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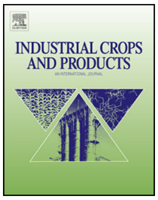

The effect of the composition of spruce and pine tannin-based foams on their physical, morphological and compression properties

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ABSTRACT

Tannin-based foams were successfully prepared, using Norway spruce and maritime pine tannins. Various parameters, including the amount of procyanidins, were varied in order to observe the effect of changes in the density of the foam, on the structure its pores, and on the homogeneity, compressive strength, and compressive modulus of the foams. It was found that an optimum amount of spruce tannin exists, which results in a foam with the lowest density whereas the amount of cross-linker affects homogeneity, and the foam morphology is defined by the surfactant. A partial replacement of pine tannin with spruce tannin decreased the foaming temperature and led to decreased compressive strength and a decreased compressive modulus of the foams. The main attribute affecting the reaction was the amount of polyphenols, or the amount of impurities (cellulosic sugars) present in the tannin extract.

1. Introduction

The development of new materials derived from bio-based sources has become a necessity (Mohanty et al., 2002). When searching for new and better materials, all relevant ecological guidelines (requiring the replacement of petroleum-based product), have to be taken into consideration (Bozell and Petersen, 2010). Tannins from trees, an abundant resource that is safe for the environment and human health, are one option (Raquez et al., 2010; Sánchez-Martín et al., 2013a). Tannin from spruce bark is an untapped resource, with a structure similar to that of the commercially available pine tannin. Due to complicated and underdeveloped extraction and cleaning processes, this very promising material has remained largely unexploited.

The use of tannin extracts from different wood species (e.g., *Castanea sativa*, *Quercus* sp., *Acacia* sp., etc.) is common in nutrition and pharmaceutical and veterinary medicine (Chiarini et al., 2013). Tannin extracts can also be used as binding agents for particle and fiberboards (Tišler et al., 1986; Roffael et al., 2000) or in the manufacturing of insulation materials (Meikleham and Pizzi, 1994; Tondi and Pizzi, 2009; Lagel et al., 2014).

Tannin can be used in the production of foam, as an insulation material obtained by the polycondensation of polyflavonoid tannins and furfuryl alcohol (Pizzi et al., 2012). Some of this end product's impressive features can easily be adapted (Tondi and Pizzi, 2009). Due to their low conductivity coefficient (Celzard et al., 2010; Lacoste et al., 2014a), these foams, with a high level of natural compounds, are comparable to more established polyurethane foams. The resulting thermosetting material can be used as a thermal or sound insulator, an absorber of metal ions, (Sánchez-Martín et al., 2013b), or a material with sufficient resistance to chemicals and fire comparable to that offered by phenol-formaldehyde foams (Tondi et al., 2009).

Foams have been prepared from tannin extracts obtained from deciduous trees, e.g., quebracho wood (*Schinopsis balansae* and *lorentzii*) (Basso et al., 2014; Martinez de Yuso et al., 2014) or acacia bark (*Acacia mearnsii*) (Tondi and Pizzi, 2009; Szczurek et al., 2013) with the predominantly prorobinetinidin/profisetinidin type of tannin. They have also been prepared from the bark of coniferous trees (*Pinus radiata* and *pinaster*) (Lacoste et al., 2013a, 2014a), in which a much more reactive procyanidin/prodelphinidin type of tannin is usually found.

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The examination of foams prepared from tannin extract from pine, which is chemically, slightly different to that of spruce (Zhang, 2011), has been described in several publications. Preparing of such foams has been investigated (Lacoste et al., 2014a), as well as their mechanical properties (i.e., their bulk density, compressive strength and moduli, thermal conductivity), their morphological properties (Lacoste et al., 2013a, 2014b), and their reaction chemistry (Garcia et al., 2014). The use of tannin extract obtained from spruce bark, one of the most commercially relevant tree species in Europe for the preparation of foams (Čop et al., 2014) is mostly unexplored, however.

The (total) purification of spruce tannin is very time-consuming and expensive process. Therefore, commercially available pine tannin, mixed with partially purified spruce tannins, was used in the investigation, the main difference between them being the content of procyanidines. The main aim of the study was to investigate the effect of the type of tannins and the foam composition on the physical, morphological, and compressive properties of tannin-based foams. The influences of the content of the surfactant, the plasticizer, and the strengthener used in the foam composition were also investigated.

2. Experimental

Tannin-based foams of different compositions were prepared, taking into account the mixture proportions of the individual components as shown in Table 1. Each mixture was defined by a label, later used in the figures and tables. The use of different types of tannins, and of certain mixes of pine tannin and non-purified spruce tannins, was verified. The most promising composition in terms of the lowest density of foam was then used for further analysis, in which the impact of the composition of the foam on the properties above was investigated in detail.

2.1. Materials

Three different types of tannins, extracted from the bark of two different tree species, i.e., maritime pine (*Pinus pinaster*) and Norway spruce (*Picea abies* L.), were used in this study. The tannin extracts differed in their grade of purity, which is directly connected to their content of polyphenols (PP). Pine tannin (PT) (which contained 92–94% of PP) is a commercially available product, known as "Phenopin". It was obtained from DRT, France. The investigated non-purified spruce tannin (NPST), extracted in a non-pressurized hot water treatment plant, contained 58% of PP and was obtained from VTT, Finland according to the procedure described by Kemppainen et al. (2014). Purification of spruce tannin (to attain the final 79% of PP) was performed by Silvateam, Italy.

Other reagents needed for the foam production (furfuryl alcohol (FUR ALC) (98%), polyethylene glycol 400 (PEG 400) (99%), para-toluene sulphonic acid (PTSA) (a 65% solution in H_2O) and pentane (PENT) (99%)) were supplied by the Merck Company, glyoxal (Glyox) (a 40% solution in H_2O), 1-methoxy-2-propanol (1-MET-2-PROP) (99%) and Kolliphor ELP (K) (hydrogenated castor oil) were supplied by Sigma–Aldrich. Glycerol (G) (99.5%) was obtained from Kemika, Zagreb.

2.2. Preparation of the foams

These foams are based on a self-blowing mixture of condensed tannins, furfuryl alcohol, cross-linker, pentane, para-toluene sulphonic acid and additives such as surfactants and plasticizers. The cross-linking reaction of tannins with glyoxal or formaldehyde and the auto-condensation of furfuryl alcohol are catalyzed by acid, producing a hard, dark resin. Since both reactions are strongly exothermic, this lead to the boiling of a blowing agent (pentane) and

Table 1
Overview of the compositions of the investigated foams, showing the proportions of the individual components (g) in the mixtures.

Name of foam composition	Nr.	TAN	Proportion of tannin		FUR ALC	H_2O	Glyox	PEG 400	G	PENT	1-MET-2-PROP	K	PTSA	Prop. G	Prop. K	Prop. Glyox
			Spruce	Pine										(%)	(%)	(%)
100 (PT)	1	30	0	100 (PT)	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5
90–10 (NPST)	2	30	10	90	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5
80–20 (NPST)[a]	3	30	20	80	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5
70–30 (NPST)	4	30	30	70	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5
60–40 (NPST)	5	30	40	60	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5
50–50 (NPST)	6	30	50	50	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5
0.5 G	7	30	20	80	18	1.5	6	1.5	0.4	5.2	4	4	9	0.5		
1 G[a]	3	30	20	80	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5
1.5 G	8	30	20	80	18	1.5	6	1.5	1.21	5.2	4	4	9	1.5		
2 G	9	30	20	80	18	1.5	6	1.5	1.62	5.2	4	4	9	2		
3 K	10	30	20	80	18	1.5	6	1.5	0.8	5.2	4	2.35	9		3	
4 K	11	30	20	80	18	1.5	6	1.5	0.8	5.2	4	3.17	9		4	
5K[a]	3	30	20	80	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5
6 K	12	30	20	80	18	1.5	6	1.5	0.8	5.2	4	4.85	9		6	
5 Glyox	13	30	20	80	18	1.5	3.9	1.5	0.8	5.2	4	4	9			5
7.5 Glyox[a]	3	30	20	80	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5
10 Glyox	14	30	20	80	18	1.5	8.22	1.5	0.8	5.2	4	4	9			10
12.5 Glyox	15	30	20	80	18	1.5	10.57	1.5	0.8	5.2	4	4	9			12.5
80–20 (NPST)[a]	3	30	20 (NPST)	80	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5
80–20 (PST)	16	30	20 (PST)	80	18	1.5	6	1.5	0.8	5.2	4	4	9	1	5	7.5

[a] The compositions 80–20 (NPST), 1 G, 5 K in 7.5 Glyox are the same. They differ only according to their names, which make it easier to understand the course of the research work.