Journal of Thermal Analysis and Calorimetry, Vol. 96 (2009) 2, 515–521

MIMOSA AND CHESTNUT TANNIN EXTRACTS REACTED WITH HEXAMINE IN SOLUTION

C. Peña[1], *K. de la Caba*[1], *A. Retegi*[1], *C. Ocando*[1], *J. Labidi*[1], *J. M. Echeverria*[2] *and I. Mondragon*[1]*

[1]'Materials+Technologies' Group, Escuela Politécnica, Dpto. Ingeniería Química y M. Ambiente, Universidad del País Vasco/Euskal Herriko Unibertsitatea, Pza. Europa, 1, 20018 Donostia/San Sebastián, Spain
[2]Hexion Specialty Chemicals S.A., Ctra. Navarra, Epele 39, 20120 Hernani, Spain

Autocondensation reactions of mimosa and chestnut tannin extracts solutions have been analysed at several pH by differential scanning calorimetry (DSC). Alkaline pH promotes autocondensation reaction of these tannins. Curing reactions between these tannins and hexamine at acid and not strongly alkaline pH have been proved by DSC. Thermal analysis gives insights not only on reactions between tannin and hexamine, but also about water presence on solutions and degradation reactions of tannins. Products obtained from reactions between tannins and hexamine have been analysed by Fourier transform infrared spectroscopy (FTIR). The obtained chemical structures are influenced by both chemical structure of tannin and pH of solution. For mimosa tannin amine and ether groups are obtained while for hydrolysable chestnut tannin amide groups have been detected.

Keywords: *autocondensation, hexamine, pH, polycondensation, tannin*

Introduction

Phenol and formaldehyde toxicity and the new requirements for increasing recycling and re-use of wastes prompted the use of renewable resources such as wood [1]. Amongst the possible alternatives, tannin is an excellent renewable resource which can be used for replacing all or part of the petroleum-derived phenolic compounds of adhesives [2–5].

Hexamethylenetetramine (hexamine) has been used for a long time as a hardener of tannin adhesives [6]. The reaction of hexamine with tannins in aqueous solutions was analysed by Pizzi, who showed that hexamine is not a formaldehyde-yielding hardener and thus it leads to cured products with low formaldehyde emissions [7, 8]. On the other hand, some works are focused on the manufacture of adhesives composed of polyphenolic tannin and hexamine. Indeed, Theis and Grohe [9] have reported the manufacture of biocomposites based in hemp and biodegradable mimosa tannin adhesive cured with hexamine. Mosiewicki *et al.* [10] have shown that composites based in pine woodflour as filler and pine tannin-hexamine adhesive have thermal and mechanical properties adequate for using in some industrial applications.

For the analysis of reactions between tannin and hexamine it must be considered that different pH can influence in chemical pathways. As it is well know, hexamine decomposition occurs easily at acid pH [11]; in these conditions tannin-hexamine solutions result in an instantaneous 'gel' formation [8–12]. At basic pH deprotonation of hydroxyl groups of flavonoid molecule occurs more easily.

In this work, autocondensation and polycondensation reactions of mimosa and chestnut tannin extracts solutions with hexamine have been evaluated by DSC. Fourier transform infrared spectroscopy (FTIR) has also been employed for the determination of the chemical structure of crosslinked materials.

Experimental

Materials and methods

Commercial powders of chestnut (*Castanea sativa*) and mimosa (*Acacia mearnsii*), wood extracts were used without purification. Fine hexamine (without stabilization) was gently provided by Hexion Specialty Chemicals (Spain). Analysed samples have been obtained by mixing water solution of every tannin at 40 mass/mass% with 10 mass/mass% of hexamine. Sodium hydroxide and clorhydric acid have been employed to control pH of solutions.

FTIR spectra of the resins were obtained in a Nicolet spectrophotometer. The acquisition conditions were 400–4000 cm^{-1} spectral range, 10 scans and a resolution of 4 cm^{-1}. Analysis was performed on KBr pellets.

* Author for correspondence: inaki.mondragon@ehu.es

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands