Thermomechanical Study of Molecular and Topological Structure of Different Kinds of Sulfur

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ABSTRACT: A novel method is used to study topological and molecular structure of different kinds of sulfur (mineral and two polymeric types). It is based on thermomechanical analysis of solid (not dissolved) polymer. It was found that a deep difference in their molecular weight distributions and in their crystallinity degrees exist. Both mineral and polymeric sulfur have polymer nature. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 499–505, 1997

INTRODUCTION

Sulfur is the most commonly used commercial vulcanizing agent for diene rubbers since the discovery of a sulfur cure by Charles Goodyear in the last century. Two types of sulfur are available in the market, mineral rhombic "soluble" and polymeric "insoluble." They differ in solubility in rubbers and differ in molecular structure. As a result, they differ in blooming to the surface of rubber stock and in dispersing when compounding.[1,2] Molecules of sulfur contain from 2 to 10^6 atoms.[3–5] Molecular weight distribution of these molecules is a very important factor needed to explain their behavior during rubber compounding and further processing.
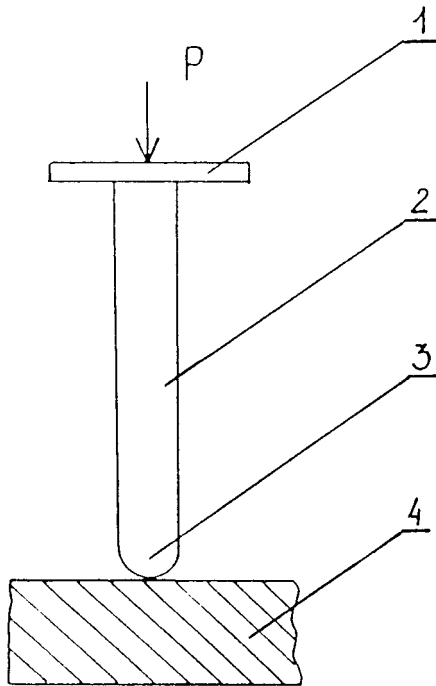
METHODOLOGY

A sample of fine, dispersed sulfur was compacted under pressure of ∼ 6 MPa to form cylindrical tablets 2–6 mm in diameter and 1–6 mm in thickness. The tablets were put into the heating chamber of thermomechanical device UIP-70M made

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by Russian Academy of Sciences. The sample was frozen without pressing under scanning rate of 2–10°C/min to a temperature of −100°C and was stored for 10–15 min to stabilize temperature. A load of 200 mg was put onto a horizontal plate of a quartz sonde (Fig. 1). This allows dilatometric expansion of the sample when heating. The sonde was moved down to contact the surface sample and further, sulfur was defrosted with a rate of 1–5°C/min. This rate of heating has no significant influence on characteristics of the studied processes when heating the sample from −100°C up to over melting temperature.[6–8] By use of a deformation-temperature recorder a full thermomechanical curve (TMC) was recorded. Figure 2 is a typical curve for polymeric sulfur (sample No. 2). It consists of a zone of glassy state (straight line AB), which is transformed at a glass transition temperature (T_g) zone into a straight line of high elastic expansion (straight line BC).

The glass transition is understood as being the temperature interval where short-range chain mobility occurred. It could be found by measurements, i.e., the change from the rate of an increase of the sample high for glassy state to that for high elastic state when any rate of heating of the sample. However, T_g is the temperature of the beginning of segmental defrosting of a sample.[9] In point C at temperature T_f the TMC is deflected from

Figure 1 Deformation measurements scheme of a sample of sulfur, (1) load P; (2) a quartz sonde; (3) a hemispherical tip of the sonde; (4) a sulfur tablet.

the straight line of a high elasticity plateau. Here a thermomechanical component of deformation is found when a hemispherical tip of the sonde penetrates into the sample of sulfur. According to "thermomechanical spectroscopy" this component of deformation is visible at temperature T_f, when molecular flow of the lowest molecular weight polymer homolog starts. Molecular weight (MW) of these macromolecules is directly proportional to the value $\Delta T = T_f - T_g$. As temperature in the heating chamber and temperature of the sample increase, the increasing molecular weights of fractions of sulfur move into molecular flow. Here, a jump in deformation $\Delta \varepsilon_i$ is noticed, a value of which is directly proportional to the weight share of this fraction φ_i. A weight share of every polymer fraction is calculated by the equation:

$$\varphi_i = \frac{\varepsilon_i - \varepsilon_{i-1}}{\varepsilon_\infty} \tag{1}$$

where i is the number of intervals (from one to n) and ε_∞ is the global thermomechanical deformation of all polymer homologies at temperature T_∞.

The network of physical crosslinks of all sulfur macromolecules loses its compaction continu-

ously as temperature increases. It is due to the permanent motion of a part of sulfur macromolecules from the zone of this network. This network holds down sulfur in the frame of thermomechanical deformation theory only up to a given temperature, over which a molecular flow starts to give a share in measured deformation. This deformation does not inform about molecular weight distribution of polymer macromolecules. Due to this, it should be removed from the measured value of deformation ε.

If the temperature at the onset flow of the lowest molecular weight of sulfur on TMC curve (point C in Fig. 2) is found sufficiently accurate, to find this temperature for the highest molecular weight of polymer homolog a procedure to divide a global deformation on its components is needed. A detailed procedure on how to establish these temperatures in a transitional zone of TMC is given in the literature.[6] A short description of this procedure is shown below when polybutadiene is given as typical polymer.

As an example, in Figure 3 a combined TMC in coordinates $\varepsilon_i - T$ and log ε_{i-T} of polybutadiene (PB 2000) mol wt 2000 (curve *ABDMOHC*) and a model polybutadiene are shown. This model is a mixture of 50% PB 2000 and 50% high molecular polybutadiene (PB 143,000) with mol wt 143,000 (curve *ABDMK'D'C'*). Individual polymers and their model mixture have the same T_g ($-100°C$). Now processes in the model mixture of polybutadienes will be studied by use a thermomechanical analysis. In Figure 3(b) is shown that mixture of polymers of the same nature but different molecular weight distributions (their cumula-
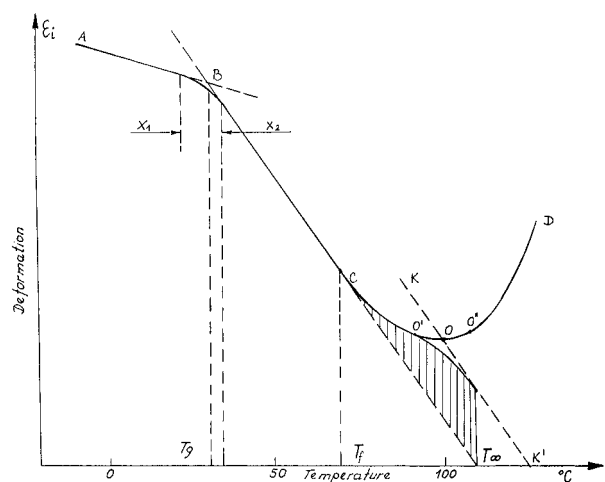
Figure 2 Typical thermomechanical curve for polymeric sulfur; x_1–x_2, a zone of glass transition processes.
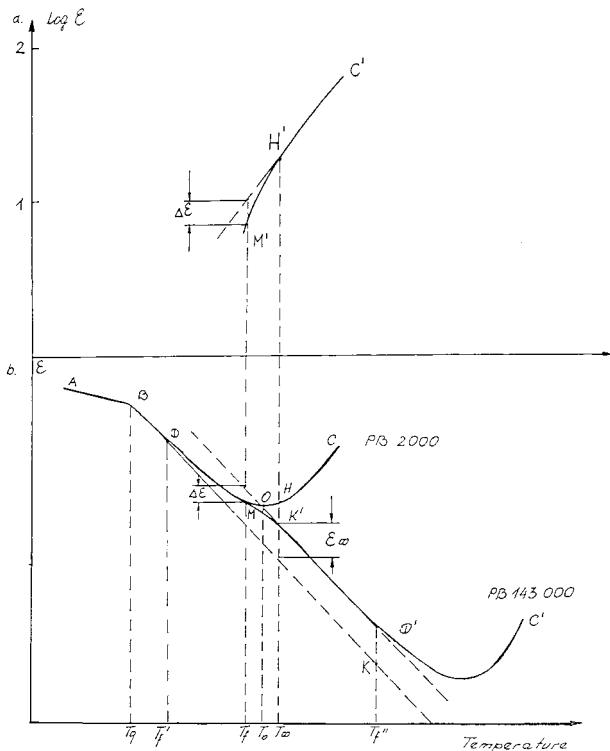
Figure 3 Combined thermomechanical curve of polybutadiene with $\bar{M}_{c(n)} = 2000$ and its model mixture with polybutadiene with $\bar{M}_{c(n)} = 143,000$; (a) in log ε $- T$ coordinates; (b) in $\varepsilon - T$ coordinates.

tive curves not overlay each other) gives a picture of successive defrosting of components. First, low molecular PB 2000, and next PB 143,000, was defrosted. Note that up to critical point M, the TMC for PB 2000 in the mixture overlay analogical curve for an individual polymer. The difference starts to be visible at temperature T_f (point M). Above this temperature for individual polymers in a combine deformation ε essential share start to give the forced molecular flow. First is consistent molecular flow of different molar polymer homologies. It is displaced as an increase of thermomechanical deformation—curve DMK' in Figure 3. It begins to be visible after reaching critical density of the network of physical bonds because of temperature–force superposition. In point O at T_o it gives an inversion of cumulative deformation (inversion from expansion to compression). At temperature a little higher than T_o a polymer is in a regime thermal molecular flow of a total polymer (curve HC).

This polymer, in a mixture with high molecular polybutadiene, is characterized by the stage of accumulation of thermomechanical deformation without

molecular flow processes. This stage is ended in point K' after beginning to flow by the highest molecular weight polymer homolog in PB 2000. Starting from this point, the cumulative pure thermomechanical deformation reaches ε_∞ value.

After ending of thermomechanical deformation in PB 2000, TMC of the model polymer start to be in the second plateau of high elasticity (straight line $K'D'$), in the frame of its thermal expansion of the polymer. Next, after reaching temperature T_f'' (point D'), when according to equation (2)

$$\log M_i = 2.3 + \frac{11(T_f'' - T_g)}{100 + (T_f'' - T_g)} \qquad (2)$$

segmental relaxation should be ended for the lowest molecular weight homologies (M_i) in polybutadiene. Here start processes of thermomechanical deformation and other phenomena, described giving individual PB 2000 as an example.

In this way a detailed study of the deformation process, taking place during thermomechanical analysis of PB 2000 and its model mixture with PB 143,000, shows relatively synonymously a picture of the processes occurring there. Based on this it is possible to list operations needed to divide cumulative deformation into components. First, determination of a point O location is necessary. Next, to draw a straight line parallel to the straight line of thermal expansion of the polymer (line BDK) a hypothetical plateau of high elasticity (straight line $BOK'D'$) is done. Furthermore, on this straight line, finding the location of point K', and on TMC point H at temperature T_∞ is necessary, when accumulation of thermomechanical deformation is ended and starts thermal molecular flow. For this purpose fragment of TMC (curve $MOHC$) is transformed into coordinates log $\varepsilon - T$. The value of ε is measured to the straight line BDK. Now location of a point H' is found. Straight line character of log ε versus T function in the interval between $H'C'$ is a rule for thermal expansion processes for polymers.

After determination in this way a location of points H', H, and K' we automatically find the T_∞ value; when processes of thermomechanical deformation are ended, cumulative deformation ε_∞ and location of a point M. This point is found along a temperature axis from point O in a distance close to the distance of point H.

After all these operations the shape of integral TMC (DMK') is found. Extracting it is easy. For

Table I Molecular Weight and Thermomechanical Characteristics of Polymeric and Mineral Sulfur

Sample	$\bar{M}_{c(n)}$	$\bar{M}_{c(w)}$	K	T_g (°C)	$\alpha_1 * 10^4$ (K^{-1})	$\alpha_2 * 10^4$ (K^{-1})	T_{melt} (°C)	φ_{er}, % by Weight
Polymeric sulfur								
No. 1	31,860	99,020	3.10	30	14.24	30.37	—	0.0
	39,650	70,420	1.78	32	8.94	14.79	—	0.0
	40,080	94,800	2.60	40	5.19	13.27	—	0.0
	46,740	100,410	2.15	40	4.86	20.00	—	0.0
	30,660	75,800	2.47	34	4.72	22.19	—	0.0
	40,200	105,000	2.50	28	7.67	18.21	—	0.0
	43,540	84,470	1.94	28	8.94	23.89	—	0.0
	34,000	76,840	2.26	29	8.00	24.31	—	0.0
Average	43,820	88,350	2.02		7.82	20.88		0.0
Polymeric sulfur								
No. 2	35,000	77,350	2.21	51	4.75	14.43	—	0.0
	50,660	101,320	2.00	31	4.00	10.30	—	0.0
	48,000	94,560	1.97	29	4.93	13.77	—	0.0
	48,650	102,620	2.11	28	7.83	13.90	—	0.0
	44,870	97,690	2.18	50	4.80	19.12	—	0.0
	34,430	79,190	2.30	54	7.89	19.80	—	0.0
Average	43,600	92,120	2.11		5.70	15.22	—	0.0
Mineral sulfur	157,500	297,690	1.89	28	3.80	10.77	98.5	95.0
	122,000	244,000	2.00	30	6.97	14.66	99.0	95.0
	131,400	223,400	1.70	43	7.51	11.76	99.0	96.7
	174,900	254,930	1.46	38	6.36	16.84	100.5	95.2
	230,000	345,000	1.50	32	6.15	13.50	99.0	94.7
Average	163,160	273,000	1.67		6.16	13.51	99.0	95.4

this purpose at some temperatures, being in this interval, finding an increment of thermomechanical deformation $\Delta\varepsilon$ is necessary as is shown in
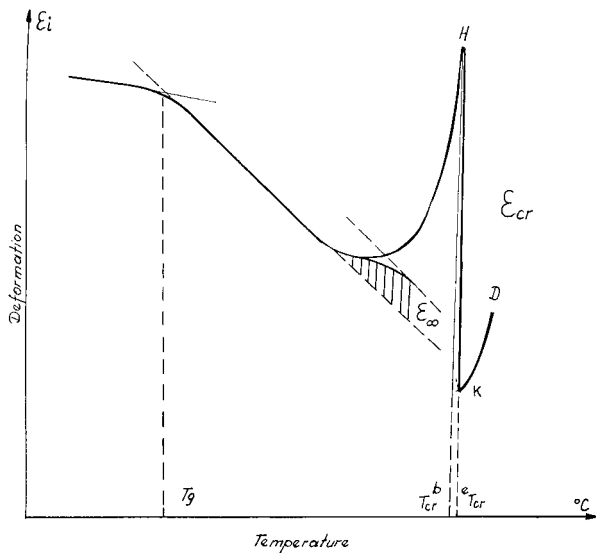
Figure 4 Thermomechanical curve for sulfur; T_{cr}^b, temperature of the beginning of melting; T_{cr}^e, temperature of the end of melting; $\Delta T_{cr} = T_{cr}^e - T_{cr}^b$.

Figure 3(a) for temperature T_f. Next, decreasing in every of these temperatures, the ε_∞ value by $\Delta\varepsilon$, location of unknown points is possible to find. This operation is shown in Figure 3(b) for temperature T_f. By junction all obtained points with points M and K' drawing a full thermomechanical deformation curve in individual PB 2000 is possible. It is practically overlapped by analogical curve for this polymer in the mixture with PB 143,000. This evidences that this procedure is applicable for dividing cumulative curve into its components. Due to this using it for study a structure of different materials, including sulfur, is possible.

In this way obtaining the real TMC of high elastic deformation being an image of integral MWD function of polymeric sulfur is possible. Next, in every point from n cross sections (Fig. 3) values of ε_i and T_i are measured. ΔT_i value is found based on these data. These data are enough to find the molecular weight[6] by using the following universal equation (2) for every point i.

To calculate values of the number-average $\bar{M}_{c(n)}$ and weight-average $\bar{M}_{c(w)}$ molecular weight, the following equations are used:

Table II   Molecular Weight and Thermomechanical Characteristics of the Blends of Polymeric and Mineral Sulfur

No.	$S_{\mathrm{polym}}/S_{\min}$	$\bar{M}_{c(n)}$	$\bar{M}_{c(w)}$	K	T_g (°C)	α_1*10^4 (K^{-1})	α_2*10^4 (K^{-1})	T_{melt} (°C)	φ_{cr}, % by Weight
1	0.15/0.85	114,900	179,190	1.56	43	6.41	14.00	98.0	88.0
		122,310	173,650	1.42	46	9.80	20.40	98.0	80.8
		135,560	191,150	1.41	50	7.60	18.80	100.0	82.0
	Average	124,260	181.330	1.46		7.94	17.73		83.4
2	0.32/0.68	106,580	196,100	1.81	31	5.85	14.92	98.5	74.2
		102,800	180,000	1.75	32	6.30	16.30	99.5	71.0
		118,500	225,100	1.90	29	6.00	15.31	99.5	68.3
	Average	109,290	200,400	1.83		6.05	15.51		71.2
3	0.52/0.48	80,340	160,680	2.00	49	7.62	18.64	98.0	51.5
		71,300	149,730	2.10	50	6.00	19.10	98.0	48.3
	Average	75,820	155,200	2.05		6.82	18.87		49.9
4	0.71/0.29	59,470	121,000	2.03	49	7.80	23.86	98.5	28.6
		50,500	108,600	2.15	48	6.24	23.00	100.0	34.7
	Average	54,990	114,800	2.09		7.02	23.43		31.7

$$\bar{M}_{c(n)} = \frac{1}{\sum\limits_{i=1}^{n} \dfrac{\varphi_i}{M_i}} \tag{3}$$

$$\bar{M}_{c(w)} = \sum\limits_{i=1}^{n} \varphi_i M_i \tag{4}$$

$$K = \frac{\bar{M}_{c(w)}}{\bar{M}_{c(n)}} \tag{5}$$

EXPERIMENTAL

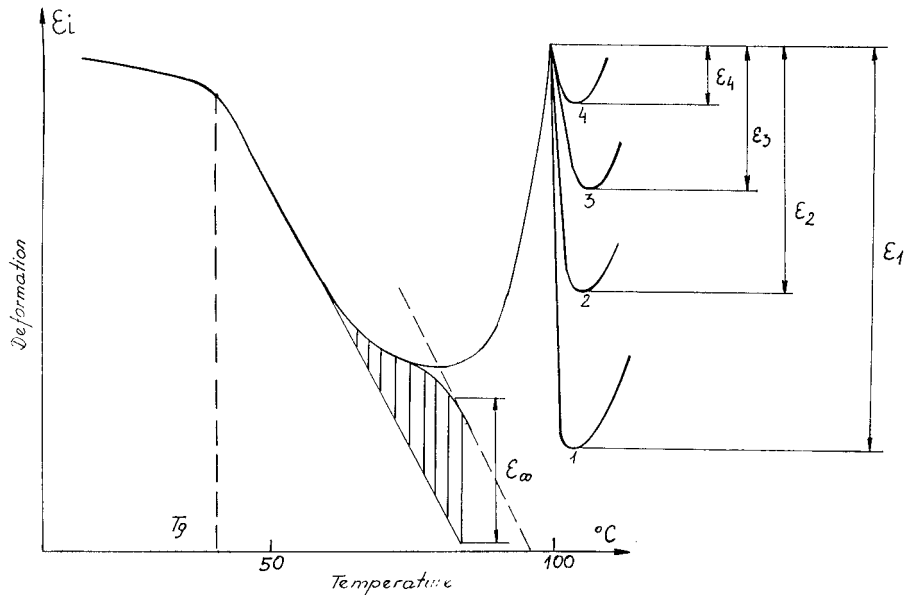Two samples of polymeric sulfur, one of mineral sulfur, and four different blends of mineral and polymeric sulfur (Table I) were tested. TMC of the sample of mineral sulfur is shown in Figure 4. Here, the shape of the curve up to 100°C is the same as for polymeric sulfur. A cristallic fraction in the sample of mineral sulfur gives a jump at a temperature of ∼ 100°C. This jump corresponds to the temperature of the beginning of its melting (point H) and accumulation of deformation up to the temperature of ending this process (point K). At this point on TMC inversion of deformation is reached from expansion during melting to molecular flow (curve KD).

The value of global deformation of amorphous and cristallic parts of sulfur being in a high elastic state gives information about their weight shares (φ_a and φ_{cr}, respectively), which is possible to be calculated by the following equation:

$$\varphi_{cr} = \frac{\varepsilon_{cr}}{\varepsilon_\infty + \varepsilon_{cr}} 100\% \tag{6}$$

In this way, values of crystallinity degree in the sample of mineral sulfur are obtained in a range between 94.7−96.7% (Table I). This result is well correlated with the data from roentgen diffraction analysis (95−97%). These data confirm an earlier formulated thesis[6] that deformation of macromolecules during thermomechanical analysis in a transitional zone is directly proportional to their weight share in the tested sample.

From the discussion shown above it is con-

Figure 5   Functions of molecular weight distributions of different sulfurs; (1) polymeric sulfur No. 1; (2) polymeric sulfur No. 2; (3) mineral sulfur.

Figure 6 Thermomechanical curves for blends of a mineral (a) and polymeric (b) sulfur (1) $a/b = 0.15/0.85$, $\varphi_{cr} = \varepsilon_1/(\varepsilon_1 + \varepsilon_\infty)$ 100%;   (2) $a/b = 0.32/0.68$, $\varphi_{cr} = \varepsilon_2/(\varepsilon_2 + \varepsilon_\infty)$ 100%;   (3) $a/b = 0.52/0.48$, $\varphi_{cr} = \varepsilon_3/(\varepsilon_3 + \varepsilon_\infty)$ 100%;   (4) $a/b = 0.71/0.29$, $\varphi_{cr} = \varepsilon_4/(\varepsilon_4 + \varepsilon_\infty)$ 100%.

cluded that the process of segmental relaxation of macromolecules in a transitional zone of TMC behave similarly (from deformation of a sample point of view) to process of transition from crystalline to amorphus state. It was found experimen-

tally that polymeric state does not contain a crystalline fraction.

Tables I and II contain values of the number-average $\bar{M}_{c(n)}$ and weight-average $\bar{M}_{c(w)}$ molecular weight and coefficient of polydispersity K, and in
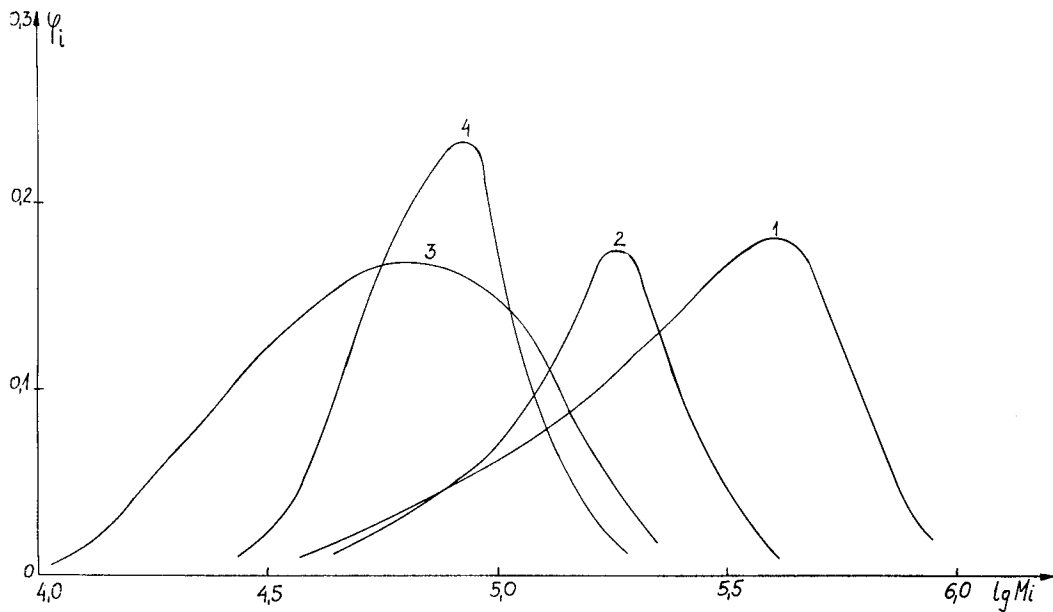
Figure 7 Functions of molecular weight distributions for the same samples of blends of mineral and polymeric sulfur showed in Figure 6.

Figure 5 functions of MWD, which were calculated from TMC of polymeric and mineral sulfur. The scatter of experimental data (variation coefficient $\sim 30\%$) is resulting, probably, from heterogeneity of sulfur structure, but not from the error of methodology used, because for more uniform polymers (e.g., standard polystyrene) variation coefficient does not exceed 10%. However, even considering this fact, deviation from the average value on 20–30% for polymers is accepted.

Figure 6 shows TMC for four model samples of sulfur with different content of crystalline fraction and different averaging MWD of amorphous fraction and Figure 7 their MWD curves. In Table II is shown good conformity between calculated and measured value of a crystalline fraction. Always measured values of molecular weights are well correlated with calculated based on the share and molecular weight of every component mixed in such a blend.

Coefficients of thermal linear expansion (Tables I and II) of sulfur being in a glassy state (α_1) and high elastic state (α_2) have values characteristic for polymers.

CONCLUSIONS

Thermomechanical mass spectroscopy used for testing materials in a solid state (i.e., not dissolved) shows that both mineral and polymeric sulfur behave as polymers.

Tested samples of mineral and two polymeric grades of sulfur have different molecular weights and functions of molecular weight distributions.

It was shown that the method used makes possible a quantitative analysis a content of a crystalline fraction in mineral sulfur. The value of a crystalline fraction is close to that obtained by roentgen diffraction analysis.

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