



Research paper

# Montmorillonite–phenolic resin nanocomposites prepared by one-step in-situ intercalative polymerisation

Miroslav Huskić<sup>a,b,\*</sup>, Alojz Anžlovar<sup>a</sup>, Majda Žigon<sup>b,c</sup><sup>a</sup> National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia<sup>b</sup> Polymer Technology College, Ozare 19, 2380 Slovenj Gradec, Slovenia<sup>c</sup> Centre of Excellence for Polymer Materials and Technologies, Hajdrihova 19, 1000 Ljubljana, Slovenia

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## ABSTRACT

Montmorillonite (Mt) resol, and Mt–novolac nanocomposites were prepared by one-step in-situ intercalative polymerisation involving the simultaneous modification of the Mt with quaternary ammonium salts (QAS), polymerisation and polymer intercalation. The Mt–polymer nanocomposites were prepared using two types of QAS – with one long (C16) alkyl chain (cetyl trimethylammonium bromide) or with three medium-sized (C8) alkyl chains (tripropyl methylammonium chloride) – as well as without a QAS. Intercalated Mt–resol, and Mt–novolac nanocomposites were formed, as confirmed by XRD and STEM. The extent of the intercalation was higher in the Mt–resol nanocomposites and with the cetyl trimethylammonium bromide modified Mt. The presence of the Mt influenced the polymerisation process, which resulted in changes in the molecular structure of the novolac resin, an increased content of p–p linkages and a lower glass transition temperature of the resin.

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## 1. Introduction

Although the phenolic resins are the oldest commercially manufactured synthetic polymers their production is still growing and new fields of applications are arising. In many areas they are almost irreplaceable with other polymers, especially in fireproofing, electronic and thermal insulation. Nevertheless, better properties are still required, which might be obtained by the addition of nanoparticles such as clay minerals. Literature reports related to clay phenolic resin nanocomposites are rather scarce, especially compared to other clay duromer nanocomposites, i.e., clay epoxy nanocomposites.

Like other Mt polymer nanocomposites, the Mt–phenolic resin nanocomposites were also prepared by either melt intercalation (Choi et al., 2000), solution intercalation (Zhang et al., 2010) or intercalative polymerisation (Jiang et al., 2006). The Mt–resol nanocomposites were synthesized by the intercalative polymerisation of phenol and formaldehyde in the presence of modified Mt (López et al., 2007) or prepared as a blend of modified Mt and pre-synthesized resin (Manfredi et al., 2007).

Dispersion polymerisation has also been performed to produce clay polymer nanocomposites (CPN) from both resol and novolac. X-ray diffraction (XRD) and transmission electron microscopy (TEM) observations showed that the Mt layers were more easily exfoliated or intercalated in

novolac than in resol. This was explained by the linear structure of the novolac, which enables its intercalation between the Mt layers (Wu et al., 2002).

The type of Mt modifier also has a significant impact on the intercalation and thermal stability of Mt–phenolic resin nanocomposites. The best exfoliation was observed when the Mt was modified with octadecylamine, while the thermal stability was increased the most when the modifier was of an aromatic nature, e.g., benzyldimethylhexadecylammonium chloride, benzyltriethylammonium chloride and benzyldimethylphenylammonium chloride (Jiang et al., 2006). Increased thermal stability was also observed in Mt–phenolic nanocomposites prepared with modified Mt (López et al., 2007; Manfredi et al., 2008) or unmodified Na<sup>+</sup>-Mt (Manfredi et al., 2007, 2008). On the other hand, some authors report that neither Na<sup>+</sup>-Mt nor modified Mt improved the thermal stability (Zhang et al., 2010).

The morphology of Mt–resol nanocomposites depends on various production parameters (different liquid resol-type phenolic resins, curing methods, modifying cations in Mt, etc.) (Kaynak and Tasan, 2006; López et al., 2012). The CPN prepared with modified Mt exhibited better mechanical properties than those with Na<sup>+</sup>-Mt. It was observed that the micro-void formation was the main problem when water-based resol resins were used. The highest strength and toughness were obtained in samples with only 0.5% Mt (Kaynak and Tasan, 2006), while the highest values of the tensile and flexural modules with only a very small concentration (<1%) of Mt were confirmed in other reports (Tasan and Kaynak, 2009; Kaushik et al., 2010).

\* Corresponding author at: National Institute of Chemistry, POB 660, 1001 Ljubljana, Slovenia. Tel.: +386 1 4760 206; fax: +386 1 4760 420.  
E-mail address: [miro.huskic@ki.si](mailto:miro.huskic@ki.si) (M. Huskić).

Wang et al. (2002 and 2004) synthesized Mt–resol, and Mt–novolac nanocomposites by using protonated Mt ( $H^+$ -Mt) as an acid catalyst and nanofiller. The  $H^+$ -Mt-resol nanocomposites exhibited higher glass-transition temperatures and impact strengths compared with the pure resol resin. No such data were provided for novolac.

Generally, the use of modified Mt ensures the good intercalation of polymers between the aluminosilicate layers and changes their properties. On the other hand, the price of the final product is increased since the modified Mt is relatively expensive. Therefore, an alternative preparation method, such as a one-step, in situ intercalative polymerisation has been proposed for preparation of CPN with various polymers: polyurethane (Kiersnowski et al., 2006), poly(methyl methacrylate) (Huskić and Žigon, 2007), and polystyrene (Weickmann et al., 2010).

A similar method has already been used to prepare Mt–novolac resin nanocomposites with dodecylamine and oxalic acid as the modifier (Pappas et al., 2005). However, this method cannot be used to prepare Mt–resol nanocomposites.

In this article, the preparation of Mt–resol and Mt–novolac nanocomposites using one-step in situ intercalative polymerisation is described. This method involves the simultaneous modification of the Mt with a quaternary ammonium salt (QAS) and phenolic resin intercalation during the polymerisation. Two types of QAS were used: (i) with one long alkyl chain (cetyl trimethylammonium bromide – CTM) and (ii) with three medium-sized alkyl chains (tricaprylyl methylammonium chloride – TC). In addition, some nanocomposites were prepared without QAS and some by pre-swelling the Mt in a water/QAS mixture for 24 h. The catalytic effect of Mt on the polymerisation of phenol and formaldehyde as well as a Mt influence on the structure of phenolic resin has been reported for the first time. The characterization of CPN was performed using nuclear magnetic resonance (NMR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning transmission electron microscopy (STEM).

## 2. Experimental

### 2.1. Materials

The phenol was kindly donated by Fenolit d.d., Slovenia. The Mt Nanofil 757 was kindly donated by Rockwood Additives. The formaldehyde (37%) and oxalic acid (p.a.) were purchased from Merck. The hexamethylenetetramine (99%) (HMTA), cetyl trimethylammonium bromide (>98%) and tricaprylyl methylammonium chloride were purchased from Sigma-Aldrich.

### 2.2. Synthesis

Mt–novolac nanocomposites were synthesized with a formaldehyde/phenol (F/P) mole ratio of 0.9. First, 0.225 mol of formaldehyde (37% aqueous solution), 0.25 mol of phenol (90% aqueous solution) and 4 ml of oxalic acid (0.5 M) were placed in a round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The Mt was added in quantities of 1%, 3%, and 5%, according to the mass of the pure reactants (without water). The required quantity of QAS was calculated from the quantity and cation exchange capacity (CEC) of the Mt, which was 85 meq/100 g, and added to the solution. The reaction mixture was heated to reflux and held there for 3 h. The resins or CPN were separated by pouring the mixture into 250 ml of ice-cold demineralised water. The product was washed several times with water and dried in a vacuum at room temperature for 24 h. Finally, it was ground to a powder and dried for another 48 h.

Mt–resol nanocomposites were synthesized with F/P mole ratios of 1.7 and 2.2 using the same procedure as described above, except that 4 ml of concentrated NaOH instead of oxalic acid was used as a catalyst.

### 2.3. Curing of phenolic resins:

All the samples were pressed into pellets and cured in an oven at 180 °C for 5 min. Mt–novolac nanocomposites were mixed with hexamethylenetetramine in the ratio of 9:1 prior to curing.

### 2.4. Characterization:

The XRD experiments were performed on an X-ray powder diffractometer PANalytical X'Pert PRO MPD, ( $CuK\alpha_1$  radiation = 1.5406 Å) in 0.033° steps from 1.5° to 15°.

The dispersion of Mt in the phenolic resin matrix was studied by scanning transmission electron microscopy (STEM) using a Zeiss Supra 35 VP microscope at an accelerating voltage of 15 kV. The samples were sectioned to a thickness of between 100 and 250 nm on the Ultramicrotome Leica Ultracut prior to the microscopy.

The degradation was studied by simultaneous thermogravimetric analysis-differential scanning calorimetry (TGA-DSC) on a Mettler Toledo TGA/DSC1 StarSystem, operating in an oxygen or nitrogen atmosphere, at a heating rate of 5 K  $min^{-1}$ , with a sample size of ~15 mg and a temperature range between 40 and 1000 °C.

The glass transition was determined on a Mettler Toledo DSC1 at a heating/cooling rate of 10 K  $min^{-1}$ , with a sample size of ~15 mg and a temperature range between –50 and 100 °C. The results were obtained from the second cycle.

$^{13}C$  NMR spectra were recorded using a Varian VXR-300 spectrometer in the solvent methanol- $d_4$  at 25 °C with an acquisition time of 1.5 s and a delay time of 2 s. Typically, 16,000 scans were recorded.

## 3. Results and discussion

The Mt was modified with QAS to determine the basal spacing of the modified Mt, which was later used for a comparison with the Mt–phenolic resin nanocomposites. The XRD spectra are shown in Fig. 1. The basal spacing of the Mt modified with tricaprylyl methylammonium chloride (TC Mt) is 1.73 nm, which is slightly higher than that of the Mt modified with cetyl trimethylammonium bromide (CTM Mt) (1.68 nm).

### 3.1. Mt–resol nanocomposites

In the XRD diffractograms of the Mt–resol nanocomposites prepared with or without the QAS there are one to three Bragg diffractions of the first, second and third orders, indicating a layered structure (Fig. 2).

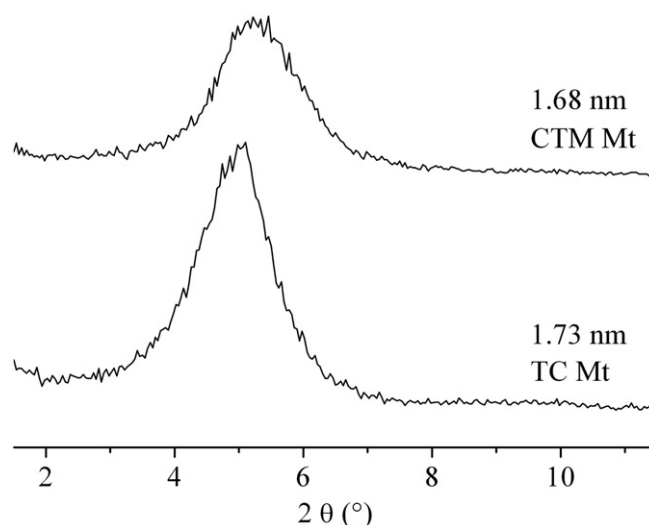


Fig. 1. XRD diffractograms of Mt modified with CTM and TC.

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