

The feasibility of using red mud in coatings based on glyptal resins

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The possibility of industrial waste – alkaline red mud to be used as the filler of glyptal resins and coatings thereof is considered. It was determined that the most effective way of compounding of said components was *in situ* combinations during the synthesis of the polymer, providing systems with filling factor up to 36 wt.% with decreased moisture absorption ability in comparison to the initial resin. It was demonstrated that the most probable cause of this performance increase is the formation of chemical bonds between the hydroxyl groups of glyptal and weak van der Waals bonds between the carbonyl group of the resin and surface groups on red mud.

Introduction

The so-called “red mud” is the industrial waste that forms during the alkaline processing of bauxite ores at the alumina production. It is a fact, that at least 35-40 % of the processed ore converts into the red mud. [1-5].

The negative environmental influence is caused by the strong alkalinity of the red mud (its pH can be in range 11-13). Considering the fact, that typically the volumes of such waste are significantly large, this leads to noticeable contamination of soil. [6]

This problem is known for a long time [7], prompting the proposal and development of numerous technical solutions, mainly through the use of this waste as the raw material for other industries: for example, the production of

alkaline activation cements, composite concrete and clinkers [8, 9].

In the research presented in reference [7], it was shown that the red mud can be successfully used as the reinforcing extender of plastic composites, for example, of polyvinylchloride base. Besides the comparatively low cost of such raw material, the outstanding advantage of it is the content of the bonded water, which varies in the range 4-8 wt. % [10], providing a certain level of fire retardant properties.

Despite the large body of work on the possible uses of red mud – plastic compounds, the application of this waste material in the formulation of protective and organic coatings has to date not been developed and is limited to its consideration as a pigment [11] or fire-

retardant additive [12]. At the same time, taking into account the high alkalinity of such waste, there is unanswered question about interphase compatibility in the thin film coating.

In particular, an conceivable interaction between the polymer matrix and the red mud at a molecular level would be of interest. In the work presented in reference [13], it was shown that a certain level of such interactions may be observed when alkyd resins are used, probably, due to the presence of alkyd functional groups in their structure. Taking into account relatively low self-cost of the red mud as raw material, we considered glyptal resins as the film forming agent due to its affordability, relatively low environmental impact and the presence of active acid groups.

The aim of this work is the establishment of the interaction in the system of glyptal resin and the red mud waste depending on the mode of the composite synthesis. The main task of the work is the comparison of the effectiveness of mechanical combination and the combination of components *in situ* during the polymer synthesis. The realization of this task would lead to the definition of a full-scale technology for the production of protective and decorative coatings as one of the ways of red mud waste disposal.

Materials and methods

The red mud of PSC “Zaporizhsky aluminium industrial complex” (GPS

47.860921, 35.129808) was employed as the raw filler material in this work.

Its chemical composition was studied by oxide analysis and is characterized by the high content of Fe₂O₃, TiO₂, the mixture of alkali and alkali-earth materials with common formula RO + R₂O = 8.62 wt. % (Table 1).

Table 1. Chemical composition of red-mud

Probe	Oxide content, wt. %									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Vol
Red mud	7.1	16.6	50.0	5.3	6.3	0.2	0.1	2.1	-	11.7

The analysis of mineralogical composition was performed with DRON-3M XRD analyzer (Fig.1). It was shown that this sample of red mud contains as its main components the minerals goethite Fe₂O₃ · H₂O, hematite Fe₂O₃, hydrargillite Al₂O₃ · 3H₂O, rutile TiO₂, and ilmenite FeTiO₃ and is minerally close to the sintered red mud from the study of Feng [14]

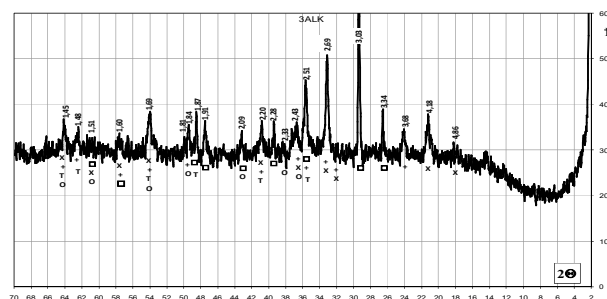


Figure 1. XRD plot of red mud sample. Symbols: x – goethite, + hematite, τ – rutile, o – hydrargillite.

The basic components for glyptal synthesis used were glycerol and phthalic anhydride. The synthesis was carried out in accordance to a known procedure [15], and the initial weight ratio of components was 1:1,65 respectively.

The mechanical combination of components was performed by the addition of the red mud to the already synthesized glyptal resin using a laboratory roll mill. The content of the red mud was 7, 15, 36 and 56 wt. %.

The *in situ* combination – preliminary mixing of the red mud with the glycerol, consequent addition of phthalic anhydride and the synthesis polymer by the predetermined procedure. The content of the red mud was 15, 36 and 56 wt. %.

The presence of interaction between the phases of the filler and the polymer was probed by Infrared spectroscopy (Specord IR 75 spectroscope, in wavenumber range from 400 to 4000 cm⁻¹) with the use of KBr pellets as the carrier.

A indication of interactions between the polymer matrix and the red mud was the shift or change in the intensity of the absorption bands of the corresponding functional groups of materials present.

To confirm the results of spectroscopic studies, an additional indirect method was used to determine the interaction by adsorption of water vapor [16], which was conditioning samples of the obtained composites in the

environment with 90 % humidity for 200 hours with dynamic fixation of the weight changes. The water absorption parameter was determined as the change of the sample weight in wt. %.

Results and discussion

Infrared spectra of the synthesized polymer (Fig. 1. (1)) show the absorption bands characteristic for vibrations of O-H bond (3543 cm⁻¹), C-H bond of aromatic ring (3062 cm⁻¹), CH- bonds of corresponding aliphatic groups (2997, 2878 cm⁻¹), double bond C=O in the carbonyl group (doublet 1738, 1724 cm⁻¹), stretching vibrations of C-H bonds inside the aromatic ring (1598, 1573 cm⁻¹), characteristic stretching bands of ethers –C-O-C – и –O-C-C (1281, 1066 cm⁻¹) [17], residual OH groups at 1155 cm⁻¹ [18], and out of plane vibrations of aromatic rings (735 cm⁻¹). Hence, the polymer obtained is an aromatic polyester and was verified to be the targeted glyptal resin with the following structure (Fig.1), accordingly to reference [19].

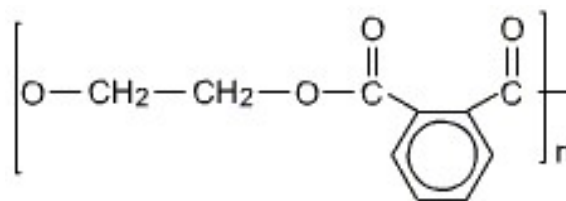


Figure 2. The general structure of glyptal polymer.

The infrared spectra of the red mud have a wide absorption band at 3000-3500 cm⁻¹, which corresponds to bond stretch vibration of the O-H bond of absorbed water and related H-O-H bending band (1450 cm⁻¹). The spectrum

also contains small C=O peaks of carbonates at 1750 cm⁻¹.

The occurrence of weak van der Waals bonds between the carbonyl group of the glyptalic polymer and the active centers of the filler surface was observed during the mechanical combination process. This fact is proved by the shifting of a vibrational band of carbonyl group from 1738 cm⁻¹ to 1715 cm⁻¹ at the filler concentration level 56 wt. % (Fig. 3.).

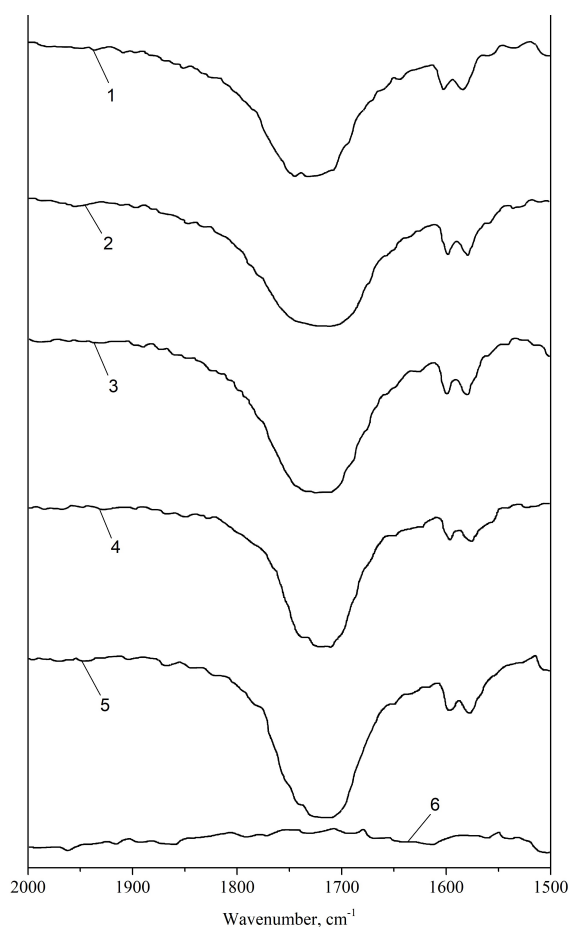


Figure 3. IR spectrum of glyptal-bauxite mechanically mixed compositions: 1. - unfilled glyptal 2. glyptal with 7 wt. % red mud load 3 - glyptal with 15 wt. % red mud load 4 - glyptal with 36 wt. % red mud load 5 - glyptal with 56 wt. % red mud load, 6 – red mud.

It should be noted that the spectrum of glyptalic resin almost completely masks the spectrum of the filler. The wide absorption band at 3450 cm⁻¹, which is corresponding to the vibrations of the surface OH-groups of the filler (Fig. 3, 6) is almost completely obscured in the spectra of the compositions.

In the spectra of compositions, obtained from the *in situ* formulations (Fig. 4), the shift of carbonyl peak to 1729 cm⁻¹ at the 56 wt. % loading also can be noted.

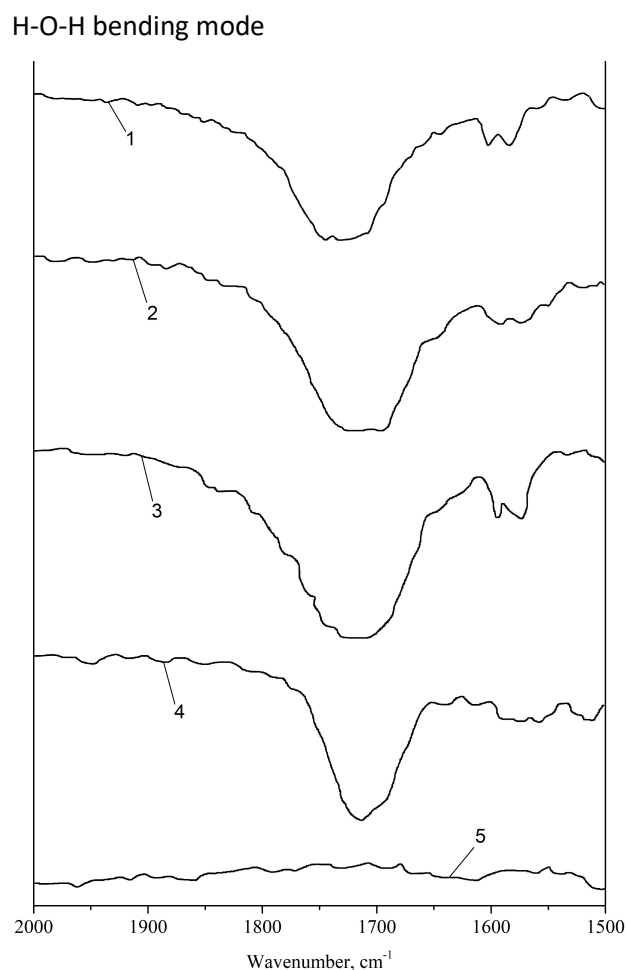


Figure 4. IR spectrum of glyptal-bauxite co-synthesized compositions: 1 – unfilled glyptal 2 - glyptal with 15 wt. % red mud load 3- glyptal with 36 wt. % red mud load 4 - glyptal with 56 wt. % red mud load 5 - red mud.

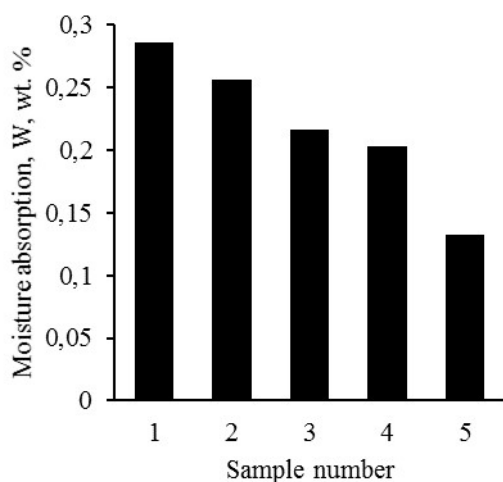


Figure 5. Water vapor adsorption of glyptal mechanically mixed composites: 1 – Mechanics 56%, 2 – Mechanics 15%, 3 – Mechanics 36%, 4 – Resin, 5 – Mechanics 7%.

It was determined that the value of the specific absorption of water vapors by the films obtained depends on their composition. In the case of systems, that were obtained by the mechanical combination (Fig. 5), the plot of the absorption curve is similar to the curve of unfilled resin (3) and, as evident, is defined by processes of molecular diffusion of the moisture inside the polymer material. However, at the 7 wt. % content of red mud in the composition the value of the peak absorption (after 200 hours) is decreased by 34 % in comparison to the pristine resin and those compositions, that have 15 and 36 wt. % load show values of absorption close to those of the native resin. In the case of 56 wt. % load, the absorption is significantly increased: by 25 %. The most probable reason for such an increase may be considered the lack of the resin for the full coverage of the red mud surface, leading to the formation of the inner capillary

structure in such systems. Taking into account the high polarity of the red mud surface, such structures will be subjected to capillary condensation.

In the case of compositions, obtained by *in situ* formulations, these trends are more evident (Fig. 6).

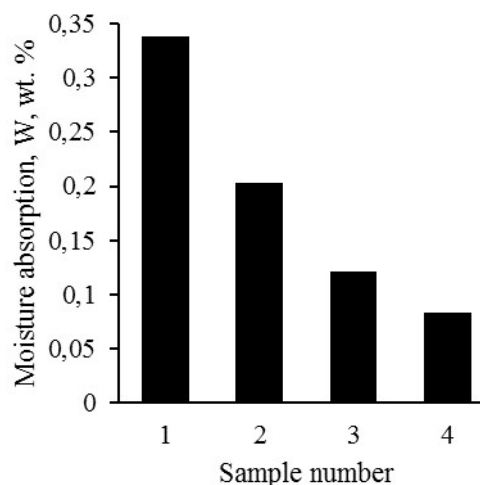


Figure 6. Water vapor adsorption of glyptal composites obtained *in situ*: 1 – Synthesis 56%, 2 – Resin, 3 – Synthesis 7%, 4 – Synthesis 36%.

At the red mud content 7 and 36 % the water absorption after 200 hours is decreased by 40 and 48 wt. % accordingly. At the same time, at the red mud content 56 wt. % the absorption value is increased almost 1,7 times in comparison to the resin.

It is evident, that at the minor loads (7 wt % for the mechanical combination and 7 and 36 wt. % for the combination *in situ*) the decrease of absorption values is caused by the interaction of the active functional groups of the resin with the hydroxyl groups of the red mud surface making them less available for hydrogen

bonding with adsorbed water. The *in situ* formulation hence may be considered as the most effective because together with a more significant decrease in adsorption value after 200 hours of testing, the value of the effective concentration of the filler increases. The effective content of the red mud in coating, therefore, is above 36 wt. %, that lets to utilize a more specific quantity of this waste material in the coating composition.

Conclusions

It was shown that red mud can be used as the filler in the glyptal resin based compositions. The *in situ* synthesis of the polymer in the presence of the red mud was proven to be the most effective way of these components combination. Effective polymer coatings with the filler loads above 36 wt. % can be obtained in this way.

There appear to be van der Waals, hydrogen bond and chemical interactions between the red mud and the polymer matrix through carbonyl and hydroxyl groups of the resin and red mud, respectively.

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