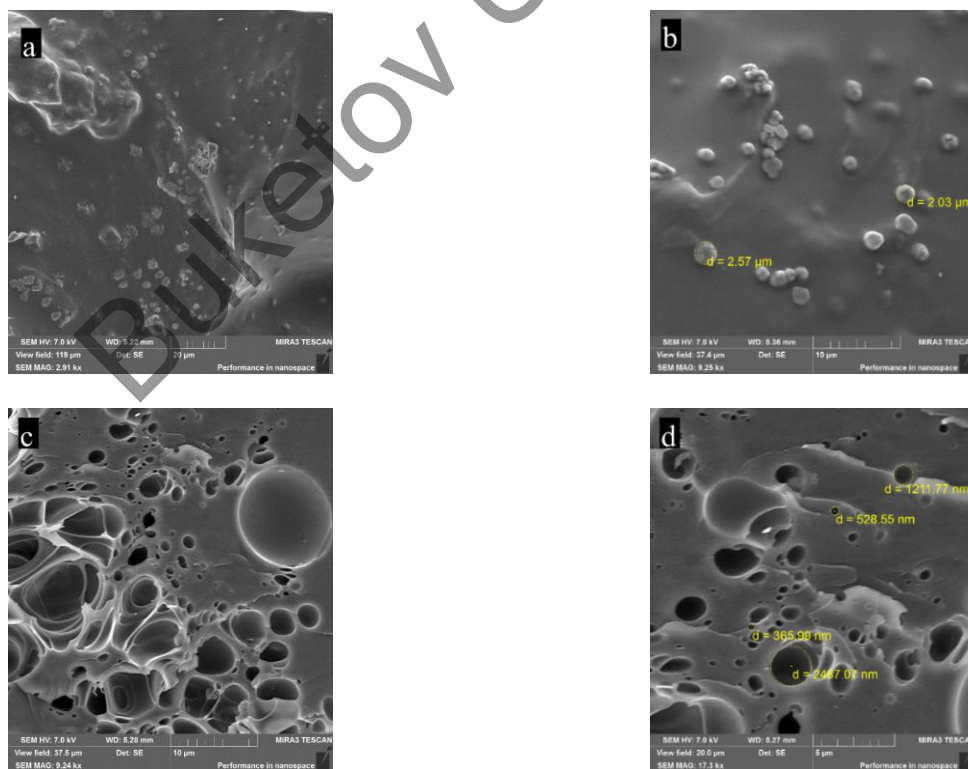
Next, micrographs of samples of the copolymer composition were obtained at the initial ratio of 86.67:13.33 mol % after heat treatment up to 440 °C (Fig. 11).

Numerous tiny convex structures with a diameter of approximately 1–5 micrometers are visible. These structures are uniformly distributed over the entire surface of the sample and may represent phase regions with distinct characteristics. The images (Fig. 11) do not show a specific orientation of pores and particles, which may indicate a random and disordered distribution of these elements on the surface. The micrograph indicates that heat treatment of the copolymer p-PGFPh:AA (copolymer at the initial ratio of 86.67:13.33 mol %) results in the formation of pores and small particles on its surface. These structural changes can have various causes, such as the release of gases, changes in the crystal structure or chemical reactions. Pores and particles influence the physical and chemical properties of the p-PGFPh:AA copolymer (86.67:13.33 mol %).



a — $\times 500$; *b* — $\times 1500$; *c* — $\times 3000$; *d* — $\times 10000$

Figure 10. Micrograph of the morphology of the p-PGFPh:AA copolymer at the initial ratio of 86.67:13.33 mol % after heat treatment up to 240 °C with successive magnification



a — $\times 500$; *b*, *c* — $\times 3000$; *d* — $\times 10000$

Figure 11. Micrograph of the morphology of the p-PGFPh:AA copolymer at the initial ratio of 86.67:13.33 mol % after heat treatment to 410 °C with successive magnification

From Figures 10 and 11 it can be seen that as the degree of unsaturation in the copolymer (p-PGFPh content in the copolymer) increases, the cured products become less hard and more viscous. This relationship is due to a reduction in the cross-linking density resulting in fewer chains to support the load.

Conclusions

The paper discusses the findings of microscopic studies carried out on copolymers of p-PGFPh:AA before and after heat treatment. In contrast, the structure of the p-PGFPh:AA copolymer (6.77:93.23 mol %) is isomorphic both before and after heat treatment to 290 °C. However, if the p-PGFPh:AA copolymer (6.77:93.23 mol %) has a “popcorn” structure, then it is completely preserved even after heat treatment up to 290 °C (Fig. 7, *b* and *c*). Consequently, the process of temperature exposure does not cause any change in the structure of the copolymer, and the morphology of polymers after heat treatment is determined only by the morphology of the original polymer. A scanning microscopy study of the cleavage surface of p-PGFPh:AA copolymers shows that the size of the smallest elements is ~20 nm (Fig. 7, *a*). Larger formations are also present in all electron microscopic images, but in some cases, at magnifications of 500 to 10,000 (e.g. Fig. 7, *b* and *c*), they can be seen to be composed of smaller spherical particles of ~10 nm in size. The p-PGFPh:AA copolymer (86.67:13.33 mol %) has a completely different morphology. The structure of the p-PGFPh:AA copolymer (86.67:13.33 mol %) turns out to be close to the structure of networks, the average size of spherical formations is 25–45 nm (Fig. 10, *b* and *c*). Despite significant differences in the morphology of p-PGFPh:AA copolymers at different component ratios, p-PGFPh:AA copolymers with monomer ratios of 6.77:93.23 mol % and 86.67:13.33 mol % have the same properties — porous structure. Consequently, these properties are not due to the nature of supramolecular formations, but to the properties of smaller structural units of the network at the molecular level. It was also shown that when heated in a nitrogen atmosphere to 800 °C, they formed the same amount of stable polymer residue, indicating the similarity of their thermal stability (Fig. 4).

The results obtained suggest that the degradation of p-PGFPh:AA copolymers is a complex process. It involves the breaking chemical bonds by heat as well as structuring reactions between macromolecules and their decomposition products. It is important to note that selecting conditions for pyrolysis plays a significant role in increasing the thermal stability of polymeric materials. This is because pyrolysis can be used to selectively modify the structure and properties of polymers.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. **CRedit: Akmaral Zhakanovna Sarsenbekova, Abylaikhan Nurlanuly Bolatbay & David Havlicek** conceptualization, data curation, investigation, methodology, validation, visualization, writing-review & editing; **Zhannur Amirgalieva Issina** & data curation, formal analysis, visualization; **Assiya Zhakanovna Sarsenbek** data curation, formal analysis; **Nurgul Almatovna Kabdenova & Muslim Anuaruly Kilybay** conceptualization, data curation, formal analysis, funding acquisition, resources, supervision, validation, writing-original draft, writing-review & editing.

Conflicts of Interest

The authors declare no conflict of interest.

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