

MODIFICATION OF ASBESTOS BY SILICONATES

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Abstract

The ability of some siliconates to hydrophobize and modify the surface of different kinds of asbestos was studied. A 6 wt% aqueous solution of potassium methylsiliconate was used in various quantities. After treatment, the asbestos samples were analysed by IR-spectroscopy, TG-DTA and electron microscopy. Structural changes were found on the asbestos surface, including the appearance of chemical bonds. The studies revealed that the sorption and lyophilic properties of asbestos are lowered, these being the basic preconditions for its injurious action on health.

Keywords: asbestos, electron microscopy, IR, siliconates, TG-DTA

Introduction

Silicon-organic polymers are finding ever-wider use in construction [1-11]. The physico-chemical properties of siliconates are defined by their composition and structure. Various authors have indicated the possibility of increasing the resistance of building materials to cold, heat, oxidation and radiation [12]. Some kinds of siliconates have the ability to hydrophobize hydrophilic surfaces [12-15].

The present work aims to establish the modifying action of some siliconates on asbestos.

Methods of investigation

Three different kinds of asbestos (M-6-40 grey, P-6-30 grey and P-6-30 yellow) were used as raw materials in the studies, with an aqueous solution of potassium methylsiliconate (PSN) in a concentration of 6% as a modifier. The main studies were carried out with M-6-40 grey asbestos treated with different quantities of PSN. After treatment of the asbestos with a mixture of appropriate quantities of siliconate and water, the resulting product was dried to constant weight at 60°C. The samples thus obtained were analysed by IR-spectroscopy, derivatographic analysis and electron microscopy. The derivatographic studies were performed on a Q-1500D device (MOM). The thermoanalytical curves obtained with a sample weight of 1000 mg, a heating rate of $\approx 10 \text{ deg} \cdot \text{min}^{-1}$ within the temperature interval 20–1000°C, a DTA sensitivity of 250 µV, a TG and DTG sensitivity of 500 µV, and a balance range of 500 mg.



Fig. 1 IR-spectrum of M-6-40 grey asbestos modified by different quantity of 6% water solution PSN. 1.) 50% towards the asbestos; 2.) 20% towards the asbestos; 3.) without PSN

Results and discussion

The IR-spectra of unmodified M-6-40 grey asbestos and of PSN are presented in Figs 1 and 2. They are used as standards for comparison with asbestos modified with a 6% aqueous solution of PSN in quantities of 20 and 50% of the asbestos weight. The absorption bands typical of PSN solution have wavenumbers of 440, 780, 860-870, 900, 1030, 1130, 1270, 1450, 1630, 2970 and 3420 cm⁻¹. The most intense bands are those with wavenumbers of 780, 1030, 1130 and 1450 cm⁻¹. The most characteristic frequency, v = 1030 cm⁻¹, relates to the Si–O–Si(C) bonds; v = 1270 cm⁻¹ to Si–CH₃; v 1450 cm⁻¹ probably to CO₃⁻¹; etc. [16].



Fig. 2 IR-spectrum of potassium methylsiliconate

The untreated asbestos spectrum is characterized by the absorption bands typical of asbestos, with wavenumbers of 302, 400, 440, 555, 614, 960, 1075, 1400, 1760, 3640 and 3688 cm^{-1} . The intensities at frequencies of 440, 960 and 3688 cm⁻¹ are the strongest. The frequencies of Si-O-Si and Si-O-Mg bonds and OH⁻ groups can to be identified. In the spectra of the samples treated with a 6% aqueous solution of PSN in a Quantity of 20% relative to the asbestos, absorption bands characteristic of the starting components are observed: those at 442, 555, 614, 960, 1075, 1760 and 3688 cm⁻¹ are typical of the raw asbestos, and those at 442, 782, 1020, 1275 and 1624 cm^{-1} of PSN. There are also a few absorption bands in the spectra that relate to neither asbestos nor PSN, at 1405, 1480, 1624, 3040 and 3160 cm⁻¹. At v = 1400 cm⁻¹, a band appears that increases considerably as the siliconate quantity is raised. The bands typical of PSN are much weaker in intensity than those of the starting PSN, which is obviously due to the presence of other components in the mixture as well. The new characteristic band at the larger quantity of siliconate in the mixture has a frequency of 455 cm⁻¹. On elevation of the siliconate content, the intensities of the new bands at 1380, 1480, 1625, 3045 and 3160 cm^{-1} increase, but not those at 1020 and 1075 cm⁻¹. These studies indicate that treatment of asbestos with a 6% aqueous solution of PSN results in new structural links. These are obviously

connected with the new coordination of OH⁻ and Si-O groups as elements of the changed asbestos structure.



Fig. 3 TG and DTG-curves of M-6-40 grey asbestos modified by different quantity of 6% water solution of PSN. TG₁ and DTG₁ - 50% towards the asbestos; TG₂ and DTG₂ - 20% towards the asbestos and TG₃ and DTG₃ - without PSN

The TG, DTG and DTA curves in the same tests (Figs 3 and 4) essentially confirm these changes in the asbestos structure. The TG curves demonstrate that, on increase of the PSN quantity in the raw mixture, the mass loss during the process of thermal treatment also increases. While the mass loss up to the end of the decomposition process for the untreated asbestos, is 14.1%, for asbestos treated with a 6% aqueous solution of PSN in a quantity of 50% relative to the asbestos it is 17.5%. The TG dependences are of a two-step character, the difference in mass loss arising in the first step within the temperature range 100-180°C. The temperature interval and the TG dependence also change during further treatment of the samples. With increase of the siliconate quantity, two intermediate stages of mass loss formation are recorded in the DTG curves. If the mass loss at lower temperatures is related to siliconate destruction, then the change in the thermogravimetric dependence and the start of the end-dehydration of asbestos at a lower temperature appears to indicate a change in the asbestos structure. This is clearly expressed in the DTA curves in Fig. 4, where enthalpy changes in the system are recorded within almost the whole temperature range of the study. The separation of the structural water from the asbestos at lower temperatures confirms the changes in number and strength of the hydrate links in the asbestos. The results suggest that the new structural links



Fig. 4 DTA-dependences of M-6-40 grey asbestos modified by different quantity of
6% water solution of potassium methylsiliconate; DTA₁ - 50% towards the asbestos;
DTA₂-20% towards the asbestos; DTA₃ - without PSN

formed between siliconate and asbestos labilize the initial OH-bonds in the asbestos. As considerable siliconate dehydration is recorded within the temperature range 650–700°C, not all of the asbestos OH-groups react with the siliconate.

The siliconate distribution on the asbestos fibres was studied by EM. EM photos show that the siliconate is captured mainly along the asbestos surface. The interaction does not produce an exact film; particles are captured only at definite sites along the asbestos surface, probably where the surface forces on the asbestos are more poorly compensated.

The results of derivatographic analysis, IR-spectroscopy and electron microscopy indicate that chemical bonds are formed between asbestos and potassium methylsiliconate, the new structure being characterized by the formula:



Conclusion

Modification of asbestos by silicone solutions involves structural changes on the asbestos surface, including the appearance of chemical bonds. The results obtained indicate that pretreatment of asbestos with various modifiers (here, with a 6% aqueous solution of potassium methylsiliconate) leads to lower sorption and lyophilic properties, these being the basic preconditions for its injurious action on health.

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Zusammenfassung — Zur quantitativen Analyse des Effektes verschiedener Faktoren bei thermogravimetrischen Messungen wie z.B. Probenmenge, Aufheizgeschwindigkeit usw. wurde eine dimensionslose Zahl entwickelt und eingeführt. Die TG-, DTG- und *T*-Angaben verschiedener gravimetrischer Messungen können direkt zur Berechnung der drei Vergleichskonstanten verwendet werden. Die unter verschiedenen Bedingungen gemessenen TG-Daten für CaCO₃ zeigen die Transformationsmethode und ihre Anwendbarkeit für die Berechnung der Korrelation der Messungen.