

Flexible-Elastic Copolymerized Polyurethane-Tannin Foams

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ABSTRACT: Open cell foams obtained by the simultaneous coreaction of condensed flavonoid tannins with an alkoxyated fatty amine and polymeric diphenylmethane isocyanate yielded highly flexible/elastic polyurethane foams. Copolymerized amine/isocyanate/tannin oligomers were identified by ¹³C NMR and MALDI-TOF spectroscopy. In general, between 30% and 50% of natural tannins is added to the components used to obtain polymerisation of the polyurethane. The characteristic of these new, partially biosourced polyurethanes is that the tannin present slows down burning, some of them can be made flame self-extinguishing and if burning they neither flow nor asperge flaming material around, contrary to what occurs with normal polyurethanes. This limits the possibility of transmitting fire to other materials in the same environment. Cyclic compression tests were carried out showing that after 50 cycles foam recovery was in excess of 80%. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40499.

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INTRODUCTION

Recent work on resins derived from natural products has led to the development of rigid foams based on polyflavonoid tannins of excellent performance and characteristics.^{1–6}

The technology developed for tannin-based foams is based on self-blowing due to a very mild exothermic reaction causing the rapid evaporation of an organic volatile solvent. The process takes place at ambient temperature.

Most of the tannin-based foams developed are rather rigid, although some tannin foams presenting evident residual elasticity and compressibility have also been developed.⁷ However, although rather flexible, these are not as flexible and elastic as some polyurethane foams such as those used, for example, for applications like bed mattresses. Thus, to be able to obtain flexible foams will open a number of additional perspectives to the application of natural materials. One approach open to prepare this type of highly flexible/elastic foams would be to coreact the tannin with a classical polyurethane foam during foam preparation, and to observe what different characteristics such a

tannin-doped polyurethane foam would present. This article then deals with the initial development and testing of flexible foams based on natural flavonoid tannin extract coreacted with a polyurethane foam during copolymerisation and foaming of the materials.

EXPERIMENTAL

2.1. Preparation of the Foams

Quebracho (*Schinopsis lorentzii* and *Schinopsis balansae*) wood tannin, thus, a profisetinidin/prorobinetinidin condensed tannin, supplied by Silva Chimica (S.Michele Mondovi, Italy) was used. This tannin was mixed in powder form by mechanical stirring with an ethoxylated fatty amine where the ethoxylated chains were between 8 and 20 Carbon atoms, with an average of 12. For the sample A10, tris (2-chlorisopropyl) phosphate, a fire retardant, was added. Stirring was continued until the mixture appeared to be homogeneous, after which polymeric diphenyl methane isocyanate (pMDI) (Bayer 44V20) was added again continuously stirring vigorously for 10 s. After this latter addition, the foam blowing of the mixture started immediately.

Table I. Elastic PUR-Tannin Elastic Foams

Formulation	A6	A8	A9	A10
Quebracho tannin (g)	12	5	5	6
Cocamine ethoxylated (g)	12	7	7	6
Polymeric diphenylmethane diisocyanate (pMDI) (g)	5	4	2,5	3,5
Polyether siloxane (g)	0.5	-	-	-
TCPP (g)		-	-	3,5

All the samples prepared had a homogeneous appearance, reddish-brown color and without any macroscopic defects or surface friability. The specimens cut into cubes were observed by scanning electron microscopy with a SEM TM 3000 Hitachi. Mechanical performance testing was carried out at ambient temperature with an INSTRON 5944 universal testing machine equipped by 2KN head. Samples of dimensions $20 \times 20 \times 20 \text{ mm}^3$ were evaluated: cyclic compression tests were done for 50 cycles to a strain of 50% at loading/unloading displacement rate of 100 mm/min with a rest period of 1 s between cycles.

The behavior to fire was tested according to the European Norm EN-ISO 11925-2.⁸ First, the foams were oven dried at 60°C until their weight was constant. The flame was applied to the lower edge of the specimens for 15 s recording the time the flame takes to reach 150 mm over the point of application and measuring the detachment of particles on fire during the 20 s which follow. Comparative tests were done on with a control foam prepared from ethoxylated cocamine and isocyanate (12 g and 4 g, respectively) not containing the tannin [foam AST (A sans tannin)] and with a commercial flexible polyurethane foam sponge as second control.

MALDI-TOF-MS

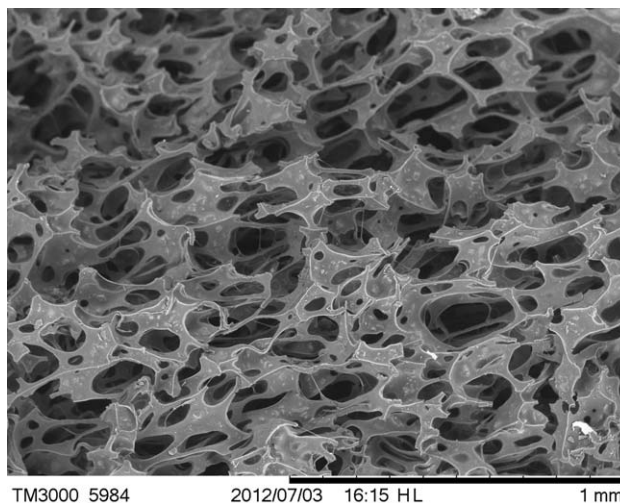
The spectra were recorded on a KRATOS Kompact MALDI 4 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns.

MALDI-TOF Sample Preparation. The samples were dissolved in acetone (4 mg mL^{-1}). The sample solutions were mixed with an acetone solution (10 mg mL^{-1} acetone) of the matrix; 2,5-dihydroxy benzoic acid was used as the matrix. For the enhancement of ion formation, NaCl was added to the matrix. The solutions of the sample and the matrix were mixed in equal amounts, and 0.5–1 μL of the resulting solution were placed on

Table II. Fire Behavior of Formulations A6, A8, A10 and AST and AC

Sample	A6	A8	A10	AST	AC
Time for 150 mm (s)	20	20	Immediate selfextinction	20	3
Dropping of inflamed material	NO	NO	NO	YES	YES

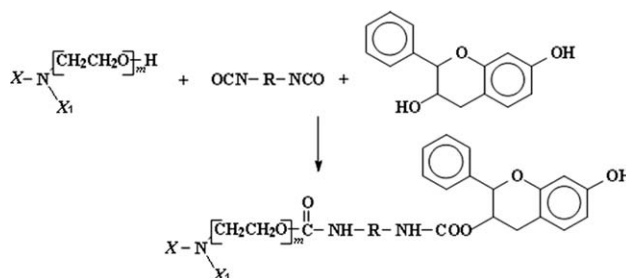
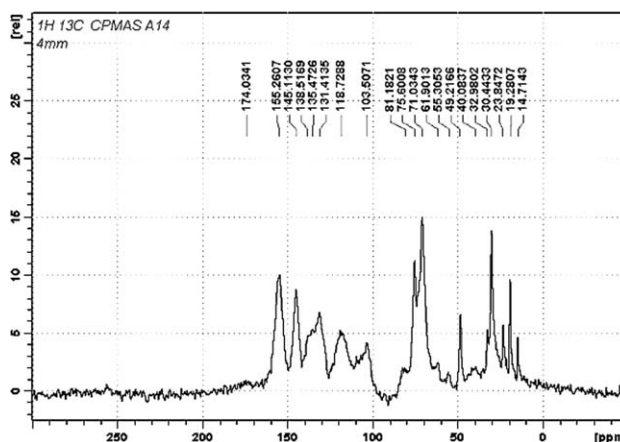
AST = A sans tannin; AC = commercial control foam.

**Figure 1.** Scanning electron microscope of copolymerized amine/tannin/isocyanate foam (A6) showing open cell structure.

the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer.

Solid State ^{13}C NMR

Solid state CPMAS ^{13}C NMR spectra were recorded on a Bruker MSL 300 spectrometer at a frequency of 75.47 MHz. Chemical shifts were calculated relative to tetra methyl silane (TMS). The rotor was spun at 12 kHz on a double-bearing 4 mm Bruker probe. The spectra were acquired with 5 s recycle delays, a 90°

**Figure 2.** Proposed reaction scheme of ethoxylated fatty amine, isocyanate, and tannin to obtain copolymerized amine/tannin/isocyanate foam.**Figure 3.** Solid phase ^{13}C NMR spectrum of copolymerized amine/tannin/isocyanate foam (A6).

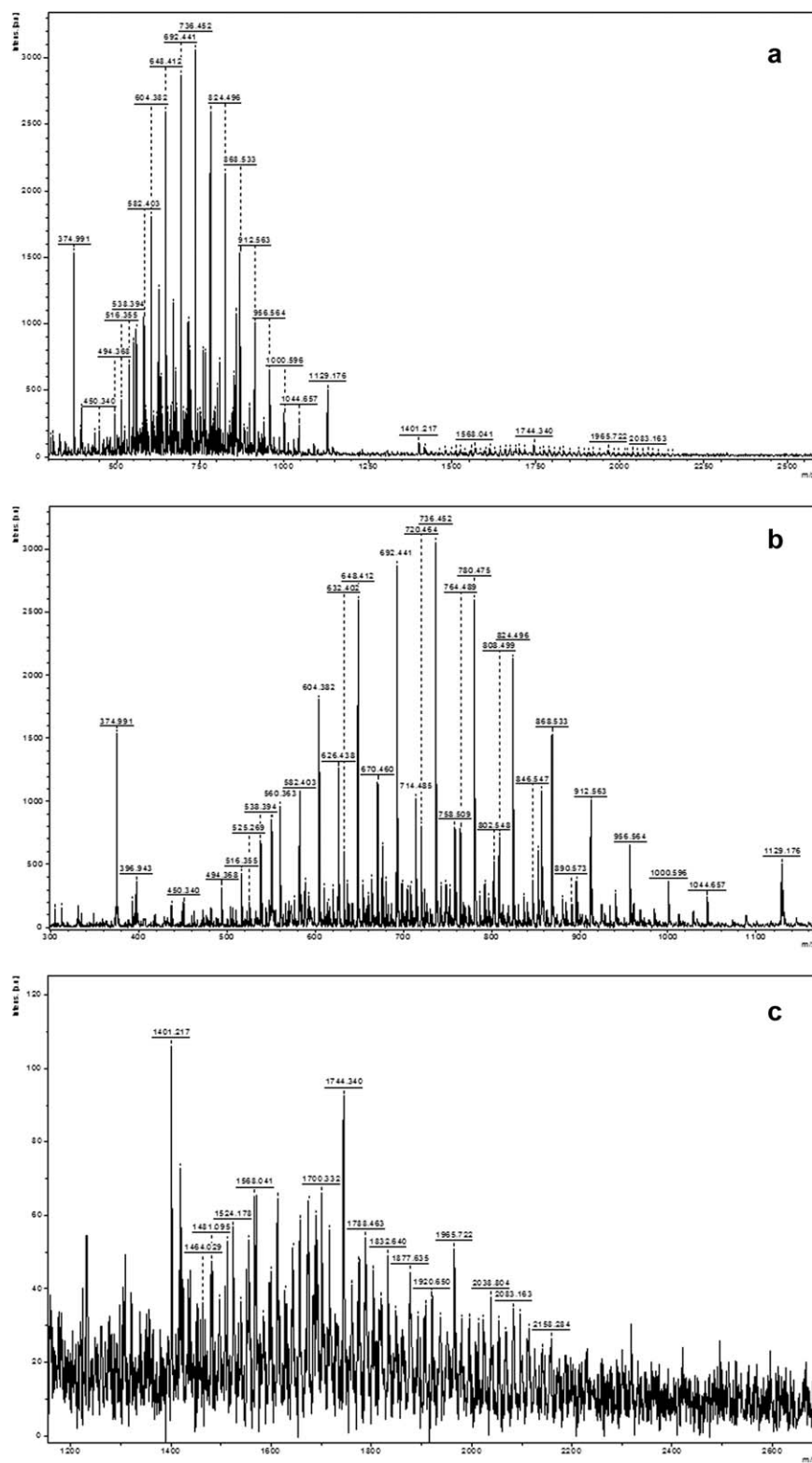


Figure 4. MALDI-TOF of copolymerized amine/tannin/isocyanate foam (A6): (a) 300 Da to 2500 Da range, (b) 300 Da to 1050 range details, (c) 1200 Da to 2600 range details.

pulse of 5 ms and a contact time of 1 ms. The number of transients was 3000. The spectrum was run with suppression of spinning sidebands.

RESULTS AND DISCUSSION

The alkoxyate amine allows to keep the tannins in suspension, reacts exothermally with the isocyanate, and conversely allows

Table III. MALDI-ToF Interpretation of Species in the Preparation of the Coreaction of Tannin-Polyurethane

Peak (Da)	Species
579 (582)	I(250)-U-Flavo(304)
693	I(382)-U-Flavo(289)
709	I(382)-U-Flavo(304)
736	Cocamine
868	(289)Flavo-U-I(250)-U-Flavo(304)
Or	A + 3xCH ₂ CH ₂ O
912	A + 4xCH ₂ CH ₂ O
982-985	(289)Flavo-U-I(382)-U-Flavo(289)
998-1000	(289)Flavo-U-I(382)-U-Flavo(304)
988 (small)	A-U-I(250)
1129	(304)Flavo-U-I(250)-U-Flavo(304)-U-I(250)
1292	A-U-I(250)-U-Flavo(304)
1401	(304)Flavo-U-I(250)-U-Flavo(304)-U-I(250)-U-Flavo(274)
1601	(274)Flavo-U-I(250)-U-Flavo(274)-U-I(250)-U-Flavo(274)-U-I(250)
1788	(274)Flavo-U-I(250)-U-A-U-I(250)-U-Flavo(274)
1820	(289)Flavo-U-I(250)-U-A-U-I(250)-U-Flavo(289)
1830-1834	(289)Flavo-U-I(250)-U-A-U-I(250)-U-Flavo(304)
1832	(274)Flavo-U-I(250)-U-A(+1x-CH ₂ CH ₂ O)-U-I(250)-U-Flavo(274)
1849	(304)Flavo-U-I(250)-U-A-U-I(250)-U-Flavo(304)
1877	(274)Flavo-U-I(250)-U-Flavo(274)-U-I(250)-U-Flavo(274)-U-I(250)-U-Flavo(274)
1916-1920	(274)Flavo-U-I(250)-U-A-U-I(382)-U-Flavo(274)
1946	(274)Flavo-U-I(250)-U-A-U-I(382)-U-Flavo(304)
2080-2083	(289)Flavo-U-I(382)-U-A-U-I(382)-U-Flavo(289)

Flavo = flavonoid, with unit molecular weight in parenthesis; A = amine; I = isocyanate with unit molecular weight in parenthesis; U = urethane bridge.

to have the pH ideal for the reaction of the polymeric isocyanate with the tannin. The elasticity of the resulting material is mainly due to the alkoxylic chains of the amine and of the urethane bridges that are generated by the reaction.

In Table I, the formulations that were used to prepare very elastic PUR-coreacted tannin-based foams are reported. The results of their exposure to a 1200°C flame by applying the European EN-ISO 11925-2 are presented in Table II. As can be seen from Table II all the three experimental foams (A6, A8, A10) had better resistance to fire than the value of the standard polyurethane foam (AC). Thus, in these new formulations, although the fire resistance is not even comparable to the much better values obtained for tannin/furanic foams,⁹ the presence of tannin cocondensed with the polyurethane retards the time, and the PURT foam starts to burn if compared to a PUR foams only. The tannin induces a slower flame propagation rate in the material. Moreover, while the foam burns the presence of the tannin stops any inflamed particles to either flow and drop, thus, avoiding propagation of the fire to other materials. Furthermore, for the A10 foam on taking away the flame, the material stops glowing, thus, this particular tannin-coreacted PUR foam is also self extinguishing. Figure 1 shows a scanning electron microscope picture of the appearance of foams A6, indicating that such flexible/elastic foams are open cell ones.

In Figure 2, the proposed reaction scheme for the three different materials to allow to better understand what type of reactions are thought to occur so that these can be traced by other analytical techniques is presented. Figure 2 advances the hypothesis that the cocamine, the flavonoid units of the tannin, and the isocyanate coreact to form species connected by urethane bridges. This is at least the idea that comes to mind. To determine if coreaction of the tannin with the PUR network chemicals does indeed occur, the system was then analysed by ¹³C NMR and by MALDI-TOF. By ¹³C NMR analysis (Figure 3), superimposed to the normal NMR pattern of the flavonoids,¹⁰ there are some peaks that appear to indicate coreaction. Thus, the peak at 138.5 ppm indicates the formation of one urethane link between the isocyanate and the aliphatic —OH group of the C3 of a flavonoid unit. This latter peak is rather marked and clearly visible. Much less visible but still contributing to the large dimension of the combined peaks they belong to are the peaks at 151.2 and 155.9 ppm. These two peaks represent, respectively, an urethane link between the —NCO group and phenolics —OHs, and an urethane linkage between the amidogroup of the cocamine and the —NCO group of the isocyanate. Furthermore, the normal signal of a C3 linked to an alcoholic —OH group is very much smaller in Figure 3 than for unreacted flavonoid tannins¹⁰ indicating that coreaction with

Table IV. MALDI-ToF Interpretation of Second Series of Species in the Preparation of Coreacted Tannin-Polyurethane Compounds

Peak (Da)	Species
1481	(274)Flavo-U-I(250)-U-A(-7x-CH ₂ CH ₂ O)-U-I(250)-U-Flavo(274)
1524	(274)Flavo-U-I(250)-U-A(-6x-CH ₂ CH ₂ O)-U-I(250)-U-Flavo(274)
1568	(274)Flavo-U-I(250)-U-A(-5x-CH ₂ CH ₂ O)-U-I(250)-U-Flavo(274)
1700	(274)Flavo-U-I(250)-U-A(-2x-CH ₂ CH ₂ O)-U-I(250)-U-Flavo(274)
1744	(274)Flavo-U-I(250)-U-A(-1x-CH ₂ CH ₂ O)-U-I(250)-U-Flavo(274)
1788	(274)Flavo-U-I(250)-U-A-U-I(250)-U-Flavo(274)
1832	(274)Flavo-U-I(250)-U-A(+1x-CH ₂ CH ₂ O)-U-I(250)-U-Flavo(274)
1876	(274)Flavo-U-I(250)-U-A(+2x-CH ₂ CH ₂ O)-U-I(250)-U-Flavo(274)
1920	(274)Flavo-U-I(250)-U-A(+3x-CH ₂ CH ₂ O)-U-I(250)-U-Flavo(274)
1965	(274)Flavo-U-I(250)-U-A(+4x-CH ₂ CH ₂ O)-U-I(250)-U-Flavo(274)

Flavo = flavonoid, with unit molecular weight in parenthesis; A = amine; I = isocyanate with unit molecular weight in parenthesis; U = urethane bridge.

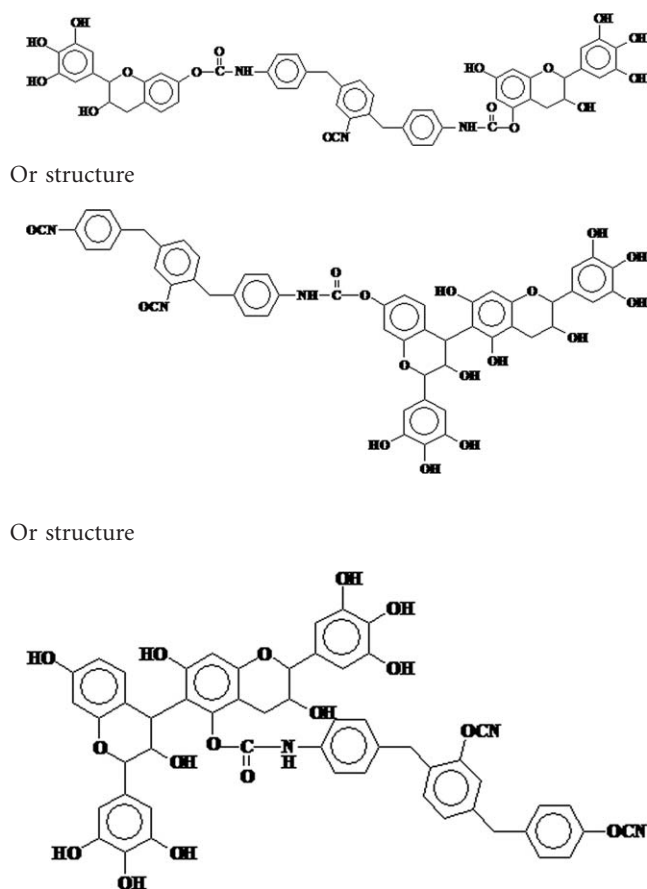
the -NCO group of the isocyanate to form an urethane bridge between isocyanate and tannin has preferentially occurred on the C3 site.

Further and determining confirmation that the isocyanate is coreacted with both tannin and cocamine and is obtained by the MALDI-TOF analysis of the complex reaction mixture (Figure 4(a,b,c) and Table III). There are two evident series of peaks in Figure 4(a,b,c), and these are described separately in Tables III and IV. First of all from Figure 4(a,b), it is noticeable that the cocamine used is a mixture of oligomers, the most abundant of which has a molecular weight of 713 Da, which gives the peak at $713 + 23 (\text{Na}^+) = 736$ Da. The other lower and higher molecular weight species are due to the distribution of cocamine oligomers with a repeating period of 44 Da, thus, of a -CH₂CH₂O- group. All the species distributed in a quasi Gaussian distribution around the 736 Da peak, thus, have a number of a -CH₂CH₂O- groups in excess or in defect of the average 736 Da peak. This distribution must also be kept in mind when evaluating species that are obtained by the reaction of the cocamine with the isocyanate to form urethane-linked cocamine/isocyanate/flavonoid species. The main compounds belonging to such a series of species is shown in Table IV, and are exclusively urethane-linked cocamine/isocyanate/flavonoid coreacted species.

A second series of coreacted compounds are shown in Figure 4(a,c) and Table III. This more heterogeneous series comprises urethane-linked tannin/isocyanate, cocamine/isocyanate, and cocamine/isocyanate/flavonoid species. Again it must be kept in mind that the polymeric 4,4'-diphenylmethane diisocyanate is in reality also composed of a distribution of oligomer species the average being the equivalent of a triphenyldimethane trisocyanate of molecular weight 382. Thus, the isocyanate molecule that is linked by one or more urethane bridges to cocamine and flavonoids is of both molecular weight 250 Da, thus, effectively 4,4' diphenylmethane diisocyanate, and of molecular weight 382 Da. To render the reaction mix of products even more complex the flavonoid units present in the extract used are of four different species, two of which of 290 Da molecular weight, and the other two of, respectively, 274 Da and 304 Da. Thus, the urethane-linked tannin/isocyanate, cocamine/isocyanate, and

cocamine/isocyanate/flavonoid species are a mix of the coreaction of all these oligomers. These species are listed in Table III.

It must also be kept in mind that the flavonoids are present as monomers, dimers, and even oligomers higher than this. Thus, the species in Tables III and IV have in some case more than one possible interpretation of their structure. To give an example, the species indicated in Table III as (289)Flavo-U-I(382)-U-Flavo(304) can equally have structure



Stress vs. strain curves of these foams tested in compression were repeated for several cycles to determine their flexibility. An

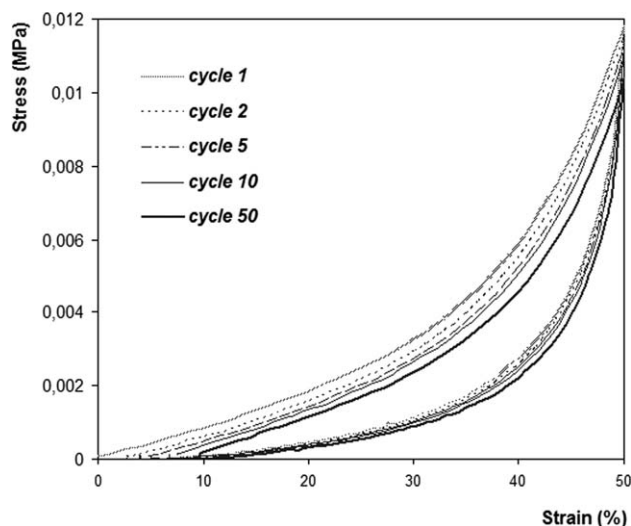


Figure 5. Stress vs. strain curves in compression during cyclic compression test. The data up to 50 cycles are shown.

example of these curves is shown in Figure 5. The reproducibility of the curves in this graph as one passes through a series of successive cycles of compression and relaxation repeated for 50 cycles clearly indicate the highly flexible/elastic nature of this material. The absence of a stress/strain plateau in these curves also confirms the elevated elasticity of these foams. As can be seen from Figure 5 such a material is highly elastic. Under the testing conditions used, recovery after the first cycle test is of 95%. After the fifth cycle is of 90% and after completing 50 cycles it is greater than 80%.

CONCLUSIONS

Condensed flavonoid tannins can be simultaneously coreacted with a fatty amine and pMDI to give highly flexible/elastic polyurethane foams. These have been shown by ^{13}C NMR and

MALDI-TOF to be composed of a series of copolymerised amine/isocyanate/tannin oligomers. In general, between 30% and 50% of natural tannins is added to the components used to obtain polymerisation of the polyurethane. The characteristic of these polyurethanes is that the tannin present slows down burning, but even more interesting they can be produced with flame self-extinguishing capabilities and, in burning, they neither flow nor asperge flaming material around, contrary to what occurs with normal polyurethanes, limiting in such a way the possibility of transmitting fire to other materials in the same environment. These foams are open cell foams.

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