

Title: The synthesis and structure of oligomers based on phenol-formaldehyde resins and montmorillonite.
The influence of concentration and acidity on their structures.

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Introduction

Montmorillonite (MMT) is among polymer fillers being studied. MMT incorporation into polymers and oligomers may result in enhancing their properties [1] Improving the polymer necessary properties is usually based on the exfoliation of MMT in the polymer during polymerization [2]. Composite polymer materials based on MMT yet may be used in various fields. However, there are no data on synthesis and application of polymer materials filled with MMT as a binding agent for grinding tools. Previous experience [3] demonstrated application prospects of phenol-based compounds as the polymer matrix for this case.

Aim

The objective of the paper was to study the synthesis of phenol-formaldehyde-based oligomers containing montmorillonite as the filler and to assess the effect of the filler quantity and acidity change.

Methods

FTIR and XRD data were used to study the structure of synthesized oligomers. FTIR spectra were registered with Nicolet is10 spectrometer within the range 400–4000 cm⁻¹. Specimens were prepared with KBr pellets in the ratio KBr : investigated material = 300 to 1.5. XRD analysis was carried out using Rigaku D/max-A X-ray diffractometer with CuK α ($\lambda=0.154$ nm) in the 2 θ range of 10–90 $^\circ$ with the step 0.02 $^\circ$ at room temperature.

Experimental part

To study the effect of the filler amount addition, phenol-formaldehyde based oligomers were prepared by changing MMT and alkali concentrations according to the following procedure: 1) Weighed portions of montmorillonite in amount of 5 g, 10 g, 20 g and 30 g were dissolved in 100 g of water; then, these solutions were heated at 40 $^\circ$ C during 4 days. 2) Four weighed portions of phenol-formaldehyde (PF) in amount of 25 g each were dissolved in 100 g of 10 % alkali aqueous solution at 60 $^\circ$ C and permanent stirring during 4 days. 3) After 4 days, MMT swollen in water was added into 100 g of phenol-formaldehyde; this mixture was stirred and held at controlled temperature 80 $^\circ$ C during 24 hours. 4) During this period, oligomers with MMT was precipitated, filtered and dried until the weight loss became less than 0.002 g. To study acidity effect on the synthesis process, oligomers were prepared by the following procedure: 1) 5 % w/w of MMY aqueous solution was prepared. 2) 10, 15, 20, 30 % w/w alkali solutions were prepared, and 4 PF weighed portions of 25 g each were dissolved in them. Then, solutions were heated. The third and fourth steps of the preparation procedure were similar with the ones described above.

Results

Figs 1 and 2 illustrate IR-spectra of prepared oligomers as well as phenol-formaldehyde and montmorillonite spectra. To identify oligomer spectra, phenol-formaldehyde and montmorillonite characteristic bands were used (Table 1).

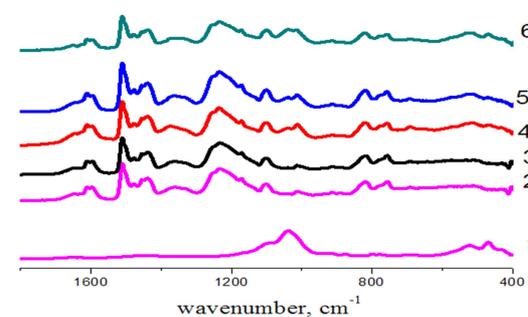


Fig.1 – Effect of MMT concentration on the oligomer structure: 1– pure montmorillonite; 2– pure phenol-formaldehyde; 3, 4, 5, 6 – spectra of the oligomers prepared from 5%, 10%, 20%, 30% w/w. MMT solutions respectively

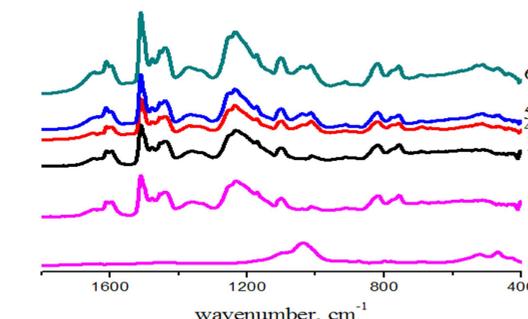


Fig.2 – Effect of alkali concentration on the oligomer structure: 1– pure montmorillonite; 2– pure phenol-formaldehyde; 3, 4, 5, 6- spectra of the oligomers prepared from 10, 15, 20, 30% w/w alkaline solutions respectively

Table 1–Characteristic bands of phenol-formaldehyde [4] and montmorillonite[5]

No	Wavenumber, cm ⁻¹	Atomic group
Phenol-formaldehyde		
1	1650	C=C aromatic ring
2	1610	
3	1536	
4	1513	
5	1478	C-H aliphatic group
6	1450	C=C benzene ring obscured by –CH2– methylene bridge
7	1370	OH in plane vibration
8	1330	
9	1237	C-C-OH asymmetric stretch
10	1170	C-O stretch
11	1100	C-O-C asymmetric stretching vibration of aliphatic ether group
12	1039	C-O in –CH ₂ OH group
13	1008	OH in –CH ₂ OH
Montmorillonite		
1	1113	out-of-plane stretching of Si-O
2	1035	in-of-plane stretching of Si-O
3	916	bending of Al-Al-OH
4	875	bending of Al-Fe-OH
5	836	bending of Al-Mg-OH
6	793	platy form of tridymite SiO ₂
7	692	quartz
8	529	bending of Si-O
9	500	

XRD pattern are shown in Figs.5 and 6:

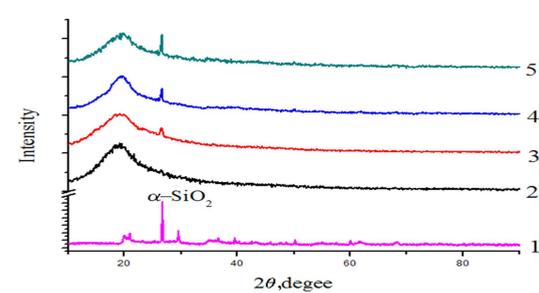


Fig.5 – XRD patterns of synthesized oligomers and MMT: 1 – montmorillonite; 2, 3, 4, 5 – patterns of oligomers synthesized using 5%, 10%, 20% and 30% w/w MMT solutions, respectively

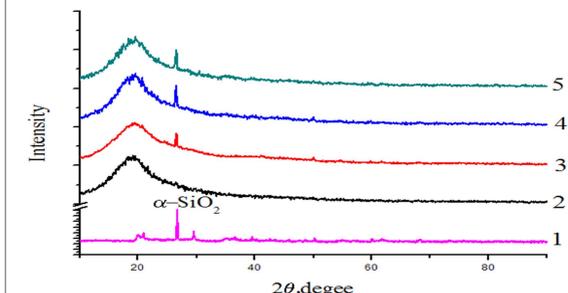


Fig.6 – XRD patterns of synthesized oligomers and MMT: 1 – montmorillonite; 2, 3, 4, 5 – patterns of oligomers synthesized using 10%, 15%, 20% and 30% w/w alkaline solutions of phenol-formaldehyde, resp.

Discussion

The influence of MMT concentration: When evaluating data(Fig.1), it was possible to propose that MMT embedding poorly affected phenol-formaldehyde oligomerization. At the same time, it influenced its structure– especially with respect to MMT aluminosilicate sheets. Probably, these layers coordinated oligomer molecules around these sheets during exfoliation. At the same time, two coordination types were possible: 1) coordination of the benzene rings with silicon atoms (Fig. 3a); 2) coordination of oligomers phenolic and methoxyl groups around oxygen atoms (Fig. 3b):

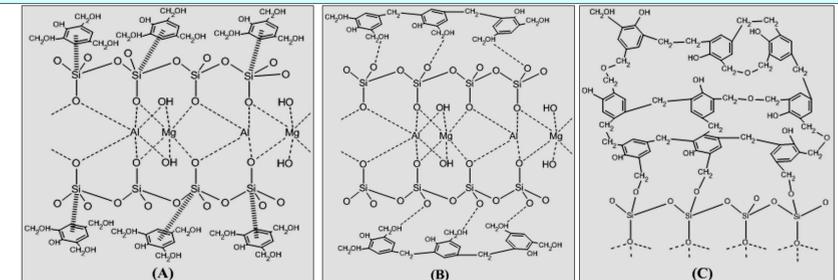


Fig.3 – Coordination structures in synthesized oligomers

The following facts served as evidences for these structures: 1) Band intensity at 1610 cm⁻¹ 1513 cm⁻¹ strongly increased; at the same time, band intensities at 1650 cm⁻¹ and 1536 cm⁻¹ were almost unchanged. All these bands featured vibration of C=C group in benzene ring. 2) Band intensity at 1234 cm⁻¹ also increased (specific for C-C-OH group) as well as at 1012 cm⁻¹ (specific for the hydroxyl group vibration in–CH₂OH). 3) At the same time, band intensities specific for –CH₂–(1436 cm⁻¹), C-H (1478 cm⁻¹) groups increased poorly while the bands specific for C-O-C (1106 cm⁻¹), C-O in CH₂OH(1039 cm⁻¹) stayed absolutely unchanged. 4) Bands at 514 cm⁻¹, 470 cm⁻¹ (attributed to Si-O bond vibration) and 916 cm⁻¹ (attributed to Al-OH) appeared in oligomer spectra. 5) When compared MMT and oligomer spectra, it was seen that the bands specific for Si-O vibration were shifted to lower frequencies – from 529 cm⁻¹ and 500 cm⁻¹ to 514 and 470 cm⁻¹.

Acidity effect: Based on the data obtained, it was possible to suppose that acidity decrease has resulted in formation of novolac-type oligomers with chemical bonds –CH₂– and –C-O-C-(Fig.3c). These oligomers formed C-O-Si type bridges with aluminosilicate layers. Existence of this structure may be reasoned in the following way: intensity considerably increased for the bands corresponded to vibration of C=C groups in benzene rings, –CH₂– methylene bridges and C-O-C ester groups. Besides, the band (1106 cm⁻¹) corresponded to C-O-C vibration may also indicate vibration of C-O-Si group. Based on these results, it is possible to suppose that phenol-formaldehyde fragments bond with each other via C-O-C and –CH₂– bridges and form C-O-Si type chemical bonds with MMT aluminosilicate layers.

XRD analyses: Peaks specific for MMT crystalline phases disappeared from oligomers XRD patterns (Fig. 5 and Fig.6, lines 2–5) meaning full lamination of the mineral in the oligomer structure. Spread-out and wide peaks of amorphous phase indicated the high dispersion degree of the formed material. Gradual increase of MMT and alkali concentration resulted in appearance of the peak corresponded to α -quartz contained in aluminosilicate sheets. Probably, part of these sheets was not capable to coordinate with organic phase or to form chemical bonds; that is why, these sheets were not included into the inter-plane space between phenol-formaldehyde layers.

Conclusions

Thus, during the study, it was revealed that almost complete MMT exfoliation into aluminosilicate sheets took place during synthesis of phenol-formaldehyde oligomers containing montmorillonite. In turn, these sheets coordinated oligomer organic components around themselves and formed chemical bonds with them. Increase of MMT concentration during oligomer synthesis resulted in increasing the amount of aluminosilicate sheets embedded in the oligomer. Sheets and organic layers were held together, probably, with coordination bonds and/or Van der Waals forces. Acidity decrease resulted in forming covalent bonds between functional groups of phenol-formaldehyde and silicon-oxygen groups of aluminosilicate sheets.

References

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