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Glucose-Biobased Non-Isocyanate Polyurethane Rigid Foams

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Abstract: Glucose-based non-isocyanate polyurethanes (NIPU) were prepared by reaction of glucose with dimethyl carbonate and hexamethylene diamine. These were used to prepare partially biobased polyurethane foams by reaction with $NaHCO_3$ as a blowing agent and addition of a silane coupling agent having different functions such as coreactant and adjuvant to obtain more uniform and smaller cells. The foams were foamed and hardened by applying heat. The foams presented very limited fire resistance indicating that as for synthetic polyurethane foams the eventual use of a fire retardant appears to be necessary. The 2 hours water absorption was used to indicate if close cells or open cells occur. More characteristic is their stress strain behaviour. While compression does indeed flatten the cell walls nonetheless the cellular structure is maintained and the cell walls have not been destroyed. This indicates a certain level of elasticity in the cell walls of formulations containing $NaHCO_3$. In effect the macro-appearance of this foams, confirms this explanation as the foam is densified and holds together.

Keywords: Polyurethane biofoams; non-isocyanate polyurethanes; NIPU; biofoams; glucose

1 Introduction

Polyurethanes are the ubiquitous material used for numerous applications and which are prepared by the reaction of a polyol with di-or poly-isocyanates. While several synthetic and natural polyols have been developed and used over the years to produce these important polymers, isocyanates are still the only reagents used industrially to produce them. To-day, the inherent toxicity of isocyanates during use has spawned a considerable research effort to try to develop alternative routes to the preparation of polyurethanes. The route to prepare polyurethanes without the use of isocyanates has been opened by some seminal work in the 1990's and early 2000's [1-3]. Since then, numerous research works have explored a considerable number of variations on the same theme of the original synthesis route [4-17]. The main approach of most of this research work has been aimed at the preparation of polyhydroxyurethanes by reacting compounds presenting hydroxyl groups with a cyclic carbonate and with a diamine, all these being of synthetic origin. The large majority of these works used synthesised cyclic or dicyclic carbonates and aliphatic diamines to react with other synthetic materials. To eliminate the additional step to prepare dicyclic carbonates in these synthesis, a different approach has been to use the simpler, non-cyclic dimethyl carbonate for the first step of carbonation [18,19] as it has neither irritating nor mutagenic effects [19]. Hydroxy groups are then carboxymethylated by nucleophilic substitution [19]. Only a few of these works linked carbonates and diamines with a biosourced material [3,14,15,17,20-23]. The technological barrier to the synthesis of biobased cyclic carbonates could be overcome either by the more simple route of using a non-cyclic dicarbonate [20-23] or by transforming epoxidized vegetable oils or using glycerine carbonate intermediates [17]. Biobased polyamines could also be produced from fatty diacids [17] or from aminated tannins [22,24].

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More recently, non-isocyanate polyurethanes (NIPU) were prepared from hydrolysable and condensed tannins [20-22] for use as wood surface finishes [21]. These latter works were remarkable first as they used the non-cyclic dimethyl carbonate; second as partially (approximately 50%) biobased NIPU were prepared; and third as, by using an aminated tannin in the place of synthetic di- and poly-amine, reached a biobased content of more than 70% [22]. In these works, it was found that the small proportion of carbohydrates always present in commercial tannin extracts also participated to the formation of urethane linkages [20,22]. As a consequence of this finding, biosourced non-isocyanate polyurethanes (NIPU) were also prepared from carbohydrates, namely glucose and sucrose, by reacting them with the non-cyclic dimethyl carbonate and hexamethylene diamine [23]. These carbohydrate-based NIPUs, in particular the glucose-based NIPUs, were used as wood and steel surface finishes and also tested as wood adhesives, in all these cases with rather encouraging results.

One of the main uses of polyurethanes is for the manufacture of foams. As NIPUs behave differently from isocyanate containing polyurethanes it was of interest to use glucose-based NIPUs to prepare rigid foams. The main challenge to achieve this is that, differently from self-blowing isocyanate-based polyurethanes, the reactions for the formation of NIPUs are not markedly exothermic. Second, catalysts for isocyanate-based polyurethanes, which help the foaming and hardening reactions to occur, do exist and are well-known. This is not really the case now for NIPUs. Thus, NIPUs can only rely on, and need application of external heat to foam and harden.

This paper then deals with initial attempts to prepare glucose-based NIPU foams through a number of different formulation approaches and thus to study what are the limitations, characteristics and foreseeable problems for the application of biobased NIPUs to rigid foams.

2 Experimental

Synthesis of the glucose based Non-Isocyanate Polyurethane (g-NIPU)

The glucose NIPUs were prepared according to a procedure already reported [23]: 160 g of glucose were mixed with 106.7 g of dimethyl carbonate and 133.36 g of water, and heated to 50°C for 40 min. Then 310.4 g hexamethylene diamine (70% solution) were added to the mixture and heated to 90°C for 30 min, then cooled to room temperature.

The reaction has been documented in reference [23] and occurs according to the following sequence of reactions: Preparation of NIPU foams: The glucose-NIPU was rotary evaporated at 60°C for 2 h, and then cooled down to room temperature ready for use. A certain amount of silane coupling agent (KH560) was mixed very well with the glucose-NIPU, and $NaHCO_3$ added as blowing agent, then the mixture was allowed to rest for a period of time (cf. Tab. 1). It was then placed in an oven at 200°C for 30 min foaming time. The foam was removed from the foaming beaker after 1 h and placed at ambient temperature (25°C and 12% relative humidity) for 2 days before its characterisation. When g-NIPU was mixed with the silane coupling agent (KH560), the mixture did start gelling. The silane coupling agent used as a compatibilizer it was also added as its addition has been found to lead to foams with smaller cells [25] as well as starting to slowly react already at ambient temperature with the NIPU polyurethane. The foams prepared were tested for their absorption by keeping them immersed in water at ambient temperature for two hours.

24 h Water absorption: In order to investigate the water absorption of glucose-NIPU foams and the effect of their densities on water absorption, 4 samples were tested for their 24 h water absorption.

Compression: The foams obtained were compression tested. Different addition amount of KH560 were added. Thus, “1” indicates only the glucose-NIPU alone, “2” is a foam formed by 20 g glucose-NIPU+2 g KH560, while “a” is a foam formed by 20 g NIPU+1.5 g KH560.

Ignition test:

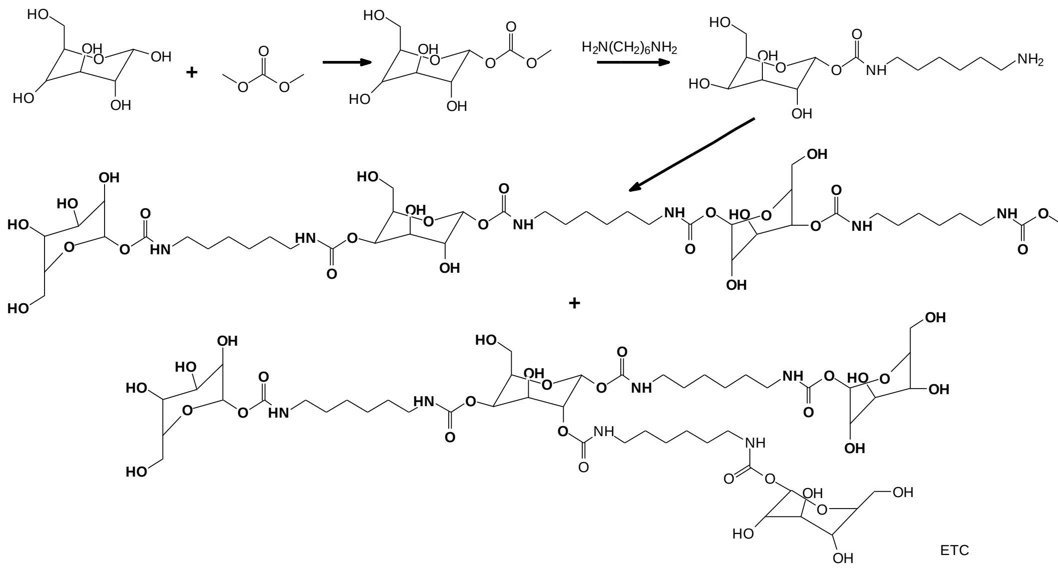


Table 1: Formulations of non-isocyanate polyurethanes (NIPU) foams and their physical characteristics

No.	Foam forrmulations	Rest time (min)	Density (g/cm^3)	2h water absorption (%)	Fire resistance (s)
1	20 g NIPU	--	0.059	362	67
2	20 g NIPU + 2 g KH560	150	0.306	72	135
3	20 g NIPU + 1.5 g KH560 + 0.2 g $NaHCO_3$	150	0.127	172	91
a	20 g NIPU + 1.5 g KH560	90	0.075	259	83
b	20 g NIPU + 1.5 gKH560 + 0.2 g $NaHCO_3$	90	0.090	320	85
c	20g NIPU + 1.5gKH560 + 0.5 g $NaHCO_3$	90	0.088	281	85

A foam sample of 2.5 × 2.5 × 2.5 cm cut from the prepared foams is placed in a porcelain crucible preheated on a Bunsen burner and with the crucible at 600°C. Heating with the burner is maintained at the same temperature until the sample chars and does not burn anymore and the time to reach this state is measured. The test is done in duplicate for each type of foam to be tested.

3 Results and Discussion

The non-isocyanate polyurethane formulations used to prepare foams are shown in Table 1. The lack of an isocyanate in the formulation precludes, at least at this stage, the preparation of self-blowing foams. As non-isocyanate polyurethanes (NIPU) cannot use catalysts the problem is to produce expansion/foaming of the mixture while simultaneous hardening occurs. Application of heat has shown to be the answer for hardening NIPU polyurethanes, at least for their applications as adhesives and surface coatings [23]. In the case of NIPU foams the further difficulty is then to cause foaming coordinated with hardening by application of heat. While the use of a blowing agent such as pentane did yield NIPU foams, unfortunately when the mixtures were heated the much lower boiling point of pentane in relation to the temperature of curing, while yielding very rigid foams, also gave foams unacceptable due to their big, disorderly and rather uneven cells. The approach was then taken to add together sodium bicarbonate as a blowing agent with a silane coupling agent as a compatibilizer, the combination of the two known to lead to controlled more even foaming [25]. This approach appeared to work and the different formulations tried are shown in Tab. 1.

The results in Tab. 1 show that the addition of sodium bicarbonate under the conditions of hardening used does yield open cells foams as indicated by the values of density and percentage water absorption after 2 h immersion in water. The absence of sodium bicarbonate and silane does yield a foam having rather short fire resistance, arriving at the formation of char in only 67 seconds, but of rather low density. The low density obtained is possibly consequence of evaporation of some hexamethylene diamine liberated from the urethane bond during the high temperature hardening and possibly of some lack of controlled even foaming due to the absence of both silane compatibiliser and bicarbonate foaming agent. The presence of a silane alone (formulation 2), without sodium bicarbonate, on the contrary depresses this effect yielding foams of much higher density, reflected in the lower percentage water absorption probably due to a certain percentage of close cells in the foams. However, comparing formulation b with the identical formulation 3 (Tab. 1) only different in the resting time used, yields a foam of much lower density and much higher water absorption. This indicates that (i) the resting time is an important parameter influencing the properties of these foams, and (ii) that the resting influences the percentage of open cells in the foam, this being high for formulation b.

Starting with formulation 3 (Tab. 1) the density starts to decrease and the influence of the resting time, although still present, is much less marked than for cases in which the sodium bicarbonate is absent. This is shown by comparing the difference between formulation 3 using 150 s resting time and similar formulations b and c for which only 90 s resting time was used. Equally, as the density decreases the water absorption increases. This indicates that the percentage of open cells appears to increase considerably. Figure 1 shows that water absorption levels after about 3 h water immersion appearing to be in direct relation to foam density for formulations a, b and c. However, this is not exactly true, as the only other conclusion that can be deduced is that the absorption of the formulations containing the $NaHCO_3$ have, as expected, slightly higher water absorptions due to the presence of the bicarbonate. The smaller size of the cells of foam "b" helps to absorb and retain water, so that the water absorption of b is higher than for other foams. The case of "20 g NIPU+1.5 g KH560 for 150 min rest time" was also tried but the results were not encouraging thus it has not been shown in Table 1, as the foam was of higher density and fire resistance than sample a and presenting a lower water absorption rendering its results very similar to those of foam 3.

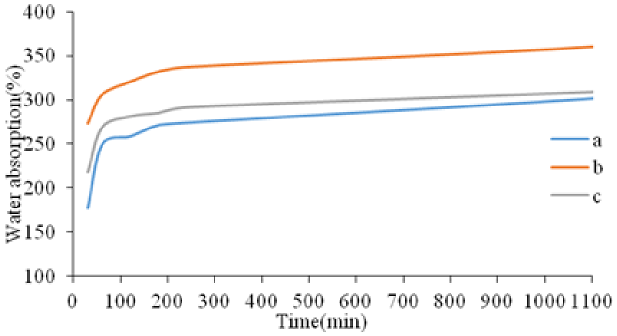


Figure 1: Water absorption curves as a function of time

The fire resistance of these foams does not appear to be very different (Tab. 1, Fig. 2). The only correlation that exists is between foam density and time taken by the foam to reach the flame-absent charred state. The higher the density the longer is the time to reach the charred terminal state. The results in Tab. 1 also clearly indicates that these foams are not fire resistants and that as for isocyanate-based polyurethane foams fire retardants would need to be added [26].

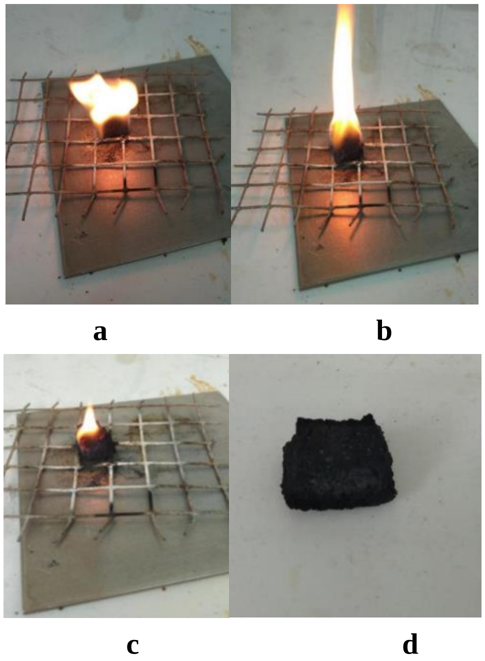


Figure 2: Ignition tests of sample 2 that formed by 20 g glucose-NIPU + 2 g KH560, (a) at ignition (b) after 90 s, (c) after 120 s, and (d) afte 150 s

Fig. 3(a) reports the stress *vs.* strain curves in compression for foam 1, 2 and a (Tab. 1). This shows that the mechanical resistance of foam 2 is better than for the others this being exclusively due to the much higher density of this foam. Fig. 3(b) shows for foams a, b and c that their stress *vs.* strain curves are comparable due to the fact that their densities are very similar, again demonstrating as for other foams that compression resistance is directly proportional to foams density [27]. Last, Fig. 4 compares the stress vs strain curves in compression of two identical formulations, namely b and 3, the main difference of which is the resting time. It appears that the longer is the resting time the higher is the stress at a given strain. The reason for using silaneKH560 is as NIPU needs a higher temperature to further the reaction and cure. KH560 does easily start to react with NIPU at lower temperature (even at room temperature) to start forming a network. This is also the reason why a resting time is used, because during the resting time, KH560 can react with NIPU and start to solidify and cure. This is the reason why the foam density is higher the longer is the resting time. Lastly, the use of KH560 coupled with resting time yields foams with more uniform and smaller cells than without.

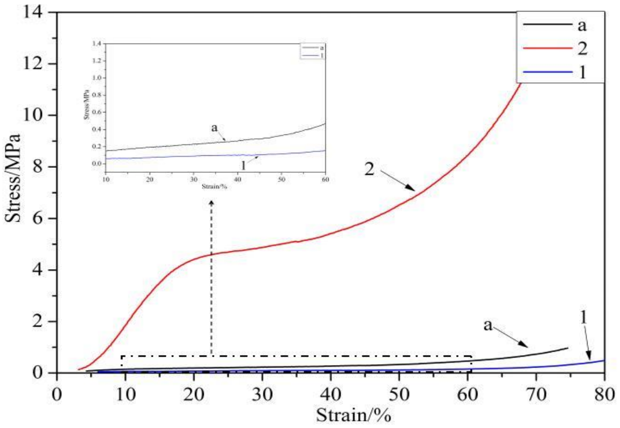


Figure 3a: Stress *vs.* strain curves where (1) indicates only the glucose-NIPU alone, (2) is a foam formed by 20 g glucose-NIPU+2 g KH560, while (a) is a foam formed by 20 g NIPU+1.5 g KH560

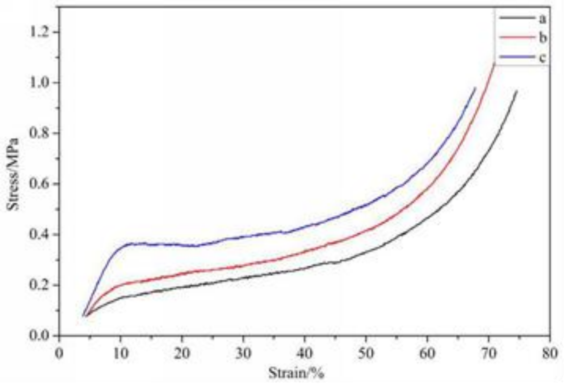


Figure 3b: Stress *vs.* strain curves where different amounts of $NaHCO_3$ were added: (a) is a 20 g NIPU + 1.5 g KH560 foam, (b) is a 20 g NIPU + 1.5 gKH560 + 0.2 g $NaHCO_3$ foam, and (c) is a 20 g NIPU+1.5 gKH560 + 0.5 g $NaHCO_3$ foam

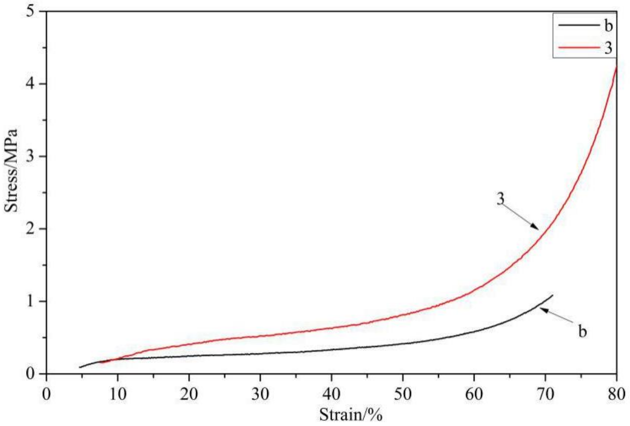
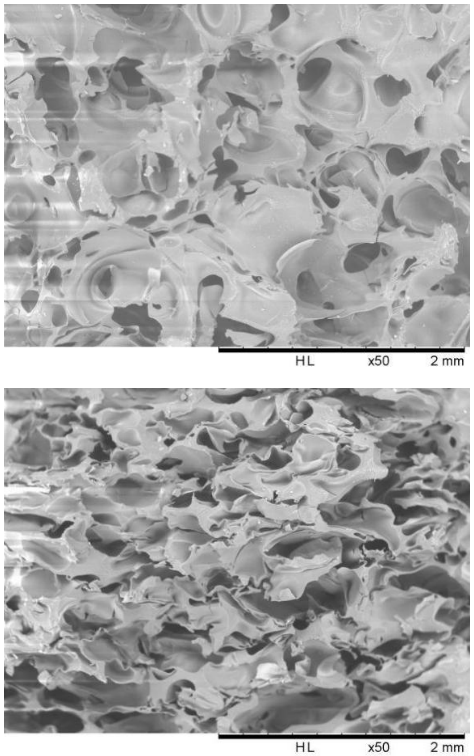


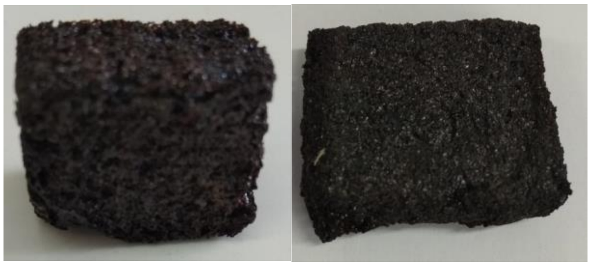
Figure 3c: Influence of the rest time to the compression performance; (b) rest time of 90 min; (3) rest time of 150 min

In particular the foams without silane KH560 are more rigid, brittle and have a cell distribution uneven and irregular. Thus, to add a small amount of a non-ionic surfactant such as a silicone coupling agent in general tends to decrease the density of the foam [25]. Furthermore, at the macroscopic level, the aspect of these foams is more homogeneous, with finer and smaller cells than foams which do not contain any surfactant. Such differences can be explained by the triple function of the surfactant: (i) to improve the compatibility of the reactants, mainly of the blowing agent with the resin and catalyst; (ii) to lower the surface tension of the system, thereby forming finer bubbles, hence smaller cells and (iii) to prevent the cell wall from becoming thin and unstable during foaming i.e., to prevent the developing foam from collapsing or rupturing [28-30]. Thus, the inclusion of a surfactant in the foam composition allows to modify the cells size independently of the density of the material, contrary to what found from previous work on other biosourced foams [31-33]. As a consequence, the capacity of thus achieving independence from the other foaming parameters greatly increases formulation possibilities and the range of materials that can be developed, hence their greater diversity of properties and applications.

Compression of the different foams in Tab. 1 yielded some information of interest. They were observed before and after by scanning electron microscopy (SEM). Figs. 4(a), 4(b) show that, after compression, foam 2 cell walls are crushed and destroyed and the cellular structure is completely lost (Fig. 4(a), right). This indicates perhaps that due to this foam higher density the cell walls are more rigid and brittle and consequently what occurs is what shown in Fig. 3(b), the cellular walls being crushed and broken. The case is different in Figs. 5(a), 5(b) for foam 3. While compression has flattened the cells structure (Fig. 5(a), right), nonetheless the cellular structure is maintained and the cell walls have not been destroyed. This indicates a certain level of elasticity in the cell walls of formulations containing $NaHCO_3$. In effect the macro-appearance of this foam in Fig. 5(b), confirms this explanation as the foam is densified and sticks together. The same is apparent from Figs. 6(a), 6(b), 6(c) for formulations a, b and c for which some of the compressed foams also do not show cellular collapse, although to different extents, but only flattening while still maintaining their cellular structure. This indicates too that while there is clearly an effect of the foam density on the residual elasticity of the cell walls there are also other effects to consider. Thus, foam c, which has a higher proportion of bicarbonate, shows much more damage after compression (Fig. 6 right) than foam b, the higher level of bicarbonate having rigidified somewhat more the cell walls. This is an indication that $NaHCO_3$ does not only play a role as blowing agent of the foam by liberating CO_2, the role for which it was added, but that it does also appear that some reaction occurs between the bicarbonate and the glucose-NIPU to rigidify the cell walls. Compression of glucose-NIPU foams gives a product which behaves differently than other rigid biobased foams, such as tannin-furanic rigid foams [27], as when compressed they are not crushed but just compacted and stronger and harder than before compression. This behaviour confirms what observed by SEM, namely that there is a certain elasticity inherent to the cell walls and these do not collapse during compression. Such a behaviour is characteristic of networks cross-linked by urethane bridges in contrast to rigid foams, synthetic or biobased, cross-linked by other types of bridges [27]. Furthermore, this residual elasticity could depend from the temperature, hence the internal pressure generated during foaming, decreasing when a surfactant/coupling agent is included in the formulation [25]. Thus, the foam with the added silane is more elastic and less brittle. Conversely, inclusion of other types of surfactants/coupling agents must be evaluated for each specific case [25] as for example addition of anionic surfactants, leads to collapse and destruction of the cellular structure. Such types of additives, if needed, must anyhow be combined with non-ionic surfactants which ease the emulsion of all the components of the formulation.

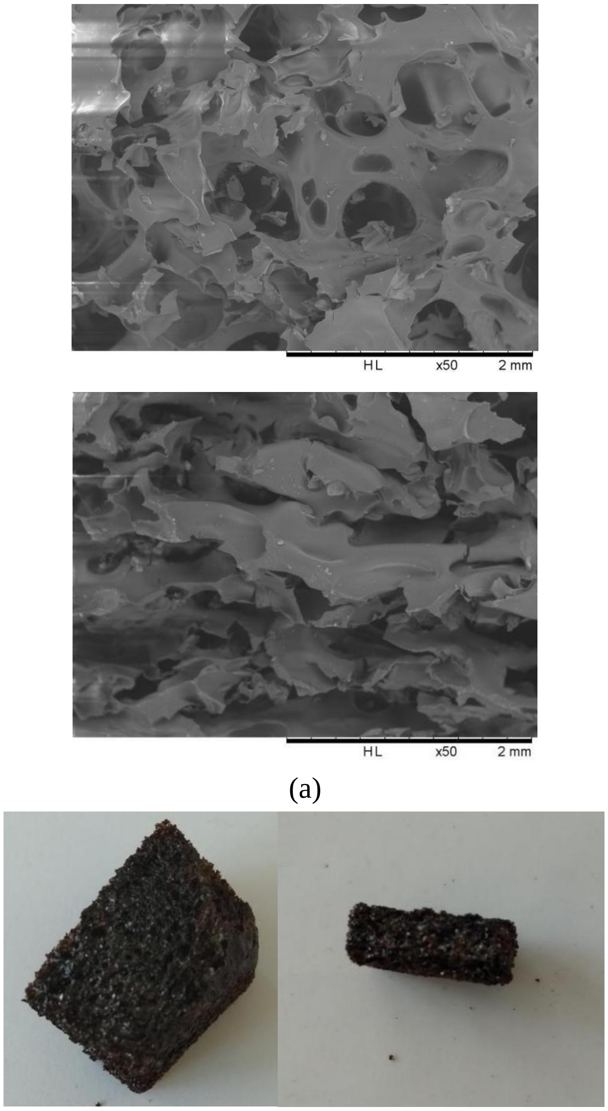


(a)



(b)

Figure 4: (a) Scanning electron microscope image of formulation 2 foam before compression (left) and after compression (right). (b) Photograph of section of foam 2 before compression (left) and after compression (right)



(a)

(b)

Figure 5: (a) Scanning electron microscope image of formulation 3 foam before compression (left) and after compression (right). (b) Photograph of section of foam 2 before compression (left) and after compression (right)

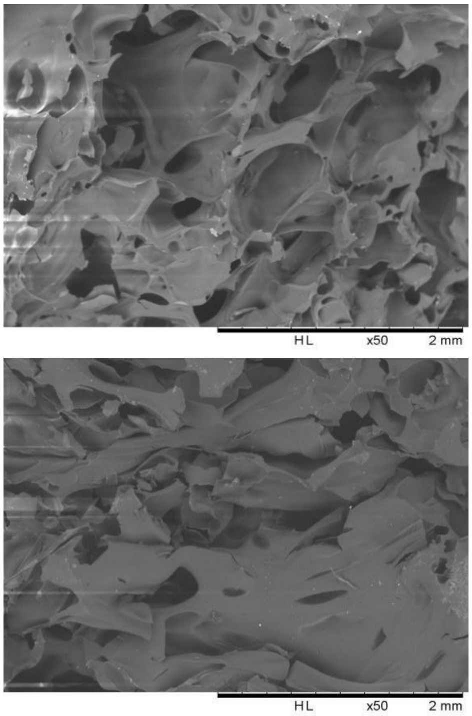


Figure 6a: Scanning electron microscope image of sample "a" before compression (left) and after compression (right)

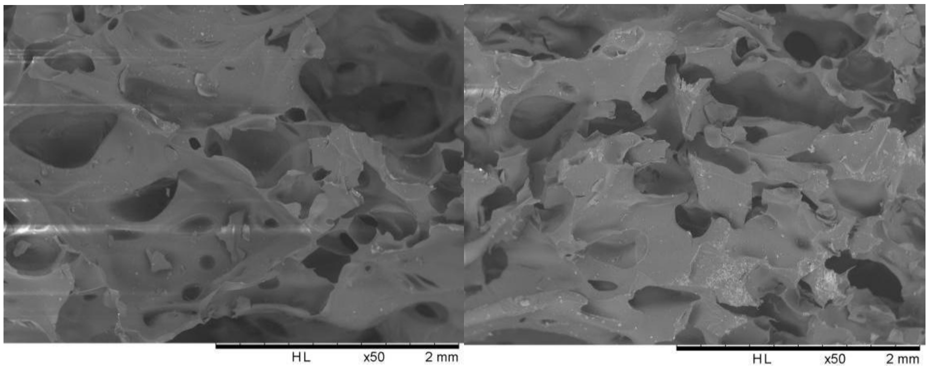
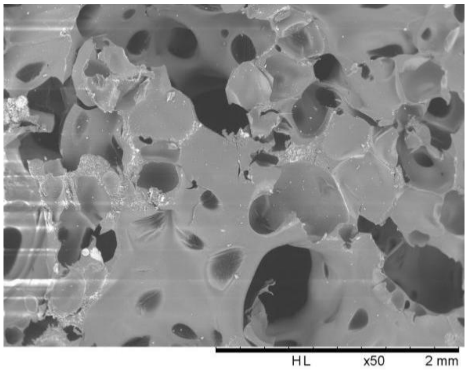


Figure 6b: Scanning electron microscope image of sample "b" before compression (left) and after compression (right)



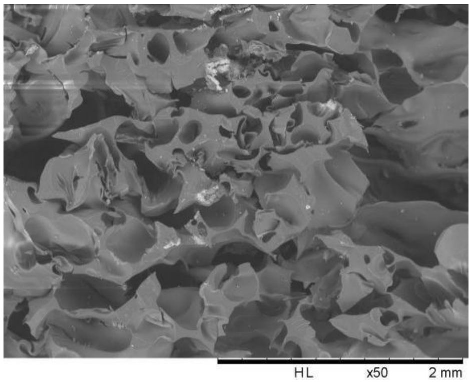


Figure 6c: Scanning electron microscope image of sample “c” before compression (left) and after compression (right)

5 Conclusions

In conclusion, glucose-based non-isocyanate polyurethanes (NIPU) have been shown to be able to be used to prepare partially biobased foams, although what presented is only an early beginning. They present two of the same characteristics of isocyanate based polyurethanes, thus (a) the flexibility of the urethane bridges cross-linked network which does constitute the foams cell walls, and (b) the limited resistance to fire that has to be addressed in the future, as for synthetic PUR, by the need to add fire retardants. The stress/strain curves and the SEM of the foams before and after compression have shown that, in the main, while the cells are flattened, the original cellular structure is not lost. This has indicated that there is a certain elasticity inherent to the cell walls and that these do not collapse during compression. This may render NIPU foams more adapt for use as a core material for sandwich composite laminates and for other broader applications.

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