

INFLUENCE OF ALUMINUM TRIHYDRATE PARTICLE SIZE ON THE COMBUSTION OF POLYDIMETHYLSILOXANE-BASED RUBBER COMPOUNDS

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The regularities of thermal degradation of $\text{Al}(\text{OH})_3$ powders and the compositions of polydimethylsiloxane and fire retardant with different size of particles (from 2 to 45 μm) were studied by the methods of the thermal analysis (TA), mass-spectrometry (MS) and the high temperature pyrolysis. It was shown that the size of flame retardant particles influences the physico-mechanical characteristics and combustion of polymeric compositions on the base of polydimethylsiloxane. The filling of the polymer with fine flame retardants improves the tensile properties of vulcanizates but the flame retardance is markedly decreased. The time of free combustion and the length of the burnt out parts are increased, the oxygen index and time of ignition delay are decreased while the flame temperature near the surface of the burning sample is increased.

The thermal degradations of $\text{Al}(\text{OH})_3$ powders and compositions of polydimethylsiloxane (PDMS) and fire retardants with different degrees of fineness were studied by dynamic thermogravimetry (DTG) (Q-1500D derivatograph), mass spectrometry (MS-80 chromatomass spectrometer) and high-temperature pyrolysis [1].

The fire-resistance was evaluated according to GOST 12.1.044-84 (oxygen index and limit of burning) and OST 1.90094-79 (time of free burning and length of burning through zone).

The fine fillers $\text{Al}(\text{OH})_3$ and Al_2O_3 catalyze the thermodestruction of PDMS accompanied by the release of low molecular volatile matter, which in turn creates favorable conditions for combustion.

One of the main ways to lower polymer combustibility is to change the heat balance in the flame by introducing inorganic fillers which decompose with heat absorption. Aluminum oxide trihydrate is applied on a large scale as a fire retardant in the production of polymers [2]. Its advantages over

other fire retardants are its non-toxicity, its non-volatility, and its stability in the processing of polymeric compositions. It does not release corrosive or toxic products on thermodegradation, and does not migrate to the polymer surface. Further, it has active smoke-suppression properties as well as ready accessibility and low cost.

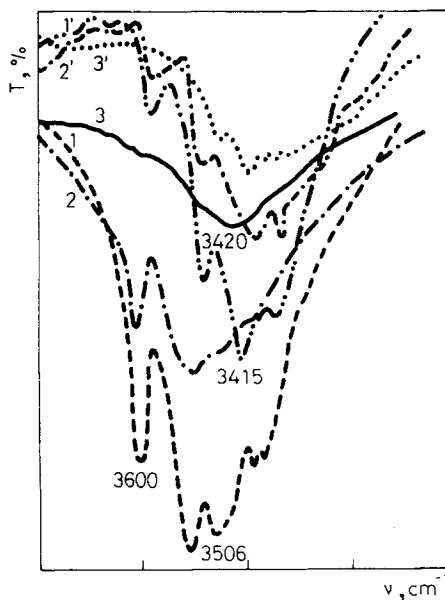


Fig. 1 IR spectra of TGOA powders (tablets with KBr) 1, 2 and 3, and films of PDMS compositions filled with TGOA 1', 2' and 3' for $\theta_{av,eq.} = 2, 10$ and 45 mm, respectively

The aim of the present work was to investigate the connection between the fineness of aluminum oxide trihydrate and its fire retardant effect on PDMS compounds.

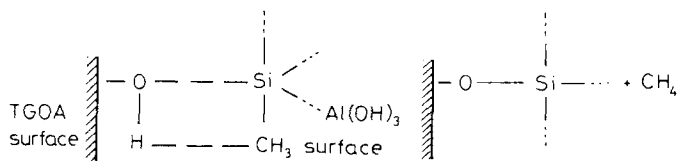
$Al(OH)_3$ is a crystalline hydrate where the bonds between the aluminum atoms and OH groups have an ion character, while all the OH groups are equivalent [3, 4]. The aluminum hydroxide obtained by the Bayer method has a lamellar crystalline lattice. The layers consist of octahedra of $Al(OH)_6$; hydrogen-bonds exist between the layers [5].

It was shown by infrared and infrared - multiplex disturbed total internal reflexion (IR-IR-MDTIR) spectroscopy that the OH groups of aluminum oxide trihydrate form hydrogen-bonds during the introduction of the filler into compositions based on DMS. The degree of this action depends on the

filler fineness (Fig. 1). It is known [6] that the valency vibrations of un-bonded OH groups occur in the interval $3700\text{--}3500\text{ cm}^{-1}$, whereas intramolecular bonds in the absence of resonance structures produce broad absorption bands in the range of $3450\text{--}3200\text{ cm}^{-1}$. It follows from Fig. 1 that as the fineness of TGOA (tablets with KBr) increases, the number of "free" OH groups increases with the decrease of $0_{\text{av.eq.}}$ for TGOA from 45 to $2\text{ }\mu\text{m}$ (curves 1 and 2); in contrast, the coarser the particles, the more OH groups take part in the hydrogen-bond interlayers in the lamellar crystal of TGOA, as the spectral absorption band at 3420 cm^{-1} proves (curve 3). It is necessary to point out that in the case of TGOA with $0_{\text{av.eq.}} = 2$ and $10\text{ }\mu\text{m}$ there are both free and bound OH groups; the absorption band of the latter is near 3500 cm^{-1} .

As shown in Fig. 1, on transition from the pure powders of TGOA to the PDMS - filler compositions the frequency of the maximum absorption band of the OH groups is practically unchanged for TGOA with $0_{\text{av.eq.}} = 45\text{ }\mu\text{m}$ (3420 cm^{-1} for pure TGOA, and 3415 cm^{-1} for the composition with PDMS), i.e. most of the hydrogen-bonds are directed to the inside of the particle crystals and the OH groups do not interact with the polymer (curve 3'). For fine TGOA with $0_{\text{av.eq.}} = 10$ and $2\text{ }\mu\text{m}$, the situation is changed. Whereas the maximum absorption band of the bound OH groups of TGOA $0_{\text{av.eq.}} = 10$ and $2\text{ }\mu\text{m}$ in the tablets with KBr is at 3500 cm^{-1} (Fig. 1, curves 1 and 2), it shifts to 3415 cm^{-1} for PDMS filled with TGOA, which testifies to the formation of strong hydrogen-bonds between the free OH groups of the ground filler and the polymer.

The formation of strong hydrogen-bonds between the OH groups of the filler surface and the methyl groups of PDMS may have negative consequences. Such hydrogen-bonds facilitate the thermodegradation of PDMS with the evolution of methane, according to the scheme [7]:



Information is available [7] about the occurrence of reaction at temperatures higher than 100° in polysiloxane compositions filled with asbestos and vermiculite. It has also been pointed out that the quantity of methane

evolved depends strongly on the content of OH groups on the surface of the filler.

It was shown by IR - MDTIR spectroscopy that the relative content of methyl groups decreased by 4.5% when a composition filled with aluminum hydroxide with $0_{av.eq.} = 2 \mu\text{m}$ was heated for an hour at 160° . The content of methyl groups was assessed via the optical density of the absorption band of the deformational oscillation bonds $\text{CH}_3 - \text{Si} - \text{CH}_3$ at 1255 cm^{-1} .

The TG data indicate that the fineness of TGOA powders has practically no influence on the overall evolution of water from them (rate of heating 10 deg/min). The weight loss on thermodegradation is close to the theoretical 34.6%. However, it is necessary to point out that the process of dehydration of fine powder $\text{Al}(\text{OH})_3$ ($0_{av.eq.} = 2 \mu\text{m}$) starts at 60-70 deg lower than for coarse powders ($0_{av.eq.} = 10$ and $45 \mu\text{m}$) (Fig. 2).

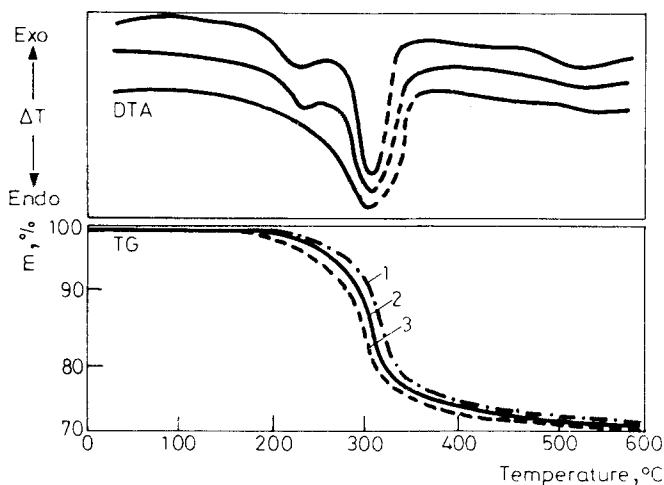


Fig. 2 TG and DTA curves of $\text{Al}(\text{OH})_3$ samples with different degrees of fineness ($V_{\text{heat}} = 10 \text{ deg/min}$)

Investigation of the destruction of filled PDMS by chromato-mass-spectrometry showed that at temperatures up to 260° dehydration and the evolution of methane proceed extensively in the composition with fine TGOA; this is due to the interaction of the methyl groups of PDMS with OH groups on the fine TGOA surface with $0_{av.eq.} = 2 \mu\text{m}$.

At temperatures over 330° , the evolution of the light volatile fragments practically stops. Products of the breaking of the main chain of PDMS -

hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) are recorded for compositions with fine filler. As concerns the composition with coarse filler where the breaking of the main chain of the polymer leads to the appearance in the gas phase of cyclosiloxane as well as methyl compounds (e.g. methane), in the same temperature range the evolution of water from the coarse filler ($0_{av.eq.} = 45 \mu m$) is still significant.

The TGA curves of weight loss of the PDMS compositions with TGOA of different fineness confirmed the data of mass-spectrometric investigations that the composition with fine fire retardant released water at lower temperatures than in the presence of the coarse filler. At temperatures higher than 400° , the difference in weight loss of the polymeric compositions, depending on the $0_{av.eq.}$ of the TGOA, is increased; the experiment with anhydrous Al_2O_3 suggests that this is due to the catalytic effect of fine Al_2O_3 , with lowering of the weight loss of PDMS on the introduction of coarse Al_2O_3 .

It has been established [7, 8] that one of the causes of the increase in the destruction velocity of rubber coverings based on siloxane is the effect of moisture adsorbed on the ingredients (in general on the fillers) and resulting in the thermal destruction of siloxane bonds at high temperatures. Accordingly, the content of free (adsorbed) moisture in the investigated samples of $Al(OH)_3$ was determined. The analysis results show that, with increase of the fineness ($0_{av.eq.}$ from 45 to $2 \mu m$), the quantity of adsorbed moisture rises (from 0.054 to 0.525%) and promotes the initiation of the following undesired processes in PDMS at high temperatures [7, 9]:

1. Hydrolysis of the main chains of PDMS, with the formation of end-fragments carrying OH groups
2. Degradation of PDMS with the participation of OH end-groups, with the formation of cycles.
3. Decomposition of PDMS with the participation of the end OH groups, with separation of the organic framing.

The methyl groups of PDMS are intensively oxidized at temperatures lower than 400° and depolymerization takes place with the formation of cyclosiloxane (D_n), accompanied by considerable heat emission. The DTA curves of the crosslinking compositions of PDMS with TGOA of different fineness are depicted in Fig. 3. Curve 4 shows that the beginning of oxidation of CH groups of rubber, accompanied by considerable heat emission, corresponds to 323° and the peak maximum to 360° . For the composition with the fine filler (curve 3), the exothermic effect is considerably less intense in comparison with the composition containing the coarse filler (curve 2) and it is shifted to the right by 10-20 deg. This confirms the mass-

spectrometric data concerning the evolution of methane into the gas phase with water from fine TGOA at lower temperatures.

Therefore, the DTA curves confirm the above-mentioned assumptions about the catalytic effect of fine aluminum oxide trihydrate in the thermal and thermooxidative degradation of PDMS.

The fineness of the filler not only influences the processes of thermal and thermooxidative degradation of PDMS rubber, but also has a marked effect on their combustion.

Studies of the high temperature pyrolysis accompanying the process of combustion have shown that, with a fine filler, temperatures 50 deg higher are observed on the surface of the composition than with a coarse filler, and the duration of the ignition delay is considerably smaller.

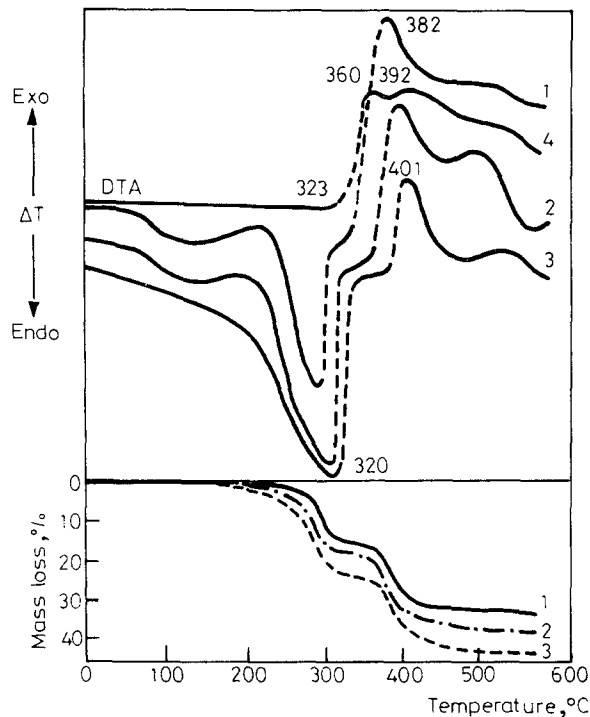


Fig. 3 TG and DTA curves of PDMS with compositions with TGOA with different degrees of fineness. 1 - 45 μm , 2 - 10 μm , 3 - 2 μm , 4 - PDMS without filler. ($V_{\text{heat}} = 10 \text{ deg/min}$)

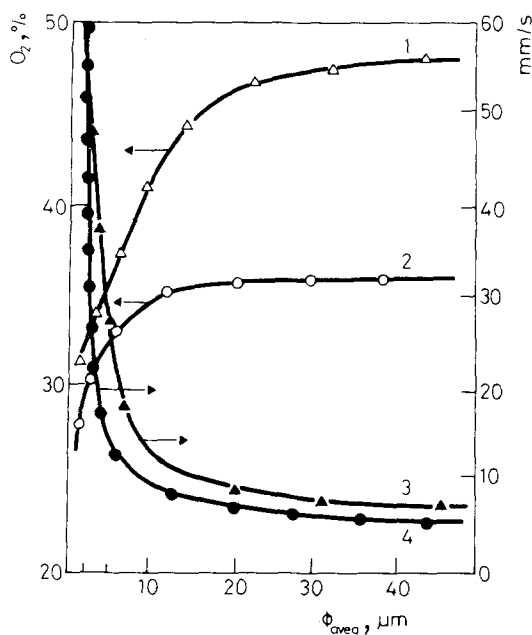


Fig. 4 Variations in the fire-retardant data for PDMS with the degree of TGOA fineness.
1 - L.O.T., 2 - limit of burning, 3 - length of burnt-out part, 4 - time of free burning

With increase of the fineness of the filler, the flame temperature is increased by 100 deg due to strong PDMS degradation and the earlier formation of volatile products of combustion.

Accordingly, with increase of the fineness of the fire retardant TGOA, the oxygen index of the system and the limit of burning become lower, while the length of the burnt-out part and the time of free burning of the sample increase (Fig. 4).

Thus, the data obtained permit the following conclusions:

-The processes of interaction of the polymer and the flame retardant under the conditions of thermodegradation undoubtedly play an important role in the general mechanism of combustion suppression.

-The fineness of aluminum oxide trihydrate markedly influences the combustion of composites containing it. The choice of the flame retardant in this case involves the optimization and the search for a composition meeting the requirements and with the necessary physicomechanical properties as concerns the combustion: with increase of the fineness of the filler, the

physicomechanical properties of the compositions are improved, but their fire retardance decreases.

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Zusammenfassung — Mittels Thermoanalyse, Massenspektrometrie und Pyrolyse bei hohen Temperaturen wurde die thermische Zersetzung von $\text{Al}(\text{OH})_3$ -Pulvern und die Mischungen aus Polydimethylsiloxan und feuerhemmenden Mitteln mit unterschiedlicher Korngröße (2-45 μm) untersucht. Man fand, daß die Partikelgröße des feuerhemmenden Mittels sowohl die physikalisch-mechanischen Eigenschaften als auch das Brennverhalten der Polymermischungen auf Polydimethylsiloxanbasis beeinflußt. Das Strecken des Polymers mit feingemahlenem flammenhemmenden Mittel verbessert zwar die Zugeigenschaften der Vulkanisate, die Flammenhemmung wird aber eindeutig vermindert. Die Zeit für den freien Brennvorgang und die Größe der verbrannten Teile wird erhöht, der Sauerstoffindex und der Zündverzug sinken, während die Flammentemperatur nahe der Oberfläche der Brennpote ansteigt.