



Comparative curing kinetics study of high char yield formaldehyde- and terephthalaldehyde-phenolic thermosets



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ABSTRACT

Phenol-Formaldehyde (PF) resoles exhibit excellent thermal properties, high temperature degradation and high char yield. The formaldehyde can be replaced by terephthalaldehyde (TPA), a non-toxic aromatic dialdehyde. The thermal performances of phenol-TPA (PTPA) resole are very interesting for further development and industrialization. The present investigation presents for the first time a thermo-kinetics study of curing of PTPA, in comparison with a commercial PF resole. Non-isothermal, at constant heating rates DSC experiments are performed on both resoles. PF shows one single exothermic peak, whereas PTPA exhibits two DSC peaks, suggesting a two-step curing mechanism which appears to be conversion-dependent. In addition, isoconversional analysis is used to elucidate the activation energies as a function of the degree of curing. Differential Friedman and integral Vyazovkin methods are considered for computations, giving equivalent results. Furthermore, the whole kinetic triplets (E , A , f) is elucidated for both resoles with Sestak-Berggren model fitting. Finally, isothermal isoconversional predictions are compared to experimental data.

1. Introduction

Phenolic thermosets are extensively used as binders in composites in many fields of applications such as microelectronics, wood industry, aerospace *etc.* [1,2]. These phenolic networks (PF) are crosslinked polymers obtained by reaction between phenol and formaldehyde. The mechanisms of synthesis of those PF, which involves two successive steps, are perfectly described in the literature [3–14]. The first reaction consists in the addition of formaldehyde onto phenol (pre-polymerization). Then, during curing, the crosslinking is achieved by condensation of methylol moieties, releasing water. Two main routes are used to produce high crosslinking density (Fig. 1). Novolacs are synthesized in acidic catalytic conditions, whereas resoles are obtained under alkaline conditions. Moreover, the resoles could reach high crosslinking and aromatic density without adding further crosslinking agent. Such high aromatic densities are required to achieve the excellent thermal resistance of resoles (high char yields) [15–19].

However, phenol and formaldehyde are rather toxic and classified as carcinogenic, mutagenic and reprotoxic (CMR) substances. Especially formaldehyde is highly volatile and is classified CMR 1B by the European Chemical Agency. Therefore there is sufficient evidence to demonstrate its carcinogenicity on mammals and as a consequence, to presume carcinogenicity for humans [20]. Thus, efforts have been

focused on the substitution of the formaldehyde in phenolic resins. Several challenging issues were reported, such as (i) poor reactivity of higher molar mass aldehyde compounds [21], (ii) enolisable aldehydes are prone to side-reactions [22] and (iii) aliphatic aldehydes significantly reduce aromatic density and thus the thermal properties [23].

In a previous study, the reactivity of several bio-based, non-toxic and non-CMR dialdehydes with phenol was evaluated [24]. Among them, terephthalaldehyde showed the best reactivity, which could be explained by the presence of the second aldehyde in para-position. Indeed, the second aldehyde acts as an electron-withdrawing group and thus enhances the reactivity with phenol (Fig. 2).

Terephthalaldehyde can be synthesized by the oxidation in vapor phase of para-xylene [25] which is also the key intermediate to obtain terephthalic acid, mainly used for the production of polyethylene terephthalate (PET). Bio-based routes to para-xylene have been developed in order to access to fully bio-based PET, as a consequence, terephthalaldehyde is being considered as a potentially bio-based building block [26].

In addition, the synthesized phenol-terephthalaldehyde (PTPA) resole showed a better thermal resistance and char yield compared to conventional PF (Table 1). The PTPA thermosets show highly cross-linked networks (networks totally insoluble in organic solvents with a low swelling index). Furthermore, the rheological behavior of both PF

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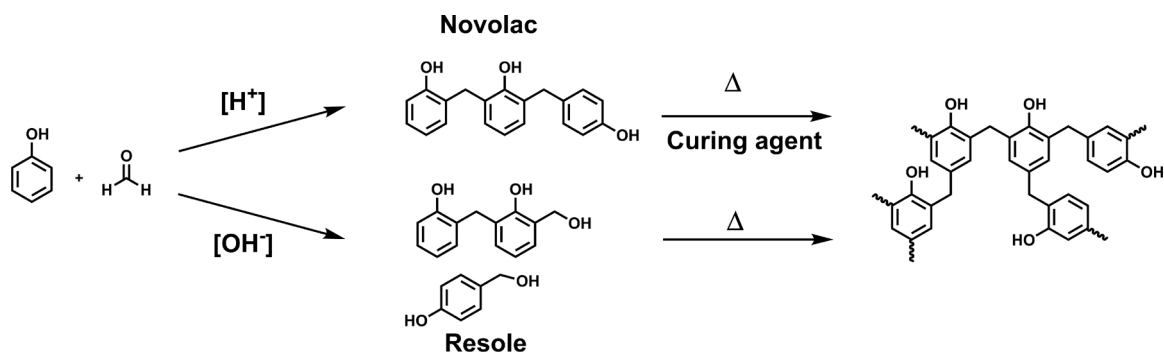


Fig. 1. The two main routes to synthesize PF thermosets: Novolac and Resole.

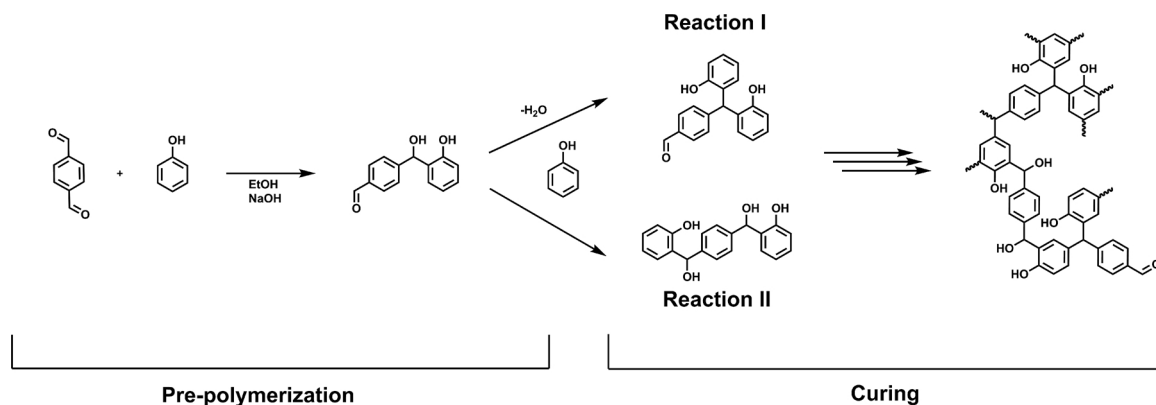


Fig. 2. Probable reactions of pre-polymerization and curing between phenol and terephthalaldehyde.

Table 1
Comparison of properties between PF and PTPA networks [24].

Properties	Phenol-Formaldehyde (PF)	Phenol-Terephthalaldehyde (PTPA)
Viscosity at 20 °C (mPa.s)	508	380
Gel time, at 125 °C (min)	31	27
Insoluble Fraction (%) ^a	99 ± 1	99 ± 1
Td10% (°C) ^b	395	500
Char yield (%) ^c	61	65

^a 24 h of immersion in acetone and drying 24 h at 60 °C.

^b 10 wt.% degradation temperature of cured phenolic resins assessed by thermogravimetric analysis (TGA) under nitrogen atmosphere at 5 °C/min.

^c Residue ratio of cured phenolic resins assessed by TGA under nitrogen atmosphere at 5 °C/min until 900 °C and one isothermal step of 1 h.

and PTPA pre-polymers are comparable. Such preliminary results are very promising for further development of formaldehyde-free networks and composites, with an excellent thermal resistance and a high char yield.

The manufacturing process of phenolic thermosets and composites is typically performed in three steps: (i) synthesis of the pre-polymer (corresponding to the addition reaction in PF), (ii) shaping (*i.e.* impregnation for composites) and pre-curing stage, within which partial hardening of the matrix is achieved (*e.g.* pre-pregs) and (iii) post-curing stage which allows complete crosslinking of the matrix. Noteworthy, the degree of curing drives all chemical and physical parameters (*e.g.* rheological behavior, chemical resistance...). It is therefore of prime importance to accurately control the curing kinetics all along the manufacturing process of final piece.

The curing of phenolic thermosets is a thermally-activated process. Previous studies report on the study of PF curing kinetics based on

differential scanning calorimetry (DSC) experimental data. In addition, several computation approaches have been studied to provide maximum information on the kinetic parameters of PF curing such as model-free [27–32] and model fitting kinetics [33]. Among them, the model-free kinetics approach, isoconversional analysis, is known to offer accurate description of the kinetics from a short experimental dataset, with a systematic and rather simple calculation process [34].

In the present paper, we suggest studying the curing kinetics of an innovative formaldehyde-free and potentially bio-based phenolic thermoset with high char yield, *i.e.* phenol-terephthalaldehyde resole, in comparison with a commercially available PF resole. Hence, the curing kinetics data are provided from non-isothermal DSC experiments, at different linear heating rates, following the recommendations found in literature [35]. In addition, kinetic modellings are performed using isoconversional analysis. Hence, quantitative kinetic data of phenol-terephthalaldehyde curing are presented. Finally, the predictability performances of the kinetics parameters are evaluated.

2. Experimental section

2.1. Materials

The phenol was purchased from Alfa-Aesar. The terephthalaldehyde and the sodium hydroxide were purchased from Sigma-Aldrich. PF resole was a commercially available pre-polymer. The reactants and the solvent were 98–99% pure and used without further purification. Pre-polymers were stored at –18 °C to avoid unwanted crosslinking.

2.2. Pre-polymerization synthesis

Phenol (1 eq.), sodium hydroxide (0.04 eq.) aqueous solution (50 wt.%) and ethanol (14 wt.%) were introduced into a two-necked flask. A condenser, a magnetic stirrer and a silicon oil bath were used.

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