Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research Paper Catalytic activity of mineral montmorillonite on the reaction of phenol with formaldehyde

Miroslav Huskić^{a,b,*}, Ema Žagar^a

^a National Institute of Chemistry, Department for Polymer Chemistry and Technology, Hajdrihova 19, 1000 Ljubljana, Slovenia
^b Center of Excellence PoliMaT, Hajdrihova 19, 1000 Ljubljana, Slovenia

ARTICLE INFO

Article history: Received 5 August 2016 Received in revised form 21 November 2016 Accepted 21 November 2016 Available online xxxx

Keywords: Phenolic resin Novolac Catalytic montmorillonite NMR SEC

ABSTRACT

Phenolic resins of novolac type were synthesized in the presence of the mineral montmorillonite in its pristine (Na-Mt) or protonated form (H-Mt), with and without oxalic acid (OA) as a catalyst. The H-Mt acts as a strong catalyst regardless of the presence of OA. Contrary, when Na-Mt was added to the OA-catalysed reaction mixture the reaction yield decreased, however, a catalytic effect was observed in the absence of the OA catalyst. The structure of novolac resins is influenced by the addition of both, the Na-Mt and the H-Mt. While the H-Mt influences only a ratio between the o-o, o-p and p-p ethylene bridges, the Na-Mt, in the absence of OA, favours the formation of methylene ether bridges. The molar mass averages of novolac resins synthesized in OA catalysed reactions were always higher than in the absence of OA. Differences in the chemical structure influence the resins' glass transition temperature, which can be even below 0 °C.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Clay minerals have been used as the catalysts in laboratory as well as on industrial scale for decades as indicated by several review papers published on this topic (Adams and McCabe, 2006; McCabe, 1996). Clay minerals catalyse various organic reactions either in the pristine form or in the differently modified versions obtained by protonation of clay mineral with acids, exchange reactions with inorganic cations (Cr^{3+} , Al^{3+} , Cr^{3+} , Cu^{2+} ...) (Adams and McCabe, 2006), polyoxocations of Al₁₃, GaAl₁₂...(Bergaya et al., 2006), organic cations (N⁺-R), and by attaching various initiator/catalyst species onto their surface, like aminoacids (Okada and Usuki, 1995), Ziegler-Natta (Abedi and Abdouss, 2014; Jin et al., 2002), diazonium (Fan et al., 2005), atom transfer radical polymerization (ATRP) (Amin et al., 2013; Zhao et al., 2004), etc. The latter method is commonly used for the preparation of clay/polymer nanocomposites.

The catalytic effect of clay minerals in the field of polymer synthesis was observed almost 50 years ago, however, it was not as explored as in the organic synthesis (Adams and McCabe, 2006). To our knowledge the first theoretical study of self-catalysed in situ polymerization of ethylenediamine with formaldehyde has been published in 2001 (Stackhouse et al., 2001). Later, the catalytic activity of clay minerals was observed in the presence of other catalysts. The synergistic catalytic

E-mail address: miro.huskic@ki.si (M. Huskić).

for the preparation of polyurethanes (Duan et al., 2011). The increase in catalytic activity (for 20%) of the metallocene catalyst during the synthesis of polyethylene polymers was observed in the presence of pristine Mt. When Mt modified with alkyl ammonium salts was used, the catalytic activity of metallocene did not change significantly, indicating a key role of acidic surface of aluminosilicate layer in catalysis (Zapata et al., 2008). This has been confirmed by the strong catalytic activity of proton-exchanged clay minerals in various types of polymerization reactions, such as the polycondenzation of tetrahydrofuran with phthalic anhydride (Ferrahi and Belbachir, 2003), the ring-opening polymerization of epsilon-caprolactone (Harrane et al., 2005; Harrane et al., 2006) and tetrahydrofuran (Benkenfoud et al., 2012), as well as five- and sixmembered cyclic phosphonate monomers (Oussadi et al., 2011). Although many polymers have been synthesized in the presence of clay minerals, their catalytic activity on the polymerization has rarely

effect of montmorillonite (Mt) was reported with bismuth compounds

clay minerals, their catalytic activity on the polymerization has rarely been mentioned. The decrease in molar mass averages and increase in molar mass dispersity during the radical in situ polymerization of methyl methacrylate in the presence of modified Mt was claimed to be due to the effect of Mt (Tabtiang et al., 2000; Kiersnowski et al., 2006). However, the latest results showed that it was not the Mt but rather the ammonium salt, influencing the radical polymerization of methyl methacrylate (Huskić et al., 2012).

Mt/phenolic resin nanocomposites have been the subject of extensive research in the last 15 years. Various preparation methods such as melt intercalation (Choi et al., 2000), solution intercalation (Zhang et al., 2010) and intercalative polymerization (Pappas et al., 2005; López







^{*} Corresponding author at: National Institute of Chemistry, Department for Polymer Chemistry and Technology, Hajdrihova 19, 1000 Ljubljana, Slovenia.

Table 1

Chemical composition of Na-Mt and H-Mt as determined by EDS analysis.

	Atomic % of								
	0	Na	Mg	Al	Si	Р	К	Ca	Fe
Na-Mt H-Mt	67.46 68.11	1.87	1.30 0.74	7.10 5.10	20.60 25.05	0.19	0.14 0.19	0.26	1.09 0.81

et al. 2007 and 2012; Jiang et al., 2006; Wang et al. 2002 and 2004; Huskić et al., 2014) have been reported. Nanocomposites based on phenol formaldehyde resin and mineral montmorillonite (Mt) were prepared by the intercalative polymerization of phenol and formaldehyde in the presence of pristine Mt (Pappas et al., 2005; Wang et al. 2002 and 2004; Huskić et al., 2014) or modified Mt (López et al. 2007 and 2012; Jiang et al., 2006).

The catalytic effect of Mt on the addition/condensation reaction of phenol and formaldehyde was for the first time observed when the proton-exchanged Mt (H-Mt) was used for the phenol-formaldehyde/Mt nanocomposite preparation (Wang et al. 2002 and 2004). The catalytic effect was also observed in the presence of pristine Mt (Na-Mt). A different structure of phenolic resin, that is a ratio between ortho-ortho (o-o), ortho-para (o-p) and para-para (p-p) bonding, as well as a strong decrease in glass transition temperature (T_g) with increasing the Na-Mt content was observed (Huskić et al., 2014).

Previous reports (Wang et al. 2002 and 2004; Huskić et al., 2014) on the catalytic effect of Mt on the reaction between phenol and formaldehyde were oriented towards the nanocomposite preparation, whereas the catalytic effect of Mt have not been deeply examined. Since the published results are very interesting from scientific as well as industrial point of view, we decided to take a deeper insight into this subject. Phenolic resins of novolac type were synthesized in the presence of either the Na-Mt or the H-Mt, with and without added oxalic acid as an acid catalyst, followed by exact determination of the structure and the molar mass characteristics of the synthesized phenol-formaldehyde resins in order to establish exact influence of the Mt on these structural parameters.

2. Materials and methods

2.1. Materials

Phenol p.a., formaldehyde (37% solution) and oxalic acid (OA) were purchased from Merck. Nanofil 757 (Na-Mt, CEC = 85 meq/100 g, medium particle size < 10 μ m,) was kindly donated by Rockwood additives. Proton-exchanged Nanofil 757 (H-Mt) was synthesized as reported by Wang et al. (2002). The abbreviation "Mt" is used as a general term for both types, the Na-Mt and the H-Mt, where appropriate.

2.2. Synthesis

The reactions were conducted in Radleys Carousel 12 Reaction Station™ To ensure the same concentration of reagents in every reaction tube, reaction mixtures with or without oxalic acid were prepared. 2.2.1. Synthesis of novolac phenol-formaldehyde resin using OA as a catalyst (OA-catalysed reaction):

44 g of phenol solution in water (90%), 31 g of formaldehyde solution in water (37%) (a molar ratio between phenol and formaldehyde was 1:0.9), and 6 g of OA (0.5 M) were mixed together. First, 65, 195 and 325 mg of Nanofil 757 (Na-Mt) or proton-exchanged Nanofil 757 (H-Mt) were put in a reactor tube equipped with a magnetic stirrer. Then, 10 g of reaction mixture was added to the Mt and mixed on a magnetic stirrer for 10 min at room temperature. The temperature was raised to 95 °C in 25 min and was held at this temperature for 4 h. The reaction was stopped by the addition of demineralized water to the reaction mixture, and afterwards the reactor tube was transferred into an ice cold bath. The mixture was left overnight to settle down the resin. Water was decanted and the product was transferred to 50 mL centrifuge tube, demineralized water was added again, mixed and centrifuged at 8500 rpm for 15 min. The water phase was decanted and the product was washed with water and centrifuged several times. After purification the product was dried, first in the air and then in a vacuum oven at 50 °C.

2.2.2. Synthesis of novolac phenol-formaldehyde resin in the presence of the Na-Mt or the H-Mt and absence of the OA catalyst (non-catalysed reaction):

The syntheses were performed in the same way as described in Section 2.2.1., only that no OA catalyst was added into the reaction mixtures.

The reaction yield was calculated according to Eq. 1, presuming the formation of only the methylene bridges between phenolic molecules.

$$Yield(\%) = m_{\rm p} / (m_{\rm th} + m_{\rm Mt})_* 100$$
(1)

 $m_{\rm p}$ – mass of the product;

 m_{th} – theoretical mass of the resin at 100% conversion; $m_{\text{H-Mt}}$ – mass of the H-Mt in the reaction mixture.

2.3. Characterization

pH of the reaction mixtures was determined by a Mettler Toledo Seven Multi pH-meter at room temperature after mixing all ingredients for 15 min with magnetic stirrer.

XRD experiments were performed on an X-ray powder diffractometer PANalytical X'Pert PRO MPD (CuK α_1 radiation = 1.5406 Å) in 0.033° steps from 1.5° to 15°.

¹³C NMR spectra were recorded on a Varian VXR-300 spectrometer in methanol- d_4 as a solvent at 25 °C with an acquisition time of 11.5 s and a delay time of 3 s. Typically, 10,000 scans were recorded.

SEM and EDS analysis were performed on a Zeiss Supra 35 VP fieldemission electron microscope at an accelerating voltage of 10 kV. The samples were coated by 10 nm of carbon.

Specific surface area was measured by N_2 adsorption, with an automated gas adsorption analyser Tristar 3000. The samples were dried in vacuum (5 mbar) at 105 °C for 1.5 h before measurements.



Fig. 1. SEM images of pristine Na-Mt (left) and H-Mt (right).

Download English Version:

https://daneshyari.com/en/article/5469106

Download Persian Version:

https://daneshyari.com/article/5469106

Daneshyari.com