
MODIFICATION
OF POLYMERS

Crosslinking Kinetics for Blends of Polyisoprene and MQ Copolymers

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Abstract—MQ resins have proved to be promising fillers for obtaining molecular composites based on silicone and carbon-chain rubbers. In the present work, MQ copolymers play the role of a complex filler with an inorganic core (Q unit) and an organic shell (M unit). Copolymers, in which the ratio of M and Q units was 1 : 2, 1 : 3, and 1 : 4, were used as fillers. Grafted methyl and decyl groups made it possible to use the MQ copolymer as a reinforcing filler of a carbon-chain polymer, polyisoprene. The thermal and rheokinetic behavior of filled compositions during the transformation of elastomers into rubbers was studied. Using differential scanning calorimetry and rheology techniques, the temperature parameters of the crosslinked structure formation process were determined and the values of the apparent activation energy of the crosslinking process were calculated. Increasing the proportion of the inorganic component from 1 : 2 to 1 : 4 resulted in an increase in the storage modulus of the crosslinked composites.

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INTRODUCTION

Among organosilicon polymers, the so-called MQ resins, or MQ copolymers, occupy a special place. These objects have a unique structure, combining the properties of inorganic particles and organic compounds [1, 2]. This “dualism” is due to the presence of an inorganic core (SiO₂) and organic peripheral groups. The ratio of M and Q units in a molecule, as well as their structure, predetermines the nature and, therefore, the basic properties of resins [3].

Traditionally, MQ copolymers are considered as fillers for silicone rubbers [4, 5]. The structure of the copolymers provides high compatibility with polydimethylsiloxane and its analogs. MQ resins with methyl substituents are in the most common use. According to [6–8], these resins can be used as modifying additives to increase the thermal resistance of materials, as well as to improve their mechanical properties. Recently, MQ copolymers have again attracted the attention of researchers, especially due to the possibility of replacing methyl groups with more complex organic groups, such as vinyl, alkyl, phenyl, substituted urea, and many others [9–14]. The replacement of terminal groups in MQ copolymers makes it possible to adjust the properties of these compounds and expands the prospects for their application in various industries. For example, silicone rubbers with the addition of ureido-modified MQ resins showed a significant increase in thermal stability and improved strength properties compared to unfilled composites [13]. The materials were proposed as candidates for

electrical insulation and exhibited tracking and erosion resistance. In a number of publications, MQ copolymers were suggested as crosslinking agents for silicone rubbers. For example, the authors of [14] developed silicone rubbers in which methoxy-MQ resins were treated as both a filler and a crosslinking agent. The crosslinked products demonstrated improved thermal and mechanical properties. This improvement was explained by the synergistic effect of the formation of a dense three-dimensional structure in a matrix and the uniform distribution of the methoxy-MQ crosslinking agent.

Currently, there is a new trend of trying to expand the boundaries of applicability of MQ resins and use them not only as an additive to silicone rubbers but also to other nature polymers. For example, phenyl-substituted MQ copolymers are potentially applicable as modifiers of polystyrenes. Such blends are optically transparent and may be of particular interest for the obtainment of special purpose coatings [15]. An MQ resin with methyl groups was used to enhance the fire resistance of composites based on an epoxy resin and hyperbranched polysiloxane [16].

In the present work, it is proposed to consider carbon-chain rubbers as a polymer matrix and to use MQ copolymers with decyl terminal groups as an active filler of polyisoprene [17]. It is expected that decyl terminal groups will enhance dispersion bonding with a carbon-chain matrix due to hydrophobic interaction. Varying the ratio of M and Q units and, consequently, the proportion of core/shell inorganic and organic

Table 1. Characteristics of MQ copolymers

M : Q	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	Si-OH*, %
1 : 2	6.55	14.15	2.16	2.4
1 : 3	4.60	9.30	2.02	4.9
1 : 4	33.40	105.70	3.16	4.8

* Weight content of silanol groups.

components will allow controlling the filler properties. An important factor influencing the use of MQ copolymers as a filler of carbon-chain elastomers is the evaluation of the rheological behavior of both the initial blends and the evolution of the rheological characteristics during the crosslinking process of the filled rubber. For polyisoprene-based filled rubbers

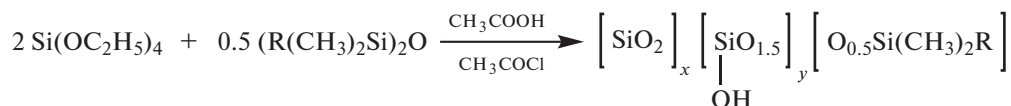
mechanical and thermal properties will be investigated.

EXPERIMENTAL

Materials

The polymer matrix was low molecular weight polyisoprene of NMPI-500 grade (OAO EZSK, Russia), molecular weight $M_n = 5.5 \times 10^4$.

MQ copolymers played the role of a “hybrid” filler consisting of inorganic (Q) $\text{SiO}_{4/2}$ and organic (M) $\text{R}_3\text{SiO}_{1/2}$ units. The copolymers were synthesized by the hydrolytic polycondensation of tetraethoxysilane with didecyltetramethylsiloxane in an active medium. The general scheme of the synthesis is outlined below:



(R is $\text{C}_{10}\text{H}_{21}$).

The synthesis procedure of MQ copolymers was described in detail in [17–19].

The resins with the ratio of M and Q units equal to 1 : 2 (**copolymer I**), 1 : 3 (**copolymer II**), and 1 : 4 (**copolymer III**) were studied. An increase in the content of Q units allowed the synthesis of copolymers with higher molecular weights and wider molecular weight distributions (Table 1). The resulting products were fully soluble in organic solvents, such as toluene, THF, and others.

The polymer matrix was crosslinked using EKh-1 grade quinol ether (OOO Angara-Reaktiv, Russia) [20]. Derivatives of *n*-quinondioxime are low-temperature crosslinking agents and are used for formulations based on unsaturated rubbers [21, 22]. Quinol ether powder was introduced into the polyisoprene–MQ resin composition in an amount of 5 phr.

Methods

MQ resins were introduced into the polymer matrix by mixing from solution. The rubber was pre-dissolved in methyl *tert*-butyl ether in an ultrasonic bath (PSB-Gals, frequency 60 kHz). A solution of a resin in the same solvent was added to the resulting solution. The obtained mixture was evacuated at a temperature of 60°C for 2 h on a rotary evaporator (Rotavapor, Buchi, Switzerland). The residual pressure was 1 mmHg. Mixing through solution ensured the uniform distribution of the filler in the matrix. For each of the MQ copolymers blends with a filler content of 30 wt % were prepared.

To measure the thermal effect of the crosslinking process, heat flow was recorded by differential scanning calorimetry on a DSC3+ DSC instrument (Mettler Toledo, Switzerland), sensor HSS9+. Thermograms were measured in the nonisothermal mode at heating rates of 2.5, 5.0, and 10.0°C/min in the temperature range of 25–200°C. Measurements were performed under argon at a flow rate of 50 mL/min.

The crosslinking rheokinetics was studied on a HAAKE MARS 60 rotational rheometer (Thermo Scientific, Germany) using a plate/plate (diameter 20 mm) measuring cell. A change in the dynamic moduli of the filled composite during crosslinking was monitored in the temperature range of 50–120°C at a constant heating rate of 1°C/min. Experiments were performed at a constant shear amplitude of 1% corresponding to the linear viscoelasticity range and a frequency of 10 rad/s.

Thermogravimetric analysis was carried out using a TGA/DSC3+ synchronous thermal analyzer (Mettler Toledo, Switzerland), sensor HSS2. Tests were done in the 30–800°C range under argon; the gas flow rate was 70 mL/min. The weighed portions of the tested samples from 40 to 100 mg were placed in 150 μL aluminum oxide crucibles. The methodology of TGA analysis was based on ISO 7111-87. Heating rate was 10°C/min.

RESULTS AND DISCUSSION

Calorimetric Measurements

The crosslinking/curing reaction is invariably accompanied by thermal effects, which makes it pos-

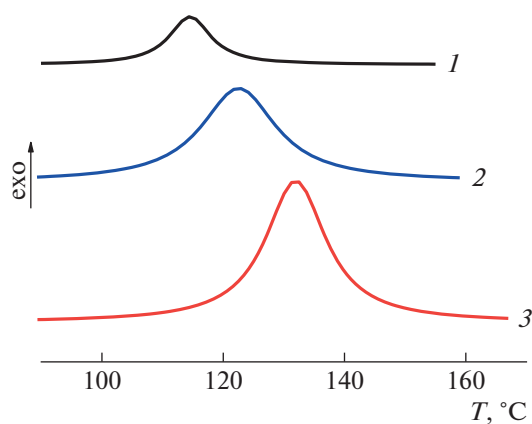


Fig. 1. Thermograms reflecting the crosslinking process of the composition based on PI and copolymer II. The heating rate is 2.5 (1), 5 (2), and 10°C/min (3). The DSC curves are shifted vertically for clarity. Color figures can be viewed in the electronic version.

sible to apply calorimetry (DSC) techniques for qualitative and quantitative assessment of the reaction.

To evaluate reaction kinetics, it is generally accepted to conduct experiments at different heating rates [23]. For all the studied systems, as the heating rate increases, the peaks on the thermograms corresponding to the process of rubber crosslinking naturally shift toward higher temperatures. Typical thermograms depicting the crosslinking process are shown in Fig. 1 for a blend containing copolymer II used as an example. Varying the heating rate from 2.5 to 10.0°C/min causes a shift in the maximum heat release from 115 to 132°C.

A similar situation is observed for all the systems under study. The values of temperatures corresponding to the maximum heat flow (T_{\max}) at different heating rates, as well as the enthalpy values of the process, are given in Table 2. The enthalpy of crosslinking reactions is independent of the heating rate and is reproducible to an accuracy of ± 0.5 J/g. The enthalpy values of the process for the filled systems were calculated in proportion to the rubber content.

The Kissinger approach was used to evaluate the process kinetics. The method is based on determining the position of the temperature maxima of the heat flow taking into account the heating rate [24, 25].

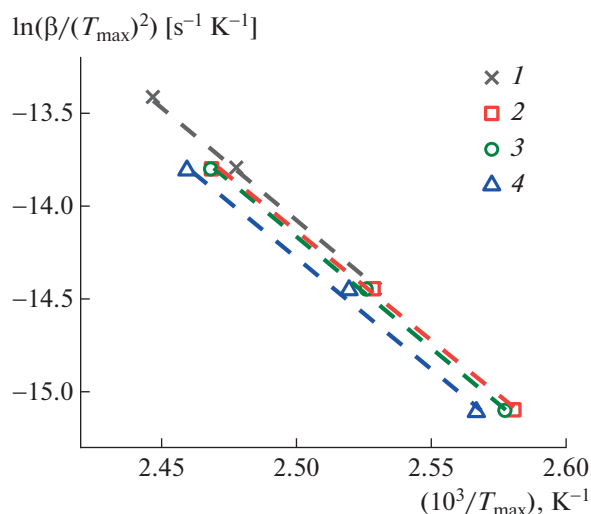


Fig. 2. Determination of the activation energy of the crosslinking process of PI-based filled compositions (1) and compositions containing copolymers I (2), II (3), and III (4) using the Kissinger equation.

$$\ln \frac{\beta}{T_{\max}^2} = -\left(\frac{E}{R}\right) \frac{1}{T_{\max}} + \ln \left(\frac{AR}{E}\right), \quad (1)$$

where E is the reaction activation energy, A is the pre-exponential factor, R is the universal gas constant, and β is the heating rate.

According to the Kissinger method, the activation energy is calculated from the maximum reaction rate. It is assumed that the temperature T_{\max} corresponds to the point in time at which the reaction rate reaches maximum values.

The initial data for calculating the activation energy in Kissinger coordinates are presented in Fig. 2. The calculated values of the activation energy are summarized in Table 2. Despite the close values of E_{act} , it can be noted that its value tends to decrease for filled systems, compared to the unfilled polymer matrix.

Rheokinetics of the Crosslinked Polymer Formation Process

Another technique that allows one to evaluate the crosslinking kinetics is rotational rheometry [26, 27]. The evolution of viscosity and dynamic moduli during

Table 2. Thermodynamic characteristics of the process of crosslinking compositions based on PI and MQ copolymers

Sample	T_{\max} , 2.5°C/min	T_{\max} , 5°C/min	T_{\max} , 10°C/min	ΔH , J/g	E_{act} , kJ/mol
PI	114.5	122.4	130.6	9.6	102
PI + copolymer I	114.5	122.5	132.1	9.1	96
PI + copolymer II	115.0	122.9	132.2	10.0	99
PI + copolymer III	116.6	123.9	133.6	8.7	100

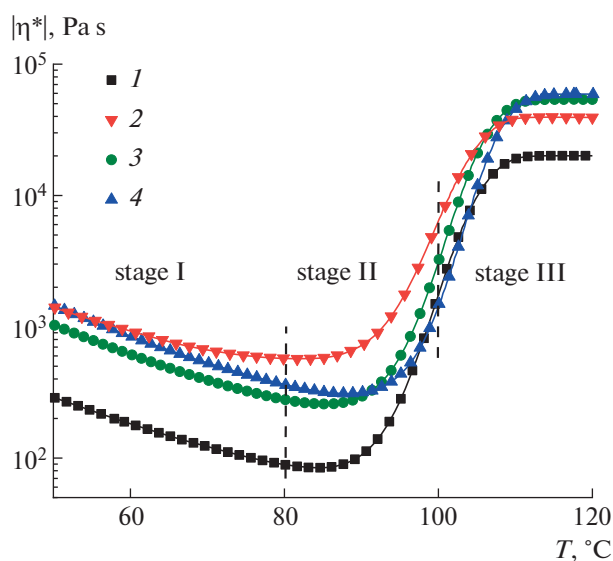


Fig. 3. Temperature dependence of the complex dynamic viscosity of PI-based composites during the curing of PI (1), PI + copolymer I (2), PI + copolymer II (3), and PI + copolymer III (4).

the nonisothermal crosslinking process reflects a change in the viscoelastic characteristics of the material. The common picture for all the studied systems is a gradual decrease of the complex dynamic viscosity and dynamic moduli with increasing temperature and their further increase due to the start of the chemical reaction [28].

The dependences of the complex dynamic viscosity on temperature during the crosslinking of the composites with MQ resins are presented in Fig. 3. Conventionally, the nonisothermal crosslinking process can be divided into three stages. In the first stage of the process, the viscosity of the systems decreases with increasing temperature. As a rule, low-temperature crosslinking often has an induction period, when the reaction is either absent or proceeds at a very slow rate, and temperature is the only factor affecting the viscosity [29]. Upon further increase in temperature the crosslinking of polyisoprene starts. The process moves into the second stage, when both the temperature factor and the chemical crosslinking reaction influence the viscosity. The minimum viscosity and its gradual increase can be observed on the graph. At the third stage, the influence of temperature on the viscosity of the composites is insignificant. The viscosity continues to increase with increasing temperature due to the active crosslinking reaction.

The typical temperature dependences of dynamic moduli for the unfilled rubber and the system with copolymer II are presented in Fig. 4. At the initial time, the loss moduli exceed the storage moduli for all the investigated systems and linearly decrease with increasing temperature, which corresponds to the first

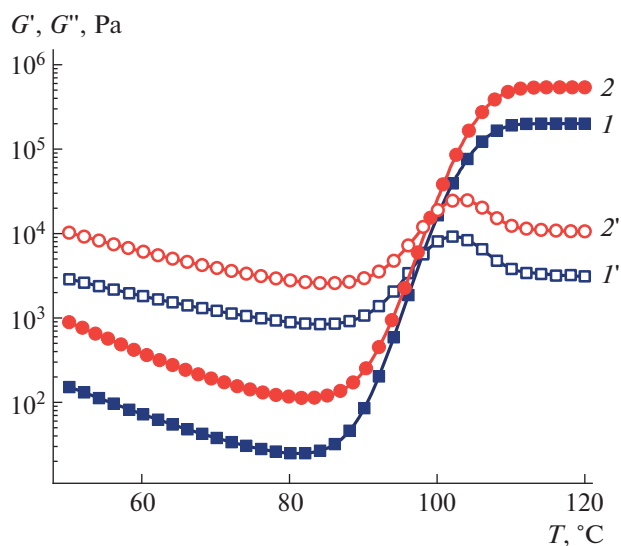


Fig. 4. Temperature dependence of the dynamic moduli G' (1, 2) and G'' (1', 2') of PI (1, 1') and PI + copolymer II (2, 2') in the curing process. The heating rate is 1°C/min.

stage of the process. When the minima are reached, the values of G' and G'' begin to increase gradually. At a certain temperature, the equality of the moduli (the crossover point) is observed. The end of the second stage of the process can be conditionally fixed at this point. Further increase in temperature leads to the growth of the moduli, and the storage modulus begins to exceed the loss modulus. The end of the crosslinking process can be recorded when the storage modulus reaches a constant value. From the point of view of rheology, at this point in time, the material is transformed to a highly elastic state and loses fluidity; that is, the chemical reaction is completed and the maximum possible number of crosslinks is formed. At the same time, the character of change in components of the complex elastic modulus for different compositions remains the same and only their absolute values change. An increase in the proportion of Q units leads to an increase in the storage modulus. Its highest value is registered for compositions based on copolymer III and the lowest value, for compositions based on copolymer I (Table 3).

In this case, the temperature, which corresponds to the most intensive phase of the crosslinking process, is defined as the first derivative of dG'/dT . The corresponding peak values can be observed on the graph (Fig. 5) by analogy with the calorimetry data. The temperatures of maxima of the compositions with MQ resins have similar values, but the following regularity can be traced, namely, the shift of the maximum to higher temperatures when the proportion of Q units increases from 1 : 2 to 1 : 4 (Table 3).

The values of temperature maxima calculated from the rheological data are much lower than the T_{\max} values obtained by DSC. This is explained by the fact that the heating rate in the case of rheological testing is 1°C/min. With increasing heating rate the peaks will shift to higher temperatures.

Dependences describing the evolution of the storage modulus during curing allow estimating the depth of the process using the so-called rheological degree of transformation β [30]. The rheological degree of transformation is calculated from the ratio of the difference of the current and initial values of the storage modulus to the difference of the plateau and initial modulus values. The value of $\beta = 1$ corresponds to the completion of the crosslinking process when the current value of the modulus G' becomes equal to the plateau modulus [31]. The evolution of the degree of transformation of the compositions with MQ resins is shown in Fig. 6. The $\beta(t)$ curves are S-shaped and shift to longer times with increasing fraction of the inorganic component in the MQ copolymer.

Thermogravimetric Analysis

To estimate the effect of MQ filler on the thermal stability of crosslinked composites their behavior was characterized by thermogravimetric analysis. The corresponding data are presented in Fig. 7. As is seen, the presence of MQ resins in polyisoprene significantly increases the thermal stability of the composites. The total weight loss is reduced to 80–85% (Table 4). The largest carbon–carbide–silicon residue at a temperature of about 700°C is observed for the composite with copolymer III, that is, with the highest inorganic unit content.

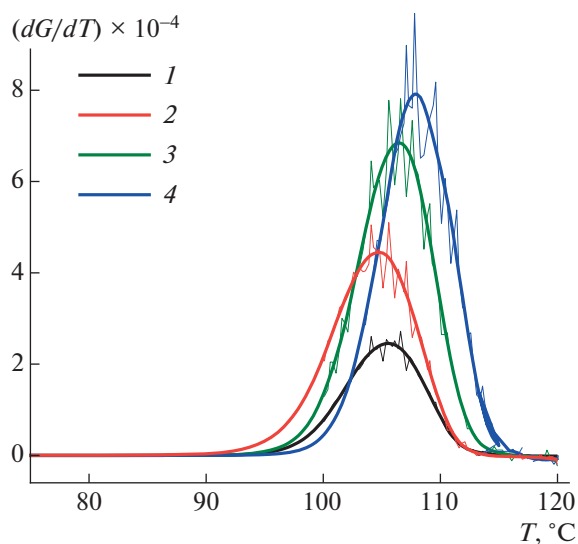


Fig. 5. Temperature maxima of the PI-based compositions in the curing of PI (1), PI + copolymer I (2), PI + copolymer II (3), and PI + copolymer III (4).

Table 3. Rheokinetic characteristics of the crosslinking process of compositions based on PI and MQ copolymers

Sample	Plateau G' , kPa	T_{\max} , °C, rheological technique
PI	2.0	105.5
PI + copolymer I	3.9	104.5
PI + copolymer II	5.4	106.0
PI + copolymer III	6.0	108.0

The onset of the intensive weight loss for all of the composites is reached in the temperature range of 210–215°C (Table 4, $T_{D3\%}$). The main weight loss is detected in the temperature range from ~376 to 380°C and is related to the decomposition of the polymer matrix. The values of temperature corresponding to the maximum weight loss rate T_{peak} for the compositions are listed in Table 4. The weight loss rate (Fig. 8) is minimum for the composites with MQ and maximum for the unfilled sample.

CONCLUSIONS

Composite materials based on low molecular weight polyisoprene and the organosilicon filler based on MQ resins with decyl end groups were obtained by mixing through solution. The ratio of M and Q units in the copolymer was 1 : 2, 1 : 3, and 1 : 4. The peculiarities of the crosslinking of polyisoprene by quinol ether in filled compositions were studied. The main thermodynamic parameters of the crosslinking process were determined by DSC techniques. With an increase

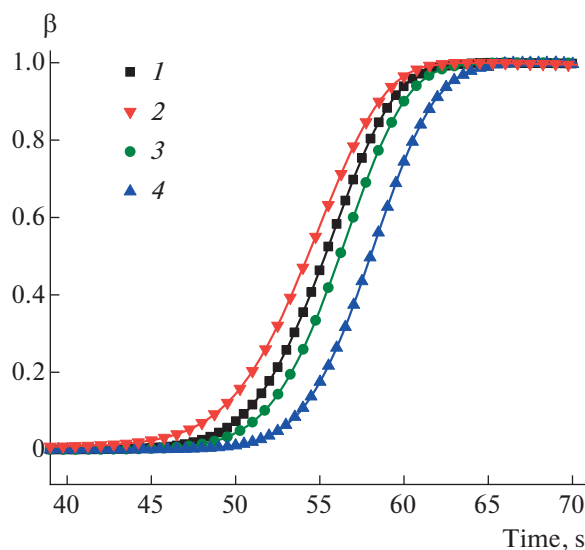


Fig. 6. Dependence of the rheological degree of transformation β for PI (1) and the compositions containing copolymers I (2), II (3), and III (4).

Table 4. Main parameters of the thermal degradation process of crosslinked composites based on PI and MQ

Sample	DTG peak, T_{peak} , °C	$T_{D3\%}$ *, °C	Total weight loss %	Ash content, %
PI	380.0	211.0	99.9	0.1
PI + copolymer I	379.0	215.5	84.4	15.6
PI + copolymer II	376.4	213.0	84.9	15.1
PI + copolymer III	378.0	210.0	80.6	19.4

* Onset temperature of the intensive weight loss.

in the proportion of Q units in the copolymer temperature maxima corresponding to the formation of crosslinks in polyisoprene macromolecules shift to higher temperatures. Using the Kissinger method describing the nonisothermal chemical crosslinking reaction, the activation energies of the process for each of the samples were calculated. Evolution of the dynamic moduli during the crosslinking process was assessed by the rheometry technique. An increase in the inorganic component in the MQ resin leads to an increase in the crosslinking time and an increase in the storage modulus of the crosslinked composite. Thus, the MQ copolymers with decyl end groups can be con-

sidered promising fillers of carbon-chain rubbers improving thermal stability and mechanical properties of the obtained composites.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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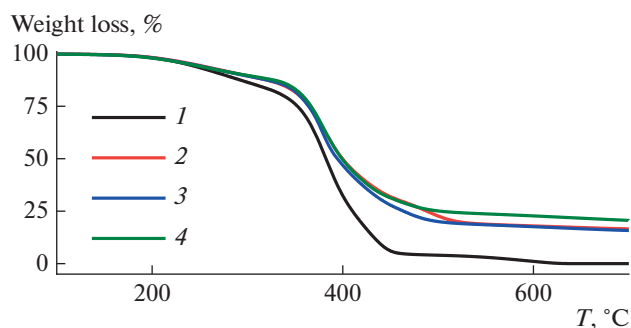


Fig. 7. TGA data for the compositions PI (1), PI + copolymer I (2), PI + copolymer II (3), and PI + copolymer III (4).

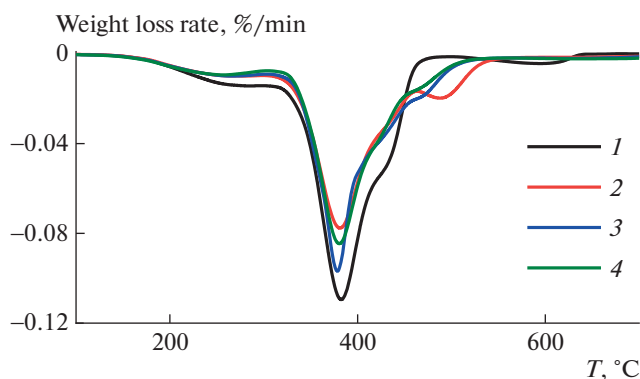


Fig. 8. Intensity of weight loss of crosslinked compositions based on PI (1) filled with copolymers I (2), II (3), and III (4).

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