

# STUDY OF INTERACTION OF SHUNGITE CARBON WITH WATER SOLUBLE POLYMERS USING MELAMINE FORMALDEHYDE AS AN EXAMPLE

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## Introduction

Composites based on water-soluble polymers are attractive as environmentally friendly materials. Incorporation of carbonaceous fillers into relatively brittle polymeric matrices with poor resistance to crack propagation aims at a multifunctional effect. First of all it relates to controlled rheology and improvements in physical mechanical properties and conductivity as well as thermal and conductive stability. Melamine formaldehyde can be taken as an example of such polymers. Random mats of cellulose fibers impregnated with melamine-formaldehyde resin (MF) are used for flooring laminates. To obtain electrically conductive composites carbon fibers and carbon black (Vulcan XC 72) were added [1]. However, the conductive composites had some drawbacks connected with the hydrophobic nature of carbon fillers, namely low adhesion of carbon fibers to MF and inhomogeneous distribution of carbon black (CB).

Shungite carbon (ShC) has naturally modified surface properties. It has been successfully incorporated into polymers of different types, thus improving composite properties such as elasticity and conductivity [2]. Its amphiphilic surface and higher concentration of oxygen containing groups in comparison with conventional carbonaceous fillers were thought to be useful in water soluble polymers as well. Furthermore, nanoparticles released from shungite carbon in aqueous solutions are of special interest. Nanosize particles liberated from ShC into aqueous dispersions were shown to be the main source of ShC reactivity in interaction between the shungite filler and polymer matrix on the molecular level in elastomers [3].

The addition of ShC was investigated towards making MF-cellulose laminates dissipative. ShC is easier to handle than CB and its inherently lower conductivity led to lower and stable conductivity of the composite. The stiffness was not affected by the presence of ShC but the strength and strain were decreased with filler content [4].

The current experiments were performed on model systems in order to estimate the reactivity of aqueous dispersion of ShC in comparison with the original powder. Its

interaction with melamine formaldehyde in aqueous solution was studied by viscosimetry, FTIR and EPR methods are the subject of the present contribution.

## Experimental

Different fillers, carbon black Vulcan XC 72, shungite type I (98 wt.% carbon), shungite type III (32 wt.% carbon) and stable aqueous dispersions of ShI (ASh), are compared. Melamine formaldehyde powder (Madurit Mw909) was used in the study in colloidal form dissolved with an equal weight of water. It is basic in nature pH=8.8.

Rheological experiments were performed on shungites in MF/water solutions at a ratio of 50/50 by weight and the viscosity measured in a rotary viscosimeter (Rheotest-2.1) with a cup and bob measuring system for different shear rates from  $13.5 \text{ s}^{-1}$  to  $437 \text{ s}^{-1}$ .

Infrared spectroscopy (FTIR) was carried out using an Equinox 55/S high performance FTIR spectrometer in transmission mode in a wavelength range of 400 and  $4000 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$ . Samples were made in the form of thick films, then dispersed, mixed with KBr at a ratio of 1:100 by weight (1:50 for CB) and pressed to form pills.

The flexibility of MF chains at room temperature has been characterized using EPR with spin label (4-amino-TEMPO) [5]. Spectra for analysis were registered on EPR spectrometer of type "Bruker EMX". Differences in polymer chain mobility under different curing conditions were observed.

Analysis of EPR spectra of MF and its composites allows us to detect a continuous distribution pattern of spin-labels with effective correlation times in the range of  $10^{-9}$ - $10^{-7}$  s characterizing a superposition of polymeric chain mobilities in wide ranges [6]. Average correlation times were estimated from the model.

## Results and Discussion

The viscosity of all three filler/solution systems is such that as the filler concentration increases first quickly in a low concentration range, then decreases somewhat in an intermediate concentration range and finally increases moderately in a high concentration range. This might be interpreted as a structuring of the mixture at low concentrations followed by destruction of this structure at intermediate concentrations. The structuring was observed at 0.5 wt.%, 1 wt.% and 5 wt.%, respectively for CB, ShI and ShIII. A concentrated aqueous dispersion of ShC structures at 0.25 wt.% The viscosities of the ShI mixture are only a third of the viscosities of the CB and ShIII mixtures. Typical values of viscosity for ShI in MF in water solutions are significantly lower and less concentration dependent. The mixtures with ShIII could show the same viscosity at higher concentration than CB in the same solution.

Differences between the FTIR spectra of the components and the composites such as shifts in the positions of absorption lines were analysed. Only the absorbance shift toward higher frequencies in the region from about  $3300 \text{ cm}^{-1}$  to about  $3500 \text{ cm}^{-1}$  on adding ShI to the matrix polymer is significant. This is in the range of stretching modes in

hydroxyl groups, alcohols and phenyls as well as N-H stretching bonds. When ShIII is added there is no shift in the peak absorption. However, the siloxy peaks at  $779\text{ cm}^{-1}$  and  $798\text{ cm}^{-1}$  are shifted to about  $811\text{ cm}^{-1}$ , likely due to hydrogen bonding. Addition of CB also produces a relatively highly structured spectrum in the range from about  $3400\text{ cm}^{-1}$  to about  $3800\text{ cm}^{-1}$ , where signatures typical of hydrogen bonding are expected. All this is compatible with the proposition that hydrogen bonds are formed between the oxygen containing groups of the filler particles and the nitrogen containing groups of the MF. These hydrogen bonds are probably the main chemical interaction mode between the filler particles and MF, and the interface bond is relatively weak.

Experimental EPR spectra of MF and its compositions with ShI and aqueous dispersion of ShC after polymerization at ambient conditions are presented in Fig.1. A model based on a rectangular distribution pattern of correlation times fits well with the experimental EPR spectra [6].

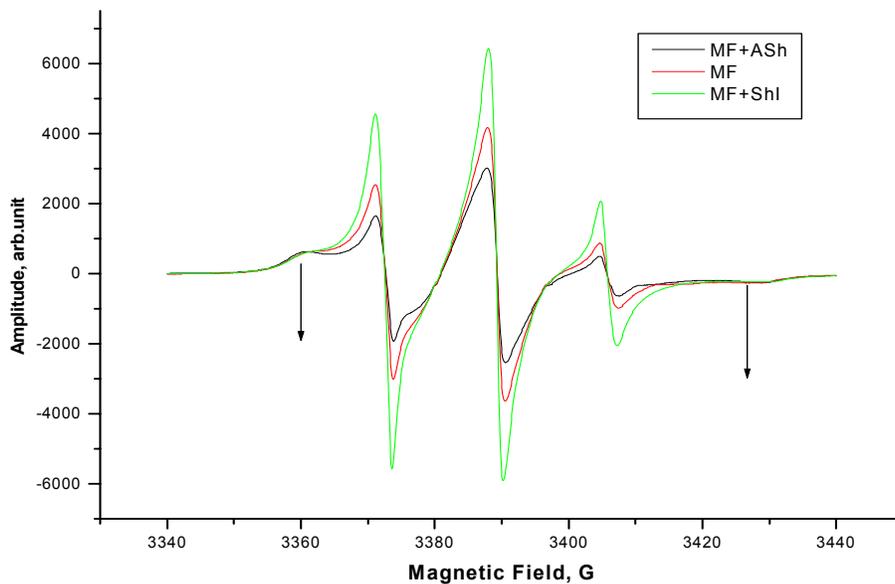


Figure1. EPR spectra of spin-labeled MF, its compositions with ShI and aqueous dispersion of ShC after heating at  $65\text{ }^{\circ}\text{C}$  for 20 min.

Correlation time distribution patterns corresponding to different curing conditions were determined (see table 1). The main difference is seen in the kinetics of the polymerization which reflects changes in the mobility of polymeric chains in the vicinity of carbon particles/nanoparticles. Incorporation of ASH leads to faster immobilization of polymeric chains which does not change during heating.

## Conclusions

The higher reactivity of aqueous dispersions of ShI was characterised by increase of chain mobility and decrease of viscosity in melamine-formaldehyde resin compositions. Probably the release of ShC nanoparticles is responsible for structuring micron size

shungite fillers in MF and for decreasing the viscosity with filler concentration. Infrared spectroscopy (FTIR) showed that hydrogen bonds are the main chemical interaction mode between ShC particles and MF.

A higher mobility of polymer molecules in the presence of ShC nanoparticles was observed. This is an advantage in regard to achieving homogeneity in distribution of components in nanocomposites. The kinetics of polymerization was higher for MF with aqueous dispersions of ShC indicating multi-functionality of ShC nanoparticles in MF. The approach worked out for the engineering polymer like MF could be applied to biopolymers with shungite.

Table 1

Correlation time ranges ( $\Delta\tau$ ) and average values ( $\tau^*$ ) for MF compositions

Samples	Just prepared	4 days at ambient conditions	Heated, 65 °C 20 min	15 days at ambient conditions
	$\Delta\tau / \tau^*, 10^{-9} \text{ s}$			
MF (control)	0.02-50/1	0.1-250/5	0.1-250/5	1-10000/100
MF+ CB 0.5 wt. %	0.05-50/1	0.04-100/2	0.04-100/2	0.04-400/4
MF+ShC 1 wt. %	0.05-50/2	0.05-50/2	0.02-200/2	0.05-500/5
MF+ShIII 1 wt. %	0.02-50/1	0.02-50/1	0.06-150/3	0.05-500/5
MF+ ASh 0.0045 wt. %	-	0.1-250/5	0.05-500/5	1-10000/100
MF+ ASh 0.045 wt. %	0.06-150/3	0.15-1500/15	0.15-1500/15	0.15-1500/15

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