

Original Article

Synthesis of High Durability Polyurethane Based on Basalt Mineral

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Abstract - This research work synthesized an oligomer based on urea, glycerol, and formaldehyde. Based on this obtained oligomer, polyurethane with high strength was obtained. Phthalic anhydride and basalt minerals were used to increase the hardness of the synthesized oligomer. According to the obtained results, the mass ratio of oligomer and phthalic anhydride and basalt minerals was 20:6:9 grams, respectively. The procedure duration was 1 hour, and the temperature was 35 °C. The physicochemical properties of oligomer and polyurethane were studied and analyzed using IR-spectroscopic, Chromato-mass spectra, scanning electron microscope SEM, and Smart EDS. Also, the hardness, elasticity, and plasticity indicators of the obtained composite polyurethane were determined by the Brinell method. In this case, polyurethane showed the highest hardness when the percentage of basalt mineral reached 3%.

Keywords - Basalt mineral, Formaldehyde, Glycerin, Oligomer, Polyurethane, Phthalic anhydride, Urea.

1. Introduction

Oligurethanes and polyurethanes are one of the most important classes of thermoplastic polymers with universal structural significance. Polyurethane elastomers are segmented copolymers consisting of hard and soft segments [1, 2]. Thermoplastic Polyurethane (TPU) is a linear polymer with relatively long, flexible, soft-chain segments joined end to end by rigid, hard-chain segments through covalent chemical bonds [3]. This work intends to novel fluorinated polyurethane hybrid latexes in the size range of 40–50 nm, fluoroalkyl acrylate as fluorinated monomers, with various fluorine content (F%=9~26 wt%) were successfully prepared via emulsion polymerization process without traditional emulsifier [4]. This work aims to enhance the fire safety of Thermoplastic Polyurethane (TPU) composites by developing an Intumescent Flame-Retardant (IFR) system consisting of ammonium polyphosphate (APP), melamine polyphosphate (MPP), and pentaerythritol (PER), with nano-silica and cone calorimeter results showed superior fire performance of the TPU/IFR composites. The combination of 40 wt% APP, 10 wt% MPP, and 1 wt% PER significantly decreased the Peak Heat Release (PHRR) and Smoke Production Rates (SPR) by 80% and 89.6%, respectively, with little dripping and without significant deterioration of mechanical properties [5, 6]. In this work, the effect of a mixture of halogen-containing flame retardants based on chloroparaffins and 1,1,9-trihydroperfl

uoronanol-1 immobilized on a montmorillonite carrier on the character of reducing the flammability of polyurethane was studied [7]. A two-step reactive process synthesized flexible polyurethane/organically modified nanoclay (organoclay) nanocomposite foams. The XRD patterns of a polyurethane foam sample containing 2 wt.% of nano clay revealed clay intercalation. Furthermore, SEM images of the prepared foams showed that incorporating clay into the polyurethane foams results in a reduction of cell size and an increase in cell density, and these phenomena were explained based on nucleation promotion in the presence of clay [8, 9]. The influence of compositions based on 1H,1H,9H-trihydroperfluorononan-1-ol, montmorillonite and polytetrafluoroethylene Fluralite on the structure and wear resistance of the polyurethane elastomer modified by them is considered. The introduction of polyelement modifiers leads to the reorganization of the amorphous structure of the polymer matrix and changes in the properties of the surface [10, 11]. In this respect, the latest advances in the production of bio-based polyurethanes are collected in this article. Thus, after a brief introduction to this subject and main tendencies towards the production of more sustainable polyurethanes, the first section reviews the feasibility of manufacturing polyurethanes from a range of natural platforms, including lignocellulosic biomass and vegetable oils, whether modified or in their original form, along with some industrial wastes [12, 13].



2. Materials and Methods

New oligomer and polyurethane synthesis obtained the following substances: Urea, glycerin, formaldehyde, phthalic anhydride and basalt mineral particles. The following devices were used to determine the physicochemical properties of the synthesized oligomer and polyurethane composition: infrared spectroscopy (IR) "IRTracer-100" (SHIMADZU CORP., Japan, 2017) spectrometer, scanning electron microscope (SEM, SmartSEM program SEM-EVO MA 10 (analyzed by Carl Zeiss, Germany). Universal testing machine. Autograph AGS-X. 10kN. Shimadzu Japan.

3. Experimental Part

3.1. Synthesis and properties of oligomer based on glycerol, urea and formaldehyde

The production of urethane oligomer OU-400 begins with the reaction of urea with glycerol. The reaction proceeds as follows:

As a result of the reaction, glycerol-based diurethane is formed. The previously obtained diurethane is reacted with

formaldehyde and urea in the second stage. The correct choice of reaction conditions makes it possible to eliminate the oligomer. Synthesis of oligomer based on glycerol. 50 grams of urea are placed in a flask equipped with a stirrer, reflux condenser and thermometer and heated to 95 - 100 °C. While stirring, add 31 grams of glycerin at such a rate that the reaction mass temperature is not lower than 100 °C. After pouring in the entire prescribed amount of glycerin, the temperature of the reaction system is raised to 120 °C. At this temperature, the reaction is carried out for 30 minutes.

Next, the temperature should be raised from 120 oC to 135-140 oC within 15 minutes. At the reached temperature, the reaction proceeds for 2 hours. When the temperature rises from 125 – 130 °C, the reaction mass begins to release ammonia. Ammonia production can be determined using wet litmus paper. The release of ammonia stops at the end of the interaction process between urea and glycerol. After completion of the reaction, slowly reduce the temperature to 70 °C and hold the light brown viscous-liquid mass at a temperature of 60 - 70 °C for 30 - 40 minutes.

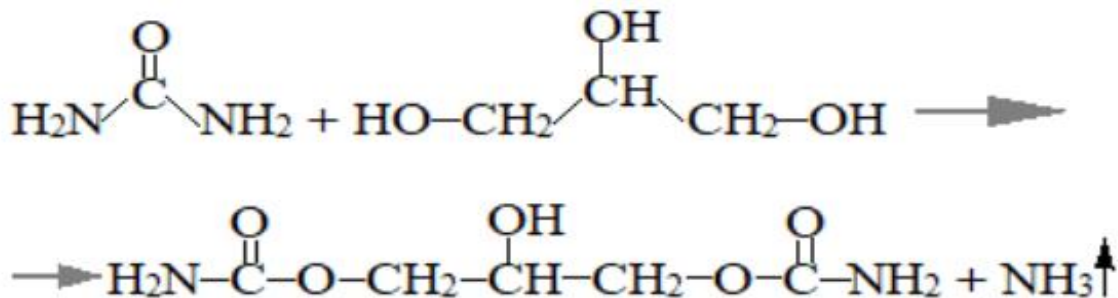


Fig. 1 Formation of a hydrazide derivative from hydrazinecarboxamide and glycerol

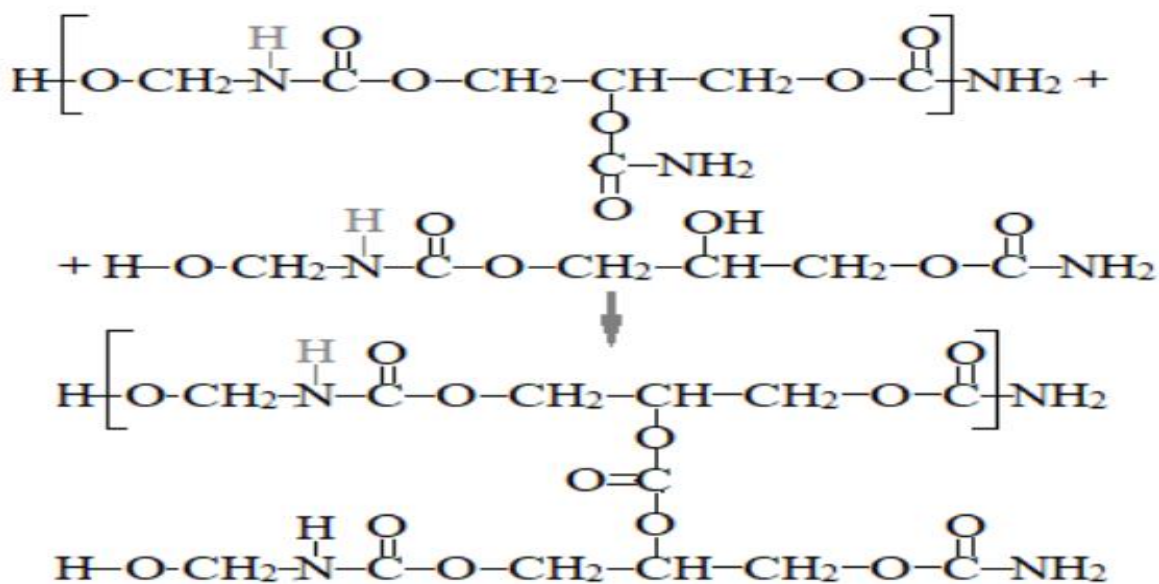


Fig. 2 Crosslinking reaction between polyhydrazides

3.2. Chromatography-Mass Spectroscopy

Based on the results of gas chromatography-mass spectroscopy, the mass spectra of oligomers were recorded (Figure 3). The macromolecular oligomers ion with the largest molecular weight has a mass of 658.

3.3. IR-Spectrum Analyses

The IR spectrum contains weak absorption bands of stretching vibrations of -C-H bonds in the 2920.3-2852.72 cm^{-1} region and bending vibrations of hydroxyl groups in the region of 1037.70 cm^{-1} .

The absorption band in the region of 1616.35 cm^{-1} explains the presence of the -CO-NH₂ group. The IR spectrum contains absorption band 59 in the region of 1653.00 cm^{-1} , corresponding to -NH₂ groups. The absorption band in the region of 854.47 cm^{-1} corresponds to the stretching vibrations of C-N groups. The C-O-C group causes asymmetric stretching vibrations in the region of 1173.68 cm^{-1} . The absorption band in the region of 1247.94 cm^{-1} corresponds to the stretching vibrations of -O-CO-O- groups. The absorption band in the region of 1732.08 cm^{-1} indicates the presence of an unsubstituted urethane group.

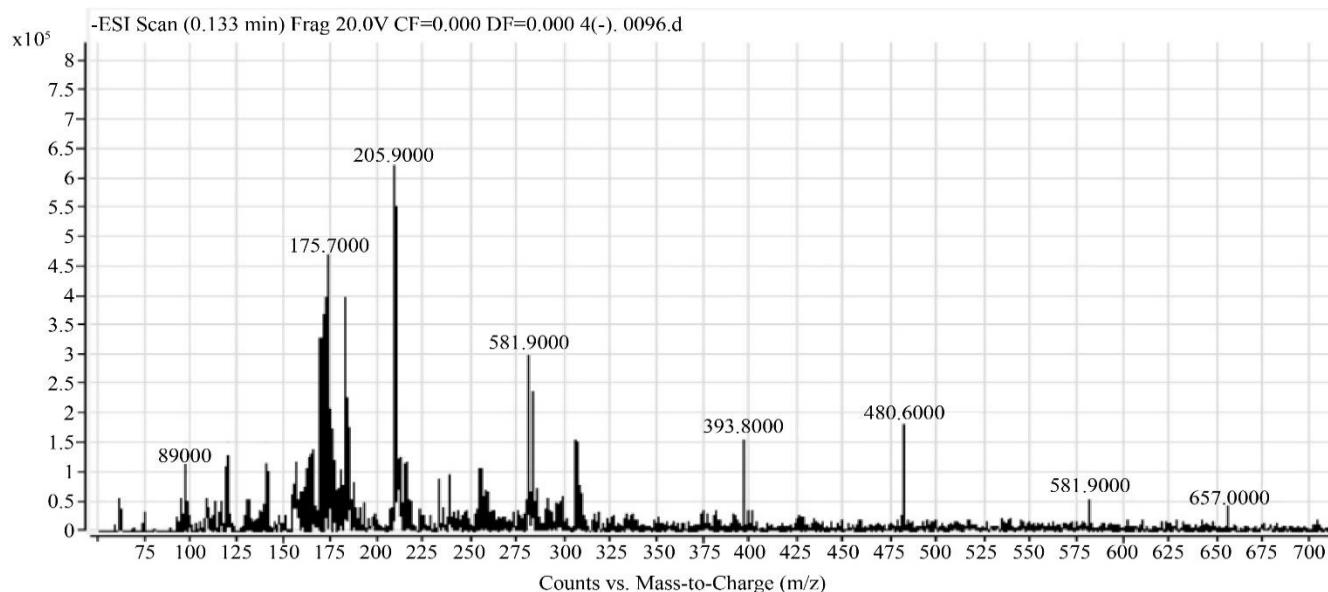


Fig. 3 Chromato-mass spectra of oligomer

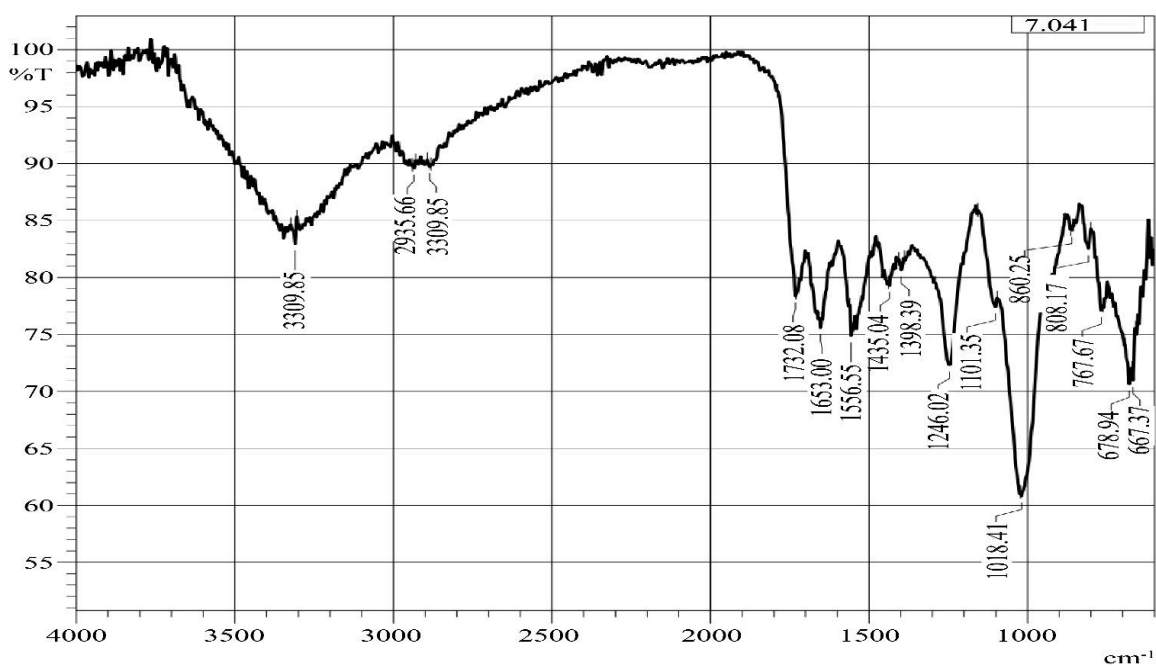


Fig. 4 IR spectrum of the oligomer

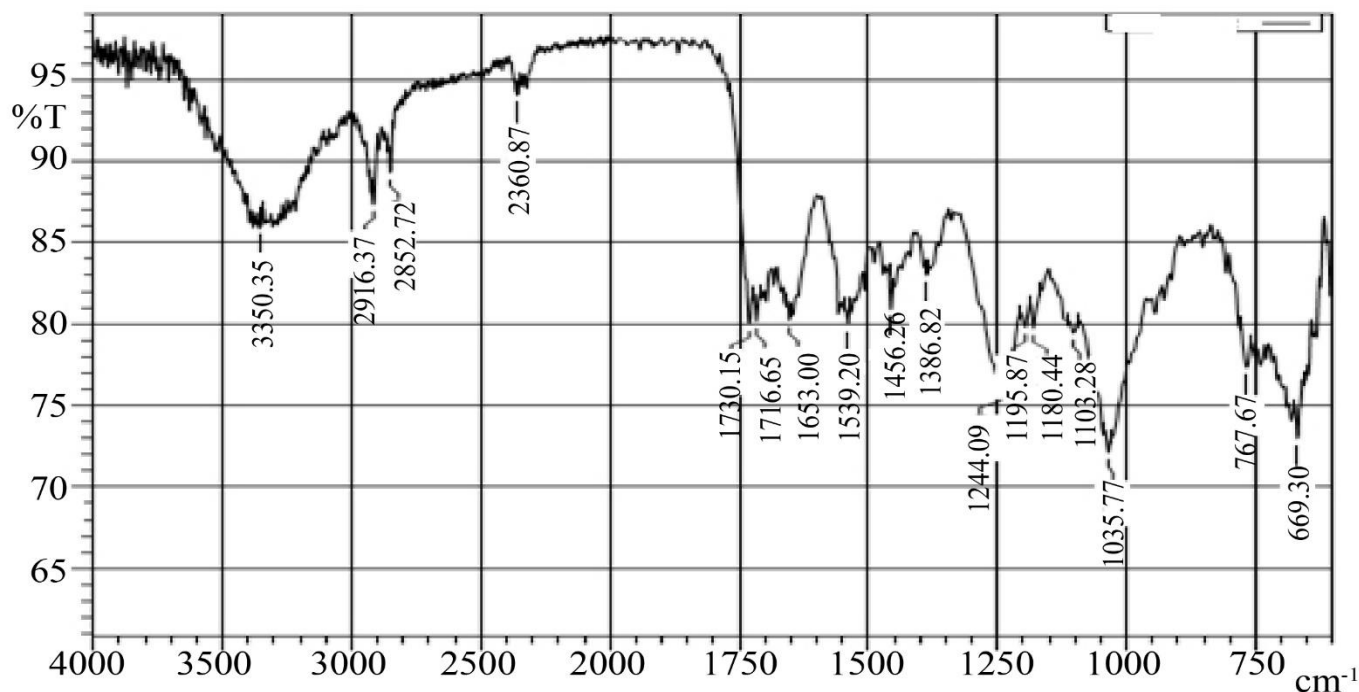


Fig. 5 IR-spectrum of the new synthesized polyurethane

The IR spectrum shows wide and strong absorption bands in the region of 3309.85 cm^{-1} . Absorption caused by hydrogen bonding appears in this region in the case of polymers. The results of IR spectroscopy show the presence of amide ($-\text{CO}-\text{NH}_2$) groups, which can only form at the ends of polymer macromolecules.

Further, from the IR spectra interpretation, one can see the presence of urethane ($\text{R}-\text{OCO}-\text{N}$) groups. This means that the polymer macromolecule contains a urethane group at the edges of the chain and in the internal segments. A carbonate ($-\text{O}-\text{CO}-\text{O}-$) group indicates that some unsubstituted urethane groups reacted with hydroxyl groups of glycerol or terminal hydroxyl groups of polymer macromolecules [14, 15].

3.4. Polyurethane Synthesis with a New Composition

Polyurethane synthesis of a new composition was carried out in a device equipped with a mixer, a cooler, and an electronic thermometer that automatically controls the device's temperature.

From the synthesized oligomer, 20 g of oligomer was placed in a flat-bottomed 250 cm^3 flask, and then 6 g of phthalic anhydride was added little by little while stirring. The reaction was continued for 2 hours at a temperature of $30\text{--}35\text{ }^\circ\text{C}$.

While stirring, it was crushed, with 9 grams of basalt added to the mineral and mixed for 1 hour until a homogeneous mass was formed. IR-spectroscopy analyzed the resulting mass.

3.5. IR-spectrum analysis of polyurethane with new composition

The IR-spectrum of the obtained polyurethane with a new composition includes absorption lines of valence vibrations of $-\text{CH}_3$ bonds in the area of $2916.37\text{--}2852.87\text{ cm}^{-1}$ and deformation vibrations of dimethyl groups of diphenylolpropane in the area of $1456.26\text{--}1386.82\text{ cm}^{-1}$. Absorption lines in the $3350.35\text{--}3045.76\text{ cm}^{-1}$ region are explained by the presence of the $-\text{CO}-\text{NH}-$ group.

The absorption line in the region of 1539.20 cm^{-1} and the absorption line at 1730.15 cm^{-1} corresponding to the $-\text{NH}-$ groups in the IR spectrum indicates the presence of the urethane group (presented in Figure 5).

4. Results and Discussion

4.1. Determination of Hardness According to the Brinell Method

The synthesized polyurethanes' hardness, elasticity, and plasticity values were studied using the Brinell method (Table-1). According to Table 1, we can see that the hardness of all samples of synthesized polyurethane polymers changes depending on the amount of added basalt mineral.

An increase in the amount of oligomer in the polyurethane composition increases the degree of elasticity, and we can see the opposite effect on plasticity. We can observe that the level of hardness increases when the amount of basalt mineral is increased to 3% in the process of polyurethane synthesis, and further increasing the amount of basalt in this process harms the level of polyurethane hardness

[16]. This can be interpreted and explained based on the graph shown in Figure 6. As can be seen from the graph results, the effect of basalt minerals in the first samples depends on the percentage level. Increasing the amount of basalt in the composition of the mass to 3% shows that it has the highest hardness. In other cases, the level of graphic display decreased. Based on the obtained data, adding up to 3% for polyurethane is optimal.

4.2. SEM and EDS Analysis

The Scanning Electronic Microscopy (SEM) and Energy Dispersion Spectroscopy (EDS) methods explored the surface characteristics of the sulfur-melamine modifier. The SEM explored the surface morphology of the modifier, whilst the EDS explored the element analysis of the surface. The SEM and EDS analyses were done in Jeol JSM-IT200LA. The morphology of the effect of basalt mineral on the synthesized polyurethane is studied below.

From the above picture, we can see that the morphological structure of the synthesized polyurethane and the modification of basalt mineral to it, i.e., the degree of mixing with it, can be seen at 250 and 650 times magnification. It was found that mixing basalt minerals in the polyurethane composition positively affects its strength.

4.3. EDS Analysis

The surface elemental analysis of the polyurethane modifier was done to identify the elemental compositions of the selected basalt minerals. Figure 8 shows EDS pictures and an EDS element map of new polyurethane based on basalt minerals.

The next picture shows the morphology of the elements in the synthesized polyurethane, and the number of elements in this polymer is shown, that is, the number of atoms of each element.

Table 1. Hardness, elasticity and plasticity indicators of rigid polyurethane polymers according to the Brinell method

Sample numbers	Name of Samples	Hardness, MPa	Elasticity, %	Plasticity, %
	Hard polyurethane			
1	HP-1%	16.9115	85.2	14.8
2	HP -2%	14.2246	51.8	48.2
3	HP -3%	46.3297	70.7	29.3
4	HP -1%+M	5.94482	61.3	38.7
5	HP -2% C ⁰	12.1271	51.8	48.2

*Note: HP- Hard polyurethane

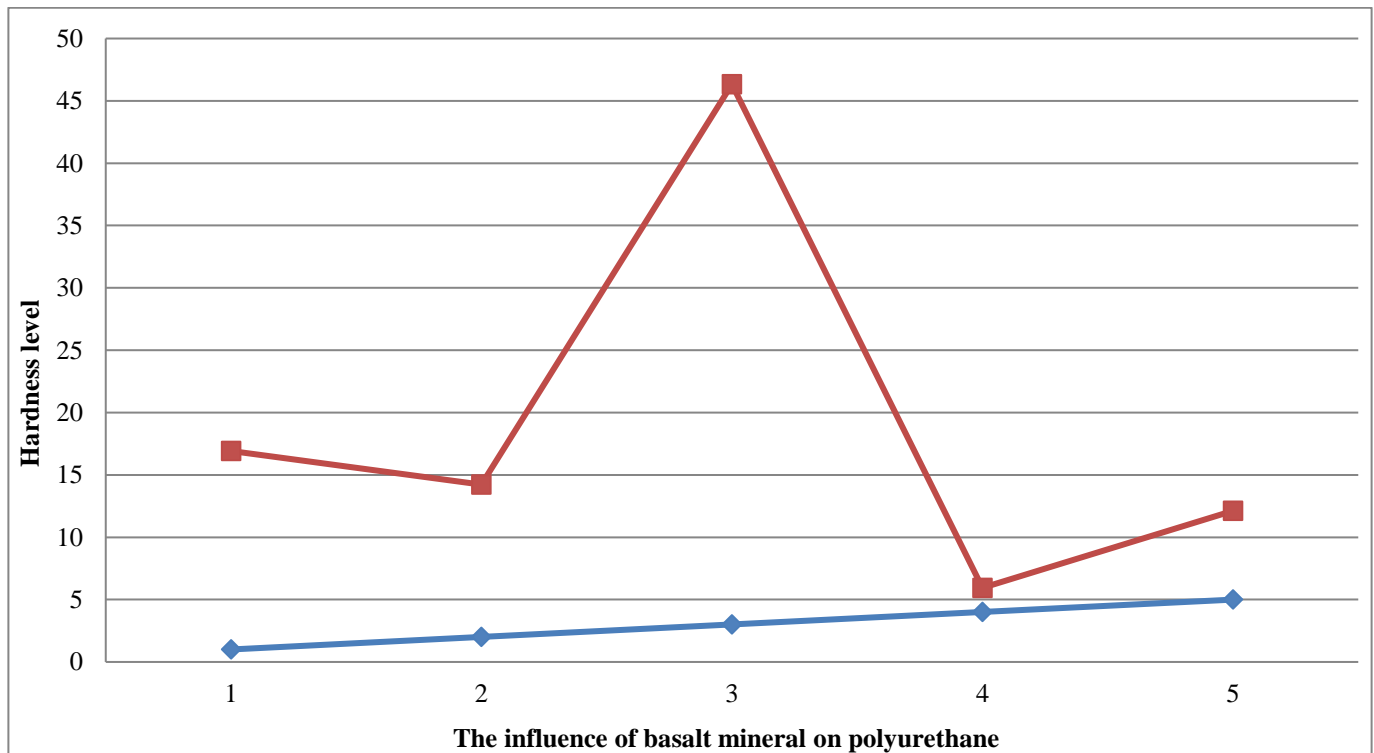


Fig. 6 Effect of basalt mineral layer on physico-chemical properties of polyurethane

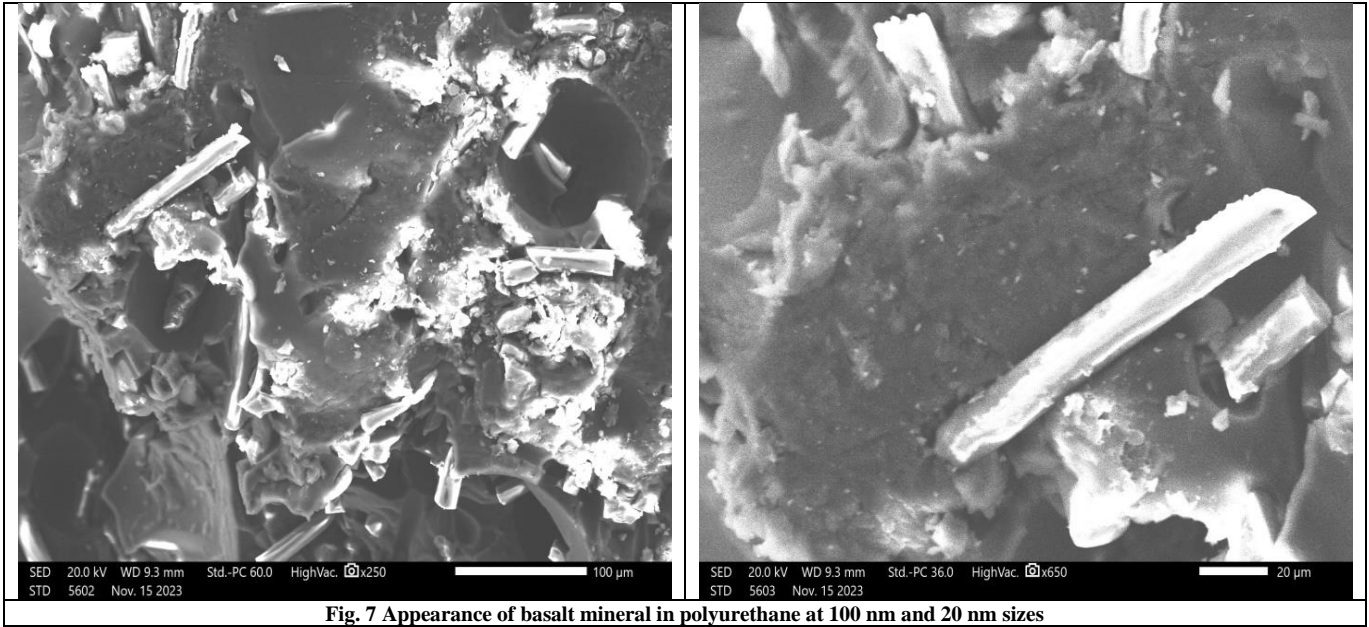
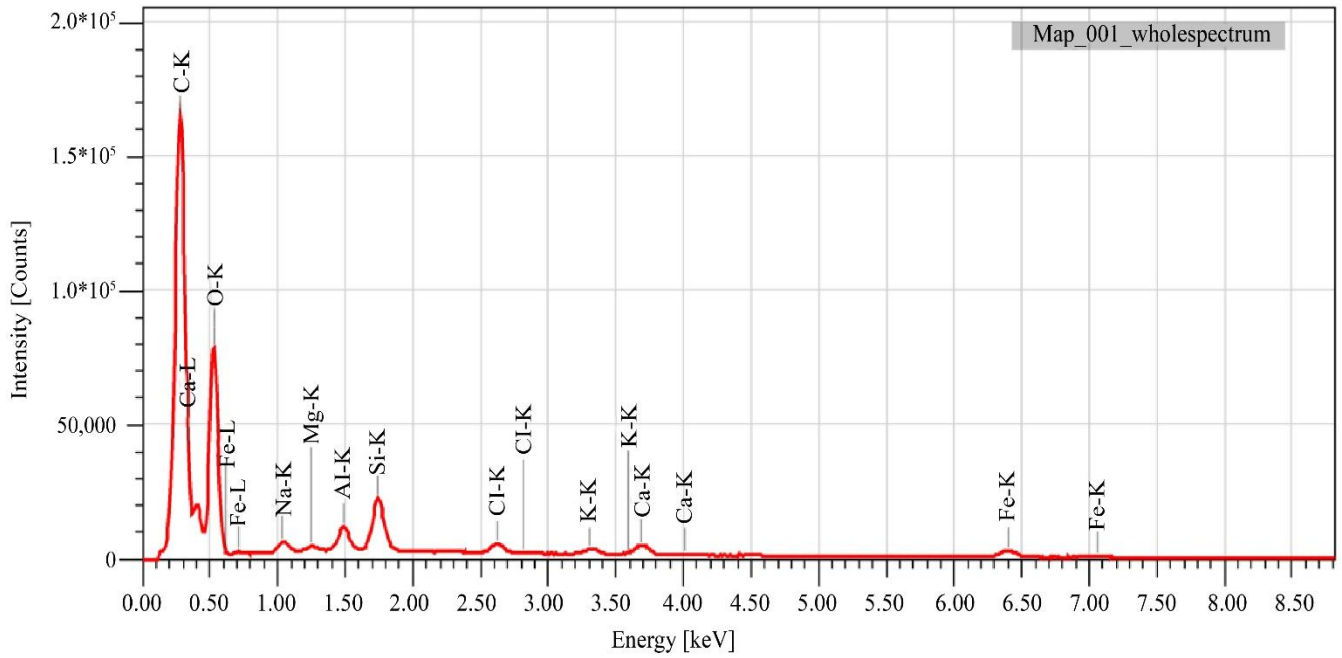


Fig. 7 Appearance of basalt mineral in polyurethane at 100 nm and 20 nm sizes



Elementlar	Massa %	Atom %
C	60.53±0.03	68.75±0.04
O	33.81±0.05	28.83±0.04
Na	0.60±0.01	0.35±0.00
Mg	0.17±0.00	0.09±0.00
Al	0.79±0.01	0.40±0.00
Si	1.72±0.01	0.84±0.00
Cl	0.43±0.00	0.17±0.00
K	0.32±0.00	0.11±0.00
Ca	0.65±0.01	0.22±0.00
Fe	0.99±0.01	0.24±0.00

Fig. 8 Elemental composition analysis of polyurethane obtained based on basalt mineral

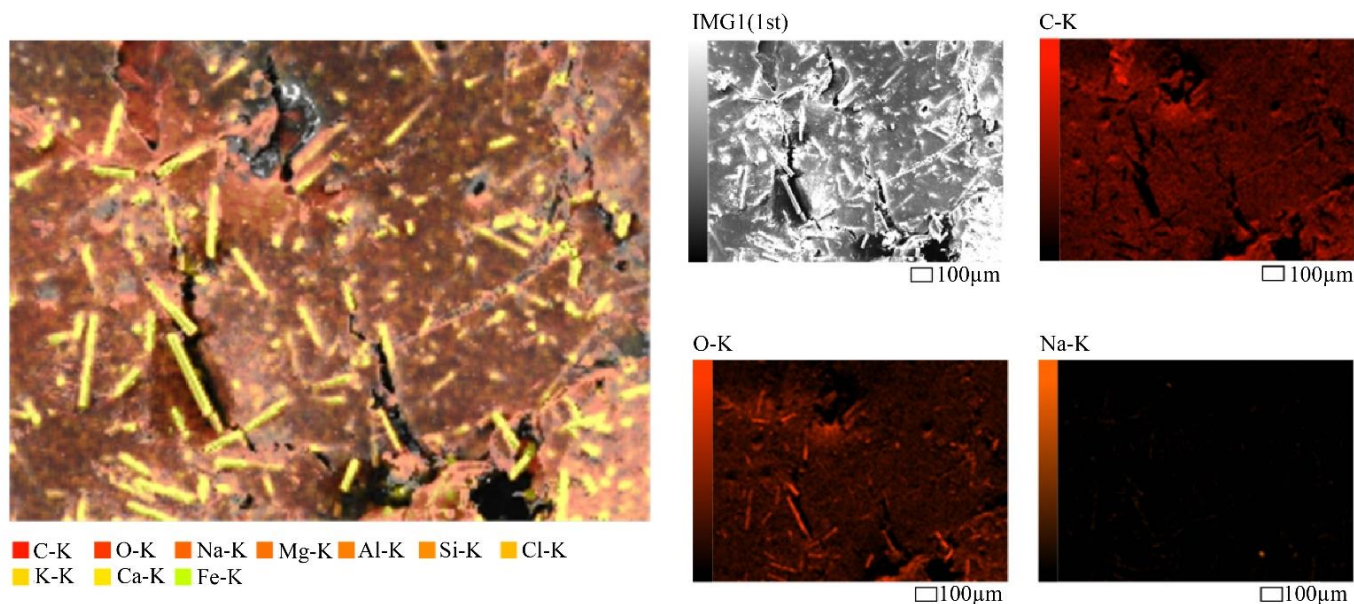


Fig. 9 EDS element map of the elemental composition analysis of polyurethane obtained based on basalt mineral

5. Conclusion

Optimum conditions for synthesizing polyurethane with high strength based on glycerol, urea, maleic anhydride, formaldehyde and basalt minerals have been determined. In this case, the optimum temperatures are 95 oC minimum and 140 oC maximum. When the structure of the obtained oligomer and polyurethane-containing basalt mineral was studied with the help of the IR spectrum, IR spectroscopy showed the presence of amide (-CO-NH₂), (R-OCO-N) and (-O-CO-O-) groups absorption lines in the region of 3350.35-3045.76 cm⁻¹ are explained by the presence of the -CO-NH-group. Also, when analyzed by Chromato-mass-spectrum analysis, the oligomer ion with the largest molecular weight has a mass of 658. Basalt-added polyurethane's surface morphology and elemental mass % composition were studied using SEM and EDS analysis. In this case, basalt has the best properties when it is 100 nm and 20 nm in size.

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Authors' Declaration

Conflicts of Interest: None.

I/We hereby confirm that all the Figures and Tables in the manuscript are mine/ours.

Authors' Contribution Statement

Safarov A.M: Writing – Original Draft. Turaev Kh.Kh: Reviewing and editing the paper. Alikulov R.V: Reviewing and editing paper. Dzhaliylov A.T: Software, Validation. Shukurov D.Kh and Kiyomov Sh. N: Writing – Original Draft, Conceptualization, Investigation, Visualization.

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