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Short communication

Horticultural/hydroponics and floral natural foams from tannins

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ABSTRACT

New formaldehyde-free Quebracho tannin foams were developed for horticultural/hydroponics and floral applications. These foams included in their composition a wetting agent and at least one compound able to neutralize the residual acidity derived from acid catalyst. Their densities were between 0.048 and 0.066 g/cm^3 and compression strength, between 0.07 and 0.09 MPa. Scanning electron microscopy (SEM) images showed open porosity and average cell size of 125–250 μm. Water absorption peaked at 98% (vol) while residual pH value was 5. The new tannin foams do not result to be phytotoxic and are apt to the conservation of fresh cut flowers and as support matrices for horticulture and hydroponics. They have shown performances comparable or superior to commercial synthetic phenolic floral foam used as reference.

1. Introduction

Tannin-furanic foams are environment friendly, cheap, lightweight materials composed of approximatetly 95% of natural products (Meikleham and Pizzi, 2000; Tondi and Pizzi, 2009; Basso et al., 2011, 2013a,b). Condensed polyflavonoid tannins are vegetal products obtained by water extraction from the wood and bark of trees, and furfuryl alcohol is obtained from agricultural wastes after hydrolysis and catalytic reduction (Aguilar et al., 2002).

These tannin- based cellular materials have already been extensively described and their performance has been evaluated for several applications, especially thermal and acoustic insulation, showing great potential for replacing commercial, synthetic phenolic foams (Meiklenham and Pizzi, 2000; Pizzi et al., 2008; Tondi et al., 2008a,b, 2009; Tondi and Pizzi, 2009; Lacoste et al., 2013a,b; Lacoste et al., 2015). Another possible application of synthetic phenolic foams, not yet explored for tannin-furanic foams, is as support of floral arrangements with cut flowers. These materials have to absorb and retain water so that the flowers remain fresh for the lifetime of the arrangement (Landrock, 1995; Pilato, 2010). Furthermore, another possible and related application is as hydroponic substrates or agricultural/horticultural foams. Thus, the foam material constitutes the “growing media” or a “propagation medium” which supports young flowers and other plants in the early stages of their development (Gardziella et al., 2000; Harper and Petrie, 2003; Pilato, 2010).

Foam properties required for floral and hydroponics/horticultural applications are then high water absorption capacity, good water retention, enough aeration, ease of flower penetration, good support of the flower stems by the foam and optimum pH value between 3.5–6 (Smithers, 1956; Pilato, 1980, 2010; Landrock, 1995). In the present work, the composition of classical formaldehyde-free tannin foams was modified in order to achieve the wanted properties: wettability of tannin foams has been increased and the typical residual strongly acid or alkaline pH was neutralized. New tannin foams were characterized and their phytotoxicity and performance in cut flower conservation and as hydroponic support was evaluated.

2. Experimental

2.1. Materials and foams preparation

Quebracho (*Schinopsis lorentzii* and *balansae*) wood extracts were provided by Silva Chimica (S.Michele Mondovi’, Italy) and sodium laureth sulphate (Zetesol 270/NS) by Zschimmer-Schwarz (Vercelly Italy). Furfurylic alcohol, gluraraldehyde, calcium hydroxide ($Ca(OH)_2$), calcium carbonate ($CaCO_3$) and pentane were purchased at Acros Organics (Geel, Belgium), phenol sulfonic acid 65% water solution (CRC 605) at Capital Resin Corporation (Columbus, OH, USA) and ethylene glycol, vermiculite (0.5–2.5 mm), dolomite ($MgCa(CO_3)_2$) and polyethylene glycol sor-

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Table 1
Composition of hydrophilic Quebracho tannin foams.

Sample name	THY	TVE	TCA	TDO
Quebracho Tannin (g)	30	30	30	30
$CaCO_3$ (g)			0.64	
$Ca(OH)_2$ (g)	0.5	0.5		
Vermiculite (g)		4		
Dolomite (g)				1.1
Furfuryl alcohol (g)	10	10	10	10
Glutaraldehyde (g)	5	5	5	5
Ethylene glycol (g)	7	7	7	7
Eau (g)	1	1	1	1
Polyethylene glycol sorbitan monooleate (g)	0.6	0.6	0.6	1.4
Sodium laureth sulphate (g)	0.5	0.5	0.5	1.3
Pentane (g)	3.3	3.3	3.3	3.3
Phenol sulfonic acid (65%) (g)	5	5	5	5
Apparent density (g/cm^3)	0.055	0.066	0.048	0.050
Compression strength$_{at20\%strain}$ (MPa)	0.09	0.09	0.08	0.07

bitan monooleate (Tween 80) at Sigma-Aldrich (Saint Quentin Fallavier, France). Vermiculite (0.5–2.5 mm) was purchased at a tree nursery its origin being from the Palabora Mining Company (Palabora, South Africa).

The hydrophilic tannin foams THY, TVE, TCA and TDO were prepared according to the mixture of components shown in Table 1 at $62 \pm 2\,°C$. They are completely formaldehyde-free and environmentally more acceptable than the synthetic foams currently available in the cut flowers and horticultural markets, which are based on oil-derived phenol-formaldehyde or polyurethane resins First a liquid mixture composed of furfuryl alcohol, gluraraldehyde, ethylene glycol, a non ionic surfactant (polyethylene glycol sorbitan monooleate), a wetting agent (sodium laureth sulphate) and water was stirred for 20 s at room temperature. The tannins in powder form and the inorganic components ($Ca(OH)_2$, $CaCO_3$, vermiculite, dolomite) were then added to the mixture and strongly stirred for 90 s. Subsequently, the blowing agent, namely the pentane, and the acid catalyst were added by stirring for 20 s after the addition of each reagent to ensure homogenization. Finally, the mixtures were put in a ventilated oven preheated at $62 \pm 2\,°C$ were foaming and hardening were carried out. The tannin foams obtained were dried at room temperature. All the formulations shown in Table 1 include a non-ionic surfactant (polyethylene glycol sorbitan monooleate) and an anionic surfactant (sodium laureth sulphate). The function of the first surface agent has already been extensively described (Zhang et al., 1999; Gardziella et al., 2000; Basso et al., 2015) while the second surface agent used is a wetting agent which increases the water absorption and water retention capacity (Gardziella et al., 2000).

2.2. Foams characterisation

Blocks of foam of dimension of $3 \times 3 \times 1.5$ cm were weighed to obtain their bulk density. The cellular morphology of prepared foams was observed by scanning electron microscopy (SEM) (TM3000, Hitachi, Japan). The mechanical resistance to compression was investigated with an Instron 4467 universal testing machine (Norwood, MA, USA) at a load rate of 2.0 mm min^{-1}. Procedure was based on NF EN 826 standard. The porous structure was investigated by helium pyncometry using a Accupyc II 1340 helium apparatus (Micromeritics)

To analyse the foams water absorption uptake, specimens of $3 \times 3 \times 1.5$ cm were weighed (M1) and then placed on the surface of water for 2, 10, 30 and 60 min. After each time period the samples were drained for 10 min on a metal grid and then weighed again (M2). In order to evaluate water retention capacity, the foam samples filled previously with water, after 60 min of soaking in water, were placed vertically on a metal grid. After a 24 h period, the samples were weighed again (M3). The percentage of water absorption (WA, in vol%) and water retention WR (vol%) were calculated according to Eqs. (1) and (2), respectively, where BV is the block volume:

$$WA = (M2 - M1) \times 100/BV \tag{1}$$

$$WR = (M3 - M1) \times 100/BV \tag{2}$$

The residual pH was measured at room temperature in the solution extracted by wringing foam samples of $3 \times 3 \times 1.5$ cm which had been previously hydrated by capillarity in deionised water during 60 min. A Hanna pH-meter (Hanna Instruments, Lingolsheim, France) was used for the purpose. No significant differences in results were noticed within the specimens coming from the 4 foam repetitions prepared for each case.

2.3. Growing and preserving cut flowers tests

Germination of garden cress (*Lepidium sativum*) grains was carried out on the tannin foams prepared from different formulations to evaluate the phytotoxicity of these new materials as well as the possibility of using them as culture substrates. For this purpose foam pieces (of dimension of 75 cm^3) were hydrated by capillarity for 5 min and then placed in small aluminium cups containing a layer of 3 mm of water. 6 garden cress grains were sown at the depth of some mm from the surface of each foam specimen. Finally, the aluminium cups were covered by a plastic film and the change in the cultures monitored during a week. The cultures were watered every three days. The conservation tests of cut flowers, *Gerberas* spp. (commonly known as 'Transvaal daisies') were comparatively conducted on foam pieces hydrated beforehand.

The performance of these hydrophilic tannin foams has been compared to that of a commercial synthetic phenolic floral foam (CF) and to that of a classical tannin foam (TB) obtained without including either a wetting agent or a compound neutralizing its residual acidity. The density of these foams was of 0.02 and 0.04 g/cm^3 respectively.

3. Results

The compositions shown in Table 1 comprise at least one compound able to neutralize the residual acidity of the phenol sulfonic acid catalyst used because this is damaging for vegetables growth and conservation (Smithers, 1956). The compounds used for this were dolomite (TDO), calcium carbonate (TCA), calcium hydroxide (THY and TVE) and vermiculite (TVE) which is simultaneously neutralizing and absorbing. These compounds, due to their low solubility, while allowing the phenol sulfonic acid to play fully its role of catalyst during the initial foaming and curing of the foam, they are afterwards able to neutralize the residual acidity (Weber, 2007). However, they also slow down foam curing. This caused that the foam curing temperature had to be higher ($62 \pm 2\,°C$) than what generally used for other types of formaldehyde-free quebracho tannin foams (Basso et al., 2015).

The new tannin foams are rather lightweight (density lower than 0.1 g/cm^3, Table 1) and grey-coloured. They generally present an homogeneous appearance with the exception of the TVE foam for which it is possible to see some cavities and some vermiculite grains not completely integrated within the structure of the foam. Such defects could be due to the granulometry of the vermiculite used and/or to a too high initial viscosity of the mixture to foam which renders difficult homogenizing the various components. This problem could be solved by using extra fine vermiculite and/or replacing the ethylene glycol in the formulation with other glycol/s. It is necessary to consider that the presence of cavities in the culture substrate is favourable to maintain aeration, but that when these