Metallurgy and Foundry Engineering – Vol. 41, 2015, No. 3, pp. 115–121
http://dx.doi.org/10.7494/mafe.2015.41.3.115

Artur Bobrowski, Beata Grabowska, Karolina Kaczmarska

Structural construction of hardeners with different hardening rates intended for geopolimer binder systems used for the preparation of moulding sands

Budowa strukturalna utwardzaczy o różnej szybkości utwardzania przeznaczonych dla spoiwa geopolimerowego stosowanego do sporządzania mas formierskich

Abstract
The paper presents the results of structural investigations of hardeners with different hardening rate for geopolymer binder system Geopol, manufactured by the Sand-Team Company. Studies have shown that these hardeners have similar chemical structures and that the hardening rate of the binder depends on the proper selection of the proportions of the respective components.

Keywords: geopolymer, hardener, hardening rates, FTIR, structural studies

Streszczenie
W artykule przedstawiono wyniki badań strukturalnych serii utwardzaczy o różnej szybkości utwardzania przeznaczonych dla spoiwa geopolimerowego produkcji firmy Sand Team. Przeprowadzone badania wykazały, że utwardzacze mają zbliżoną strukturę chemiczną, a szybkość utwardzania zależy od doboru właściwych proporcji poszczególnych składników.

Słowa kluczowe: geopolimer, utwardzacz, szybkość utwardzania, FTIR, badania strukturalne

1. Introduction

In the foundry industry, many types of binders for molding and core sands are used. Producers offer both organic and inorganic binders. Increasingly popular are binders based on geopolymers that can become an alternative to the water glass. These are inorganic

---

Artur Bobrowski Ph.D. Eng., Beata Grabowska Ph.D., D.Sc. Eng., Karolina Kaczmarska, M.Sc. Eng.: AGH University of Science and Technology, Krakow, Faculty of Foundry Engineering, Krakow, Poland; arturb@agh.edu.pl

materials belonging to the group of alkali silicates, containing silicon, aluminium and alkaline elements such as sodium or potassium which play a stabilizing role. The Sand-Team Company offers this product under the trade name Geopol. It is a colorless liquid that is basic (pH = 11–13) and of an amorphous structure, soluble in water. In the moulding sand technology, the binder is based on an inorganic geopolymer and liquid hardeners. It is used for making moulds and cores for casting iron, steel, and non-ferrous metals from all available types of foundry sands.

According to the data obtained from the manufacturer as well as studies carried out by the authors of this publication, this Geopol binder is characterized by low emissions of toxic compounds during the casting and knocking-out processes. Its primary advantage is the possibility of reusing up to 90% of its reclaim. The moulding sand with a geopolymer binder system is characterized by good knocking-out properties and susceptibility to mechanical reclamation. The available data indicates that, in the binder geopolymers (unlike water glass), the cause of destruction of the connection between grains and the binder is an adhesive. After hardening, the geopolymer obtains great strength, and by the action of the external load, it detracts an adhesive layer from the sand grain surface without affecting the continuity of the binder. Such behavior may be important during the reclamation process, since it is reflected in the significant improvement of the effectiveness of the mechanical reclamation process of the spent moulding sands [1–5].

A lot of research was carried out on the modification and improvement of inorganic binders as well as the effect of the curing method on the obtained properties of molding sands and the efficiency of activities [6, 7].

As mentioned above, the binder Geopol's hardening occurs due to the addition of an appropriate amount of liquid hardener. In the manufacturer's series, there are hardeners that allow for the regulation of the working time of molding sands as well as the hardening time. The aim of this survey was to identify the relationship between the structural construction of the hardener and its ability to accelerate binder curing time. IR spectra analyses will also allow us to identify which group of compounds includes a hardener or its individual components. Based on the structural construction of hardeners, it will be possible to determine a relationship between the curing rate of the geopolymer and the hardener composition.

2. Materials, apparatus, and research methods

The series of five commercial hardeners (SA71–SA75) manufactured by the Sand-Team Company, dedicated to the geopolymer binder Geopol and used for the preparation of molding sands, were tested. According to the manufacturer, data hardeners have different curing rates in the binder. The hardener SA71 causes the slowest curing rate of the binder, while SA75 causes the fastest. Figure 1 shows the allowable times of model removal from the mold depending on the applied hardener.

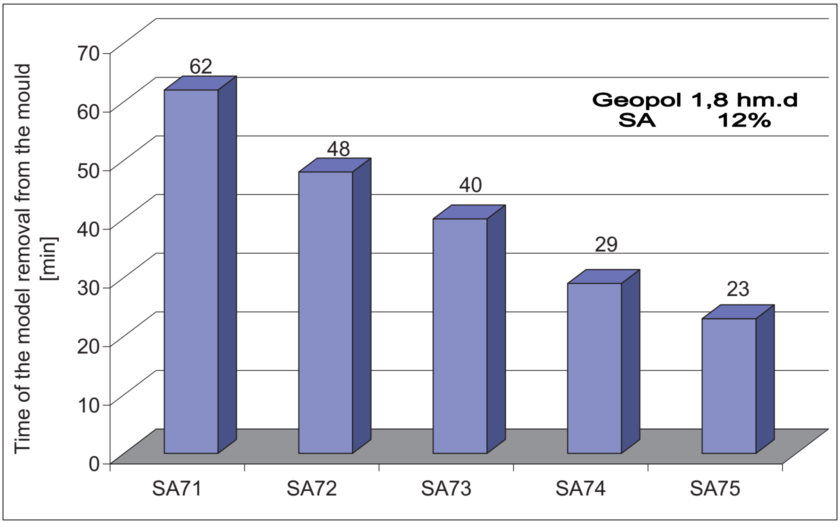

Fig. 1. Allowable times of model removal from the mold – in its dependence of the applied hardener [4]

The Excalibur 3000 FTIR spectrometer with a DTGS standard detector was used in the carried-out studies. Spectra were recorded in the range of 4000–400 cm^{-1}, with a resolution power of 4 cm^{-1}. The transmission technique was used in making samples. This involves the preparation of pellets of potassium bromide (KBr). A thin layer of the resin sample was applied to the pellet surface. The spectra for the sample in the fresh state (immediately after application) were recorded.

3. Results of investigations and their discussion

Figure 1 shows the IR spectra of the investigated hardeners for the geopolymer binder in the wave-number range of 4000–400 cm^{-1}.

The spectra of a series of hardeners can be identified by weak bands in the wave-number range of 3700–3400 cm^{-1}. Their occurrence indicates the presence of valence vibrations of OH bonds. It is difficult to indicate deformation vibrations of OH groups in the obtained spectra. Therefore, it can be assumed that these bands are associated with the first overtone vibrations of C=O bonds [8]. The characteristic band derived from the stretching vibration of C–H bonds (CH_2 or CH_3) registered in the range of 3100–2900 cm^{-1} can also be seen [9]. With the increase of the curing rate, its maximum moves towards the higher wave numbers.

To make a detailed structural analysis, the IR spectra of the investigated hardeners (in the wave-number range of 2000–400 cm^{-1}) are shown in Figure 2.

The band at a wave number of about 1800 cm^{-1} is not observed in the spectrum of hardener SA 71 (the smallest curing rate). In the spectra of other hardeners (SA72–SA75), this band is observed, and its intensity increases according to the following relationship: the higher the hardening rate, the higher the intensity of the band. Its position suggests that it is associated with the vibration of carbonyl bonds (C=O), probably from the ester groups in the compounds.

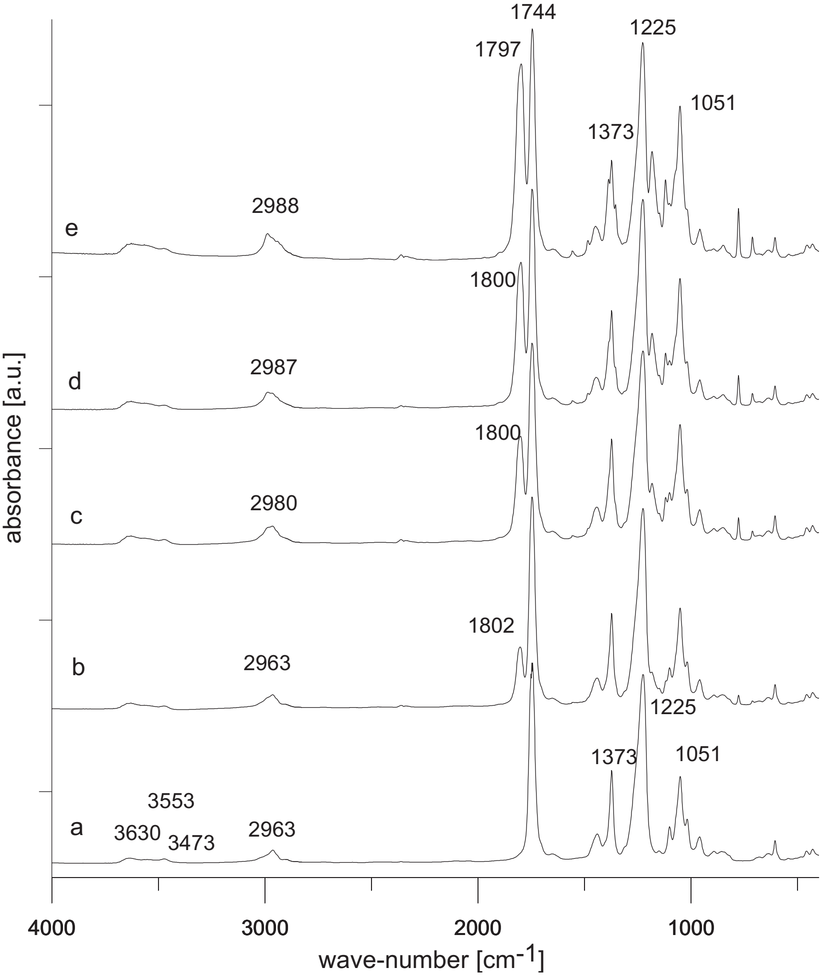

Fig. 2. The IR spectra of the investigated hardeners, in the wave-number range of 4000–400 cm^{-1}: a) SA71; b) SA72; c) SA73; d) SA74; e) SA75

The absorption band at a wave number of 1744 cm^{-1} has the highest intensity among all of the bands in the spectrum. Just as discussed above, the band (1800 cm^{-1}) is derived from the organic component and is associated with the carbonyl bond C=O vibrations (in esters) [9]. The band at 1373 cm^{-1} probably comes from the C–H deformation vibrations [10]. The spectrum of hardener SA75 (the highest curing rate) extracts additional bands at 1387 and 1354 cm⁻¹, which are also derived from C–H bond vibrations. It can be concluded with high probability that a strong band at wave number 1225 cm⁻¹ is related to C–O bond vibrations [10, 11]. For the bands at wave numbers 1225, 1183, 1051, and 777 cm⁻¹, an increase of the absorbed amount coincides with the hardener's ability to accelerate the curing process. Their positions can suggest an association with C–H deformation vibration bonds and C–O stretching vibrations bonds [8, 12, 13].

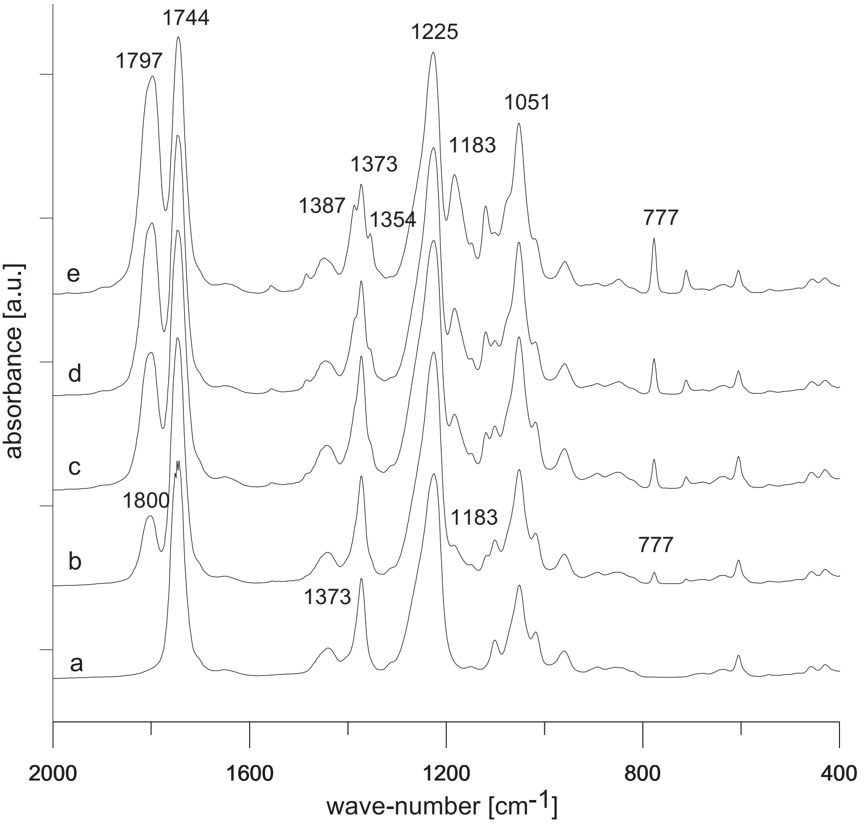

Fig. 3. The IR spectra of the investigated hardeners, in the wave number range of 2000–400 cm⁻¹
a) SA71; b) SA72; c) SA73; d) SA74; e) SA75

4. Summary

This study shows that hardeners for the geopolymer binder Geopol belong to the ester groups. The slowest of them (SA71) is probably a single-component material. The other hardeners (SA72–SA75) have the ability to accelerate the curing process of the geopolymer binder by introducing an additional component. The location of the characteristic bands suggests that they also belong to the ester group and the increases in the rate of curing depend on the proportion of components in the mixture. This study did not reveal structural bands indicative of the presence of other organic components.

5. Conclusions

- The hardeners for the geopolymer binder have similar structural constructions.
- Based on the analysis of the obtained infrared spectra, it can be concluded that the hardeners belong to the ester group. Hardener SA 71 (the slowest) is probably a one-component material, while the others (SA72–SA75) are mixtures of two or more components - also from the group of esters.
- The curing rate control of the geopolymer binder Geopol is dependent on the quantity ratio of individual components in the mixture of esters.
- The proper selection of the proportion between the hardener components allows for the smooth regulation of the curing rate, the provision of the required technological properties during the preparation of molding sand, and the maintenance of the recommended mechanical properties of the finished casting molds.

References

[1] Pezarski F., Smoluchowska E., Izdebska-Szanda I.: Application of geopolimer binder in manufacturing of casting from ferrous alloys. The Transactions of the Foundry Research Institute, 2 (2008), 19–34

[2] Fridrich R., Jelinek P.: Polysialates binders preparation and their influence to shear strength of foundry sand mixtures. Archives of Foundry Engineering, 8, 2 (2008), 37–40

[3] Jelinek P., Skuta R.: Modifikovane sodne silikaty, nova alternativa anorganickych slevarenskych pojiv. Materials Engineering, 10, 3 (2003), 283–286

[4] Holtzer M., Drożyński D., Bobrowski A., Plaza W.: Influence of binding rates on strength properties of moulding sands with the GEOPOL binder. Archives of Foundry Engineering, 14 (2014), 37–40

[5] Burian A., Novotny J.: Produkcja form i rdzeni z ekologicznym systemem spoiwowym [Production of moulds and cores with ecological bonder system]. Proceedings of XI Foundry Conference TECHNICAL 2008, Nowa Sól, 2008, 81–91

[6] Stachowicz M., Granat K., Nowak D.: Studies on the possibility of more effective use of water glass thanks to application of selected methods of hardening. Archives of Foundry Engineering, 10 (2010), 135–140

[7] Stachowicz M., Granat K., Nowak D.: Effect of hardening method and structure of linking bridges on strength of water glass moulding sands. Archives of Foundry Engineering, 10 (2010), 141–146

[8] Kęcki Z.: Fundamentals of molecular spectroscopy. Wydawnictwo Naukowe PWN, Warszawa, 1992

[9] Farinha J., Caiado M., Castanheiro J.E.: Valorisation of glycerol into biofuel additives over heterogeneous catalysts. In: A.M. Éndez-Vilas (ed.): Materials and processes for energy: communicating current research and technological developments. Formatex Research Center, Badajoz, 2013, 422–429

[10] Gokulakumar B., Narayanaswamy R.: Fourier transform – infrared spectra (FT-IR) analysis of root rot disease in sesame (sesamum indicum). Romanian Journal of Biophysics, 18, 3 (2008), 217–223

[11] Stuart B.H.: Infrared spectroscopy: Fundamentals and applications. John Wiley & Sons Ltd, University of Technology, Sydney, Australia, 2004

[12] Romão B.M.V., Diniz M.F., Azevedo M.F.P., Lourenço V.L., Pardini L.C., Dutra R.C.L., Burel F.: Characterization of the curing agents used in epoxy resins with TG/FT-IR technique. Polímeros 16, 2 (2006), 94–98

[13] Holtzer M., Dańko R., Dańko J., Kubecki M., Żymankowska-Kumon S., Bobrowski A., Śpiewok W.: Ocena szkodliwości materiałów wiążących stosowanych do mas formierskich i rdzeniowych nowej generacji [The assessment of harmfulness of binding materials used for a new generation of core and moulding sands]. Wydawnictwo Naukowe Akapit, Kraków, 2013