

# Poly(vinyl chloride) Composition. I. Mechanical Properties and Structure of Poly(vinyl chloride) and Fire-Retardant Additives

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## SYNOPSIS

Natural, activated, and modified microzeolites were studied individually and in combination with ammonium sulfamate as high-melting dispersed additives. The strength-deformation properties of poly(vinyl chloride) were improved within the interval of 3–8 wt % additive. The strengthening effect due to the considered dispersed additives can be ascribed to the optimal adhesive interaction of the phase-boundary surface and to the formation of a partially ordered dispersed phase. The tetrahedral configuration of the modified microzeolite that contains 3.5–4% zinc in its crystal lattice remains unchanged, but exhibits a reduced birefringence. These relationships are of exceptional importance for the use of poly(vinyl chloride). The introduction of certain amounts of the additives improves the melt flow of the polymer and facilitates the processibility of the compositions. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The materials based on poly(vinyl chloride) have a leading position by volume alongside polyethylene, polypropylene, polystyrene, and polyurethanes in the world production of polymers. In particular, poly(vinyl chloride) (PVC) is widely applied as a construction material in the building industry, in the electrical and chemical industry, in the production of various appliances for the use in the home, etc. Apart from its valuable good practical points, the consumption of PVC remains constant because of its smoke-forming ability and the freeing of toxic and corrosive substances on combustion.<sup>1</sup> The combustion and smoke-forming processes of PVC have received considerable attention.<sup>2–6</sup> The powdered fillers—oxides and hydroxides of aluminum, zinc, magnesium, and iron as well as the finely dispersed kaolin, bentonite, and chalk—have found wide use in improving the fire resistance of PVC. Natural zeolites also can find application in polymer compositions.<sup>7,8</sup> Aluminum hydroxide can be replaced

by some of these that contain significant amounts of water in their crystal structure.<sup>7</sup> It has been established that natural zeolites saturated with various hydrogen halides (HF, HCl, HBr, HI) reduce significantly the combustibility of polyethylene on mixing with it.<sup>8</sup> The processes of inhibiting combustion remain unclear in spite of the considerable results achieved. One of the complicating factors is the fact the physical properties of the fire-resistant polymers differ considerably from those of the unmodified polymers.<sup>9</sup>

The aim of the present investigation was to study the effect of powdered inorganic material—natural microzeolite with the general formula  $\text{Me}_{2/m}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n \text{SiO}_2 \cdot p\text{H}_2\text{O}$ , and an organic additive—the ammonium salt of sulfamic acid combined with ammonium sulfate, on the mechanical properties and structure of unplasticized PVC.

## EXPERIMENTAL

### Materials

PVC suspension with a Ficentcher constant of 67.0 was used. The ammonium sulfamate in combination

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with ammonium sulfate was obtained on the basis of polyisoprenic rubber.<sup>10</sup>

The natural microzeolite has the following composition: SiO<sub>2</sub>, 65.10%; Al<sub>2</sub>O<sub>3</sub>, 10.74%; Fe<sub>2</sub>O<sub>3</sub>, 0.98%; CaO, 0.88%; MgO, 0.88%; K<sub>2</sub>O, 3.40%; Na<sub>2</sub>O, 0.44%; H<sub>2</sub>O, 6.45%. The average dimensions of the particles were 8 microns; the pH of the aqueous extract, 8.36; and the active surface after BET, 108 m<sup>2</sup>/g. The crystalline water content drops to 1% after thermal treatment (activation) at 360°C for 2 h. The natural microzeolite contains 3.5–4% zinc because of the high exchange capacity of CaO (82.6%) after treatment with a 0.3*N* zinc chloride solution at 75°C. The modified zeolite was washed with distilled water until a negative reaction for chloride ions was observed, dried at 105°C for 2 h, and calcined at 360°C for 2 h. It contained about 1% crystal water.

Ammonium sulfamate in combination with ammonium sulfate (AS-1A), the natural microzeolite with 6.5% water (MZ-6.5% H<sub>2</sub>O), the activated microzeolite with 1% water (MZ-1% H<sub>2</sub>O), and the modified microzeolite containing 3.5–4% of zinc (Zn-MZ) was added to PVC in the amounts of 3, 5, 8, 10, and 15 wt %. The following system of stabilizers was employed: calcium stearate, 1.0 wt %; dibutyltin maleinate, 4.0 wt %; and Irganox 1010, 0.25 wt %.

The ingredients were mixed by plastication on rolls in the interval of 170–180°C for 7 min. After that, sheets were pressed at 180°C under 3.0 MPa and at a cooling rate of 25°/min.

### Measurements

The strength–deformation indices (i.e., yield stress,  $\sigma_Y$ ; stress at break,  $\sigma_B$ ; elongation at break,  $\epsilon$ ) were measured according to CMEA<sup>†</sup> standard 1199-78 at a stretching rate of 50 mm/min. The sizes of the specimens were as follows: length of the operating section,  $22 \pm 1$  mm; width,  $4 \pm 0.2$  mm; and thickness, 0.4 mm. The value of each parameter ( $\sigma_Y$ ,  $\sigma_B$ ,  $\epsilon$ ) was determined as an average one of the 8–10 specimens of each composition examined. The notched Sharp impact strength ( $\sigma_{IM}$ ) was measured according to CMEA standard 1491-79.

The melt index ( $I_m$ ) was determined on a capillary plastometer IIRT (USSR) at 200°C and a load of 21.6 kg. The equilibrium torsional moment ( $M_{equil.}$ ) was evaluated using a Brabender PLV 151 plastograph with a W30H kneader at 60 rev/min and 180°C.

Differential scanning calorimetry employing a DSC-111 instrument (Setaram, France) gave the

glass transition temperature ( $T_g$ ) at a rate of heating 10°/min and a sample mass of 100 mg.

The morphological observation was performed using a polarized light microscope Amplival POL-U, Carl Zeiss-Jena. Microtome sections 20–30  $\mu$ m thick were immersed in Canada balsam prior to observation. The cuts were perpendicular to the pressing direction of the samples. Microphotographs of the fracture surface of some compositions and a powdery MZ were made by using a scanning electron microscope BS-340 (Tesla, Czechoslovakia). The fracture surfaces were obtained by thermostating the specimen at –196°C for 2 h followed by breaking by means of an impact stress. The X-ray diffraction curves of MZ-6.5% H<sub>2</sub>O, and Zn-MZ were made on a TUR-M 61 apparatus (Germany) using CuK $\alpha$  irradiation.

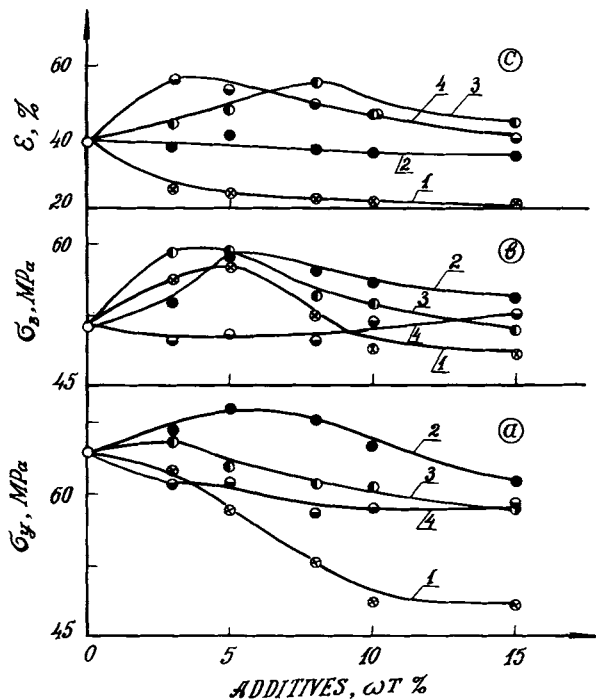
### RESULTS AND DISCUSSION

One of the problems of modern chemistry of polymers is linked with the creation of polymeric materials with improved fire-resisting properties. Other important characteristics regarding PVC are the smoke-suppressing and strength indices as well as the ease with which they are subjected to further treatment. It is known<sup>11</sup> that PVC free of plasticizers often contains small amounts of high-melting dispersed additives that improve its properties on further treatment.

The strength–deformation indices of the PVC compositions containing stabilizers and respective amounts of the studied organic or inorganic admixtures are listed in Figure 1. Comparatively good characteristics are noted, i.e., a constant or improved value of yield stress ( $\sigma_Y$ ), stress at break ( $\sigma_B$ ), and elongation at break ( $\epsilon$ ) when a natural MZ in inactivated, activated, or modified form in amounts of 3–15 wt % is used. The yield stress and the elongation at break are reduced by the combination of ammonium sulfamate and ammonium sulfate, the effect being most notable in the case of  $\sigma_Y$  with 8–15% admixture (Fig. 1, curve 1). In Figure 2 is given the relationship between the stress at break ( $\sigma_B$ ) of PVC compositions with AS-1A and different microzeolite concentrations (3–15 wt %). The  $\sigma_B$  is higher than in the initial PVC (51.2 MPa) in the interval of 3–10 wt % MZ. The elongation at break of these mixtures varies within 19–28%.

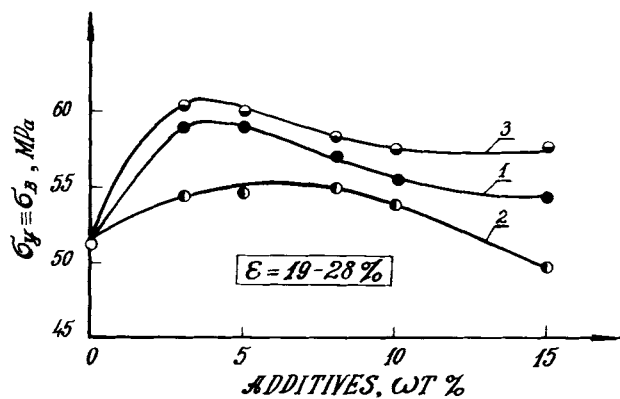
The powdered fillers strengthen the polymeric material, i.e., they improve stress at break and the elongation in a complex way. In the usual case, the improvement depends on the interaction between

<sup>†</sup> Council for Mutual Economic Assistance.



**Figure 1** The relationship between the (a) yield stress, (b) stress at break, and (c) elongation at break of PVC and the content of [1 (⊗)] AS-1A, [2 (●)] MZ-6.5% H<sub>2</sub>O, [3 (○)] MZ-1% H<sub>2</sub>O, and [4 (◐)] Zn-MZ.

polymer and the filler on the phase-boundary surface, on the size and degree of particle aggregation of the filler, and on its amount.<sup>12</sup> Of particular importance for this improvement of the polymer is the structure-forming role of the filler. This is reflected in the latter's capacity to form thin adsorption layers of the polymer on the surface of the dispersed particle. The improvement effect for PVC compositions



**Figure 2** The relationship between the stress at break of PVC + 5% AS-1A mixtures and the content of [1 (●)] MZ-6.5% H<sub>2</sub>O, [2 (○)] MZ-1% H<sub>2</sub>O, and [3 (◐)] Zn-MZ.

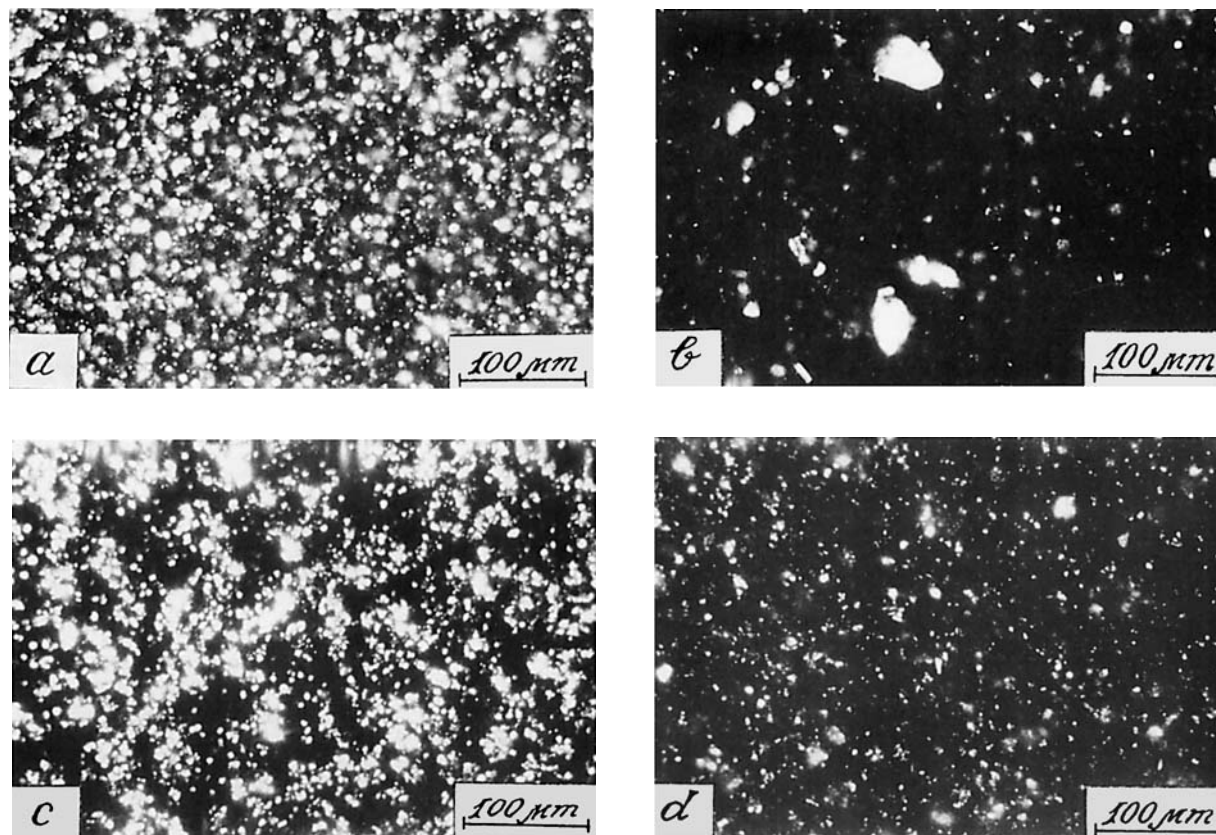
with 3–8 wt % additive is probably due to complex causes, among which two are of importance: (a) the existence of optimal adhesive interaction between the particles of the filler and the polymer; and (b) the formation of aggregates and agglomerates of the primary filler particles with a certain degree of order.

The adhesive interactions between the microzeolite (dispersed phase) and PVC (dispersed medium) are caused by van der Waals and dispersion forces between the active centers of the two components: Si—OH, Me—OH (where Me = Zn<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>), Si—O—Si, and Si—O—Al of the MZ and the polar chloromethylene groups of PVC. The microglobule PVC formations are strongly attached to the surface of the dispersed particle due to the physical bonds. The restricted mobility of the polymer chains near the phase-boundary surface causes an insignificant increase in the glass transition temperature<sup>12</sup> that can be observed with Zn-MZ and AS-1A (Table I). The high-melting dispersed additives specifically affect the temperature transitions of PVC.<sup>11</sup> Their activity depends on the chemical nature of the particles, on the state of the polymer layer near its surface, and on the atomic radius of the metals present in the additive. The segment mobility of PVC is higher probably with natural and activated microzeolites than with Zn-MZ and AS-1A, thus increasing the deformability of the system and lowering  $T_g$  (Table I).

Second, the strengthening of PVC in the case is assisted by the presence of a dispersed phase with a certain degree of ordering. The light-microscopy photographs of thin layers of rolled mixtures show the presence of separate particles of the filler and agglomerates [Fig. 3 (a) and (b)]. A similar distribution of the additives containing microzeolite and AS-1A can be observed on SEM microphotographs of the fracture surface of the pressed samples [Fig. 4 (a) and (b)]. In those microzeolite agglomerate formations, numerous effective contacts between the primary particles take place. On applying a stress, they can be stretched and bent, i.e., they deform,

**Table I** Characteristics of Mixtures of PVC, Microzeolites, and Ammonium Sulfamate (AS-1A)

No.	Composition	$T_g$ (°C)	$M_{max}$ (N × m)	$M_{equil.}$ (N × m)
1	PVC + stabilizers	78.0	30.5	17.0
2	PVC + 5% MZ—6.5% H <sub>2</sub> O	76.9	29.0	15.0
3	PVC + 5% MZ—1% H <sub>2</sub> O	76.3	28.7	15.0
4	PVC + 5% Zn-MZ	78.6	27.0	15.0
5	PVC + 5% AS-1A	79.0	29.0	15.5



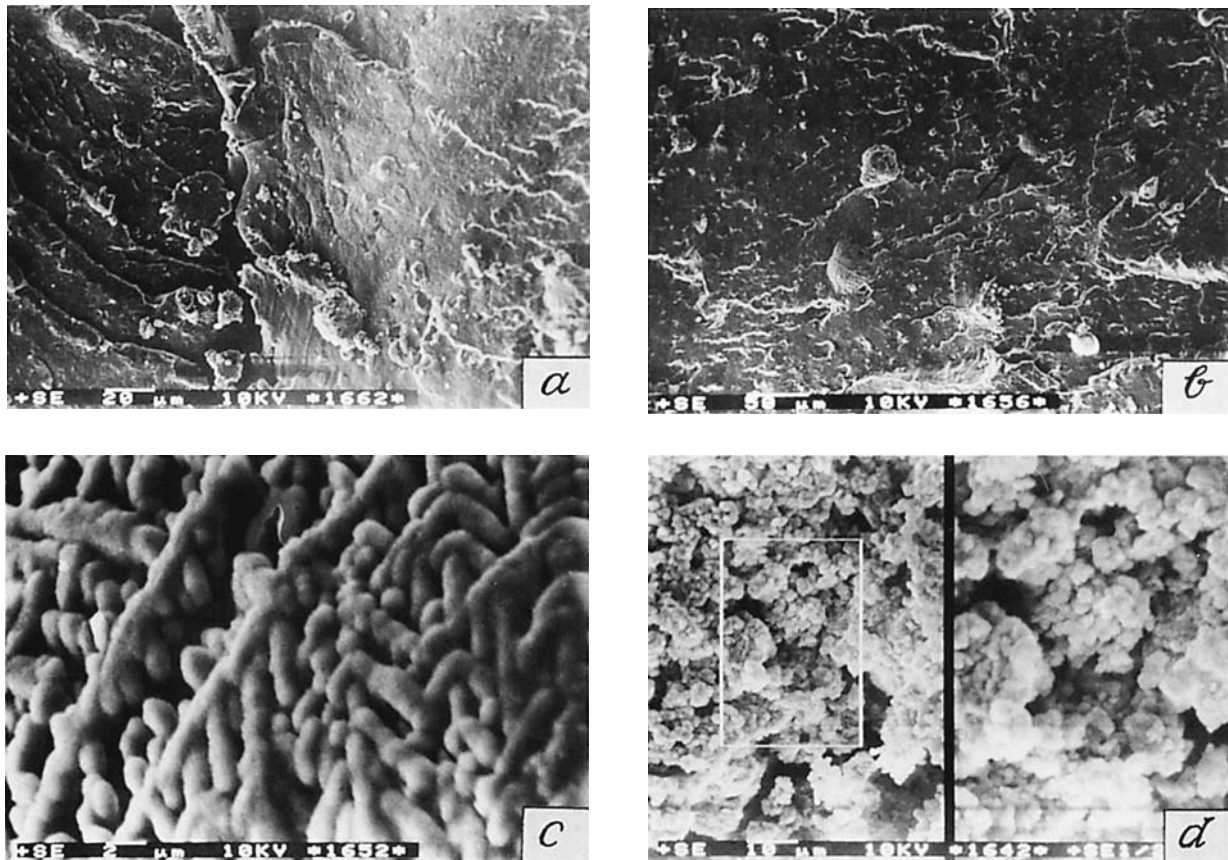
**Figure 3** Optical micrographs of thin layers of (a) PVC + 5% MZ-6.5% H<sub>2</sub>O, (b) PVC + 5% Zn-MZ + 5% AS-1A, (c) MZ-6.5% H<sub>2</sub>O, and (d) Zn-MZ; cross-polaroids,  $\times 180$ .

and in this manner, they absorb a significant amount of the destructive energy, improving the strength of the material. Moreover, the formation of a sorption layer of the polymer onto the particle surface is believed to be of real importance to the increase of the strength. The microphotography in Figure 4(c) indicates with a higher magnification one of the objects of Figure 4(b). Accordingly, it should be concluded that the particles of additives are wrapped by a polymeric layer, thus promoting an interaction between the polymer and the filler. From Figure 3, it can be also seen that the modified MZ (Zn-MZ) possesses a lowered birefringence in comparison with the natural MZ-6.5% H<sub>2</sub>O. Simultaneously, an agglomeration of the particles has been observed [Fig. 4(d)]. The structure of agglomerate becomes looser with more pronounced limits between the single particles.

The X-ray data indicate that the introduction of zinc into the structure of the zeolite does not change its tetrahedral configuration since no change in the intersurface distance ( $d_\alpha$ ) of the characteristic diffraction maxima is observed. Significant changes in

the relative intensity ( $I_{rel}$ ) have been observed for the following diffraction lines:  $d_\alpha = 3.87 \text{ \AA}$ ; 3.51–3.54  $\text{\AA}$ ; 3.01–3.05  $\text{\AA}$ ; 2.77  $\text{\AA}$ ; and 2.46–2.48  $\text{\AA}$ . The new strong diffraction maxima appear with  $d_\alpha = 2.93 \text{ \AA}$  and  $I_{rel} = 45$  and  $d_\alpha = 2.56 \text{ \AA}$  with  $I_{rel} = 38$  associated with the introduction of Zn<sup>2+</sup> in the zeolite crystal lattice (Table II). The difference in the birefringence of MZ-6.5% H<sub>2</sub>O and Zn-MZ can be ascribed to vulcanic glass, quartz, and clay impurities, which form aggregates with the clinoptilolite crystals in the initial zeolite. Ion exchange and repeated washing of the chloride ions purifies the clinoptilolite tufa. The microcrystal aggregates in it are destroyed, thus reducing their dimensions and birefringent activity.

In agreement with Manson and Sperling's<sup>12</sup> conclusion that the strengthened elastomers have improved impact strength, it can be noted that PVC-containing active fillers also exhibit improved impact strength characteristics (Fig. 5). This can be best seen at the 3–8 wt % concentration interval of the additive. In fact, the use of microzeolites and ammonium sulfamate in combination with ammonium



**Figure 4** SEM micrographs of the fracture surface of (a) PVC + 5% MZ-6.5% H<sub>2</sub>O, (b) PVC + 5% Zn-MZ + 5% AS-1A, (c) PVC + 5% Zn-MZ + 5% AS-1A, and (d) Zn-MZ.

sulfate does not lead to a deterioration of the impact strength of the initial unplasticized PVC, which is 3.0 kJ/m<sup>2</sup>.

The introduction of small amounts of high-melt-dispersed additives, up to ca. 10–15 wt %, to the unplasticized PVC affects specifically the flowability of the melt. This depends mainly on the nature of the additive. In Figure 6 is shown the change in the melt index ( $I_m$ ) as a function of microzeolite and AS-1A content. The introduction of the MZ in unmodified and activated forms improves the melt flow (Fig. 6, curves 2 and 3). PVC shows lower or approximately the same flow—about 1.4 g/10 min, independently of the concentration of the modified zeolite (curve 4). The melt flow of PVC decreases continuously with the increase in the concentration of the organic additive combined with ammonium sulfate (curve 1). It is advisable that this additive not exceed 3–5 wt % with respect to PVC. The compositions containing 5 wt % of AS-1A and up to 10 wt % of microzeolites lead to comparatively good flows.  $I_m$  varies within 1.95 g/10 min (initial PVC)

to 1.32 g/10 min (for composition that contains 5% of AS-1A and 10% Zn-MZ). The increase of the flow of PVC compositions containing natural and activated MZ is probably due to the immobilization of macromolecules of the polymer on the surface of the dispersed particles. This is also accompanied by a decrease of intermolecular interaction. Conditions are created that facilitate the mobility of the globulous formations along the direction of the flow.<sup>11</sup>

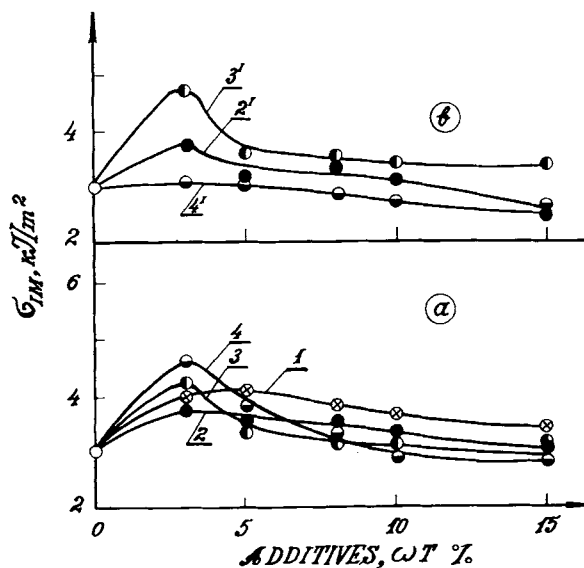
The observed changes of  $I_m$  correspond to the changes in  $T_g$  of PVC that contains 5 wt % of the studied additives (Table I). These relationships are also supported by the data for the changes of the torsional moment  $M$ , or  $\lg M$ , respectively, as taken from the Brabender plastograms (Table I and Fig. 7). As can be seen from Figure 7, the torsional moment that is directly linked to the viscosity characteristics of PVC-composition melts containing 5 wt % additive is lower than the one of PVC containing only stabilizers. Depending on the nature of the dispersed additive plastification (the time until  $M_{max}$ ) for PVC compositions is achieved within dif-

**Table II** X-Ray Data on Micronized Natural Zeolite (MZ—6.5% H<sub>2</sub>O) and on the Zinc Form (Zn-MZ)

No. of the Line	Clinoptilolite Samples			
	MZ—6.5% H <sub>2</sub> O		Zn-MZ	
	$d_{\alpha}$ (Å)	$I_{rel.}$	$d_{\alpha}$ (Å)	$I_{rel.}$
1	8.69	36	8.69	38
2	7.79	19	7.76	17
3	6.51	14	6.51	11
4	5.01	13	5.01	20
5	4.56	9	4.59	11
6	3.87	70	3.87	100
7	3.51	11	3.54	33
8	3.36	20	3.38	35
9	3.29	23	3.14	34
10	3.01	100	3.05	33
11	—	—	2.93	45
12	2.77	24	2.77	64
13	2.72	16	—	—
14	2.70	18	—	—
15	—	—	2.56	38
16	2.48	25	2.46	85
17	2.42	21	—	—
18	2.30	19	2.29	20
19	2.08	20	2.11	15
20	1.90	23	1.90	17
21	1.86	28	1.86	12
22	1.76	10	1.73	8
23	1.59	10	1.60	27

ferent periods of time (from 30 to 100 s). Then, the torsional moment, i.e., the viscosity of the melt, decreases until an equilibrium value is reached. The time for destruction of the agglomerates of the primary globules and for beginning of the melting (i.e., the time for gelation) is almost the same for all PVC compositions containing 5 wt % additive (approx. 4.5 to 5 min) and is less than the time necessary for gelation of PVC without additives (Fig. 7, curve 1). The PVC compositions presently considered can be processed in a conventional manner used for treating solid PVC.

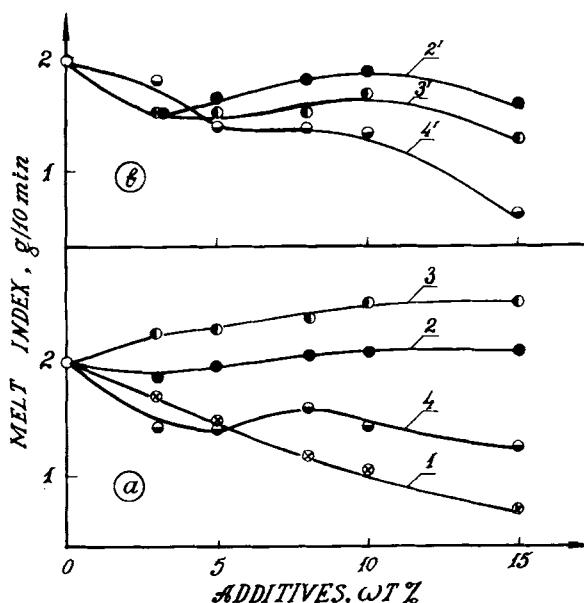
The heat resistance of PVC varies under the influence of the dispersed additives depending on their nature and amount in the polymer composition. In all cases, it is higher or the same as that of the initial PVC (83.3°C). Thus, PVC containing 5 wt % of AS-1A—82.9°C has the lowest heat resistance, whereas PVC + 5% AS-1A + 5% Zn-MZ—85.3°C has the highest.



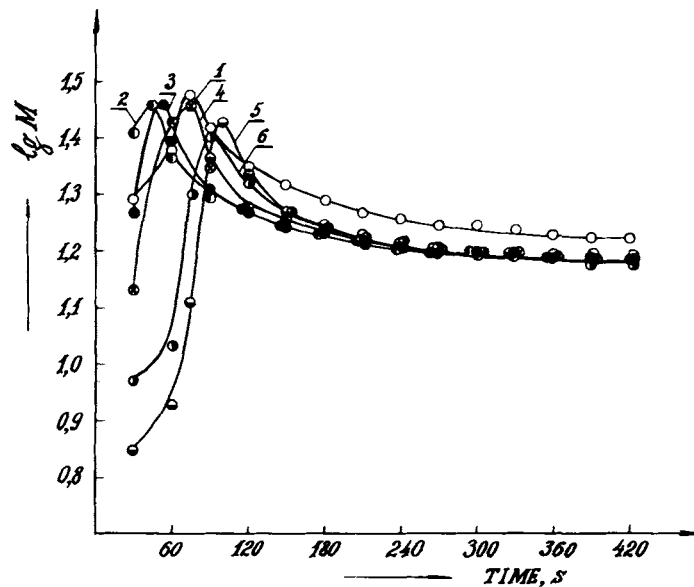
**Figure 5** Dependence of the notched Charpy impact strength on (a) PVC from content of [1 (⊗)] AS-1A, [2 (●)] MZ-6.5% H<sub>2</sub>O, [3 (●)] MZ-1% H<sub>2</sub>O, and [4 (●)] Zn-MZ; (b) mixtures of PVC + 5% AS-1A from content of [2' (●)], MZ-6.5% H<sub>2</sub>O, [3' (●)] MZ-1% H<sub>2</sub>O, and [4' (●)] Zn-MZ.

## CONCLUSION

The operational properties of unplasticized poly(vinyl chloride) are improved by the introduction



**Figure 6** Dependence of the melt index ( $I_m$ ) at 200°C, 21.6 kg load on (a) PVC from content of [1 (⊗)], AS-1A, [2 (●)] MZ-6.5% H<sub>2</sub>O, [3 (●)], MZ-1% H<sub>2</sub>O, and [4 (●)] Zn-MZ; (b) mixtures of PVC + 5% AS-1A from content of MZ-6.5% H<sub>2</sub>O [2' (●)], [3' (●)] MZ-1% H<sub>2</sub>O, and [4' (●)] Zn-MZ.



**Figure 7** Dependence of  $\lg M$  on time for [1 (○)] PVC, [2 (●)] PVC + 5% AS-1A, [3 (●)] PVC + 5% MZ-6.5% H<sub>2</sub>O, [4 (⊙)] PVC + 5% MZ-1% H<sub>2</sub>O, [5 (●)] PVC + 5% Zn-MZ, and [6 (●)] PVC + 5% Zn-MZ + 5% AS-1A.

of natural, activated, and modified microzeolite alone or in a combined form with ammonium sulfamate. The strengthening effect of these high-melting dispersed additives is determined by the optimal adhesive interaction on the phase-boundary surface and by the formation of a dispersed phase with a given degree of ordering. The introduction of certain quantities of these structurally distributed additives improves the flowability of the polymer melt.

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