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Incorporation of Aminoalcohols to Tune the Properties of Polyurethane Systems

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Incorporation of Aminoalcohols to Tune the Properties of Polyurethane Systems

Alexandre Adam, Saadane Rezaiguia, Romain Severac and Michel Bouquey[1]

Abstract: It is common practice to incorporate low molecular weight molecules, known as chain extenders, to enhance the performance of polyurethane (PU) material. They usually increase the phase separation between the soft and hard domains, which has a significant impact on the density of hydrogen bonds. Aminoalcohols, molecules with both hydroxyl and amine functional groups, are important building blocks in the synthesis of pharmaceuticals but are also widely used in cosmetics or paints and coatings. Easily derived from abundant natural sources, such as amino acids, aminoalcohols align with the need for renewable and sustainable sources. Despite their importance, the specific reactivity of aminoalcohols towards isocyanates and their contribution to PU-based formulations remain underexplored. They can act as chain extenders as well as crosslinkers and catalysts. This study addressed this knowledge gap by assessing the feasibility of adding various aminoalcohols to create hybrid poly(urethane-urea) formulations. By measuring the exothermicity of the polymerization and gel times, we calculated that all tested aminoalcohols have a catalytic activity on the formation of the polymer network. We also identified DMAMP as a promising reactive catalyst whose integration into the network is of primary interest to formulate products that do not emit volatile organic compounds. Moreover, increasing the amount of aminoalcohols stiffened the foams while maintaining the density constant. X-ray tomography completed the characterizations of the foams. Taken together, these results open possibilities for using aminoalcohols to enhance and tune material performances while contributing to more environmentally friendly PU formulations.

Keywords: Aminoalcohols, Polyurethanes

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Introduction

PU foams represent more than half of total PU consumption worldwide and can be divided into two main groups: rigid and flexible foams [1]. Rigid foams are used mainly for insulation purposes in the building industry, refrigeration, and transportation industry. On the other hand, flexible foams are recognized for their excellent reversible deformation and are widely used in the transportation industry, with cars, aircraft, seats, and for applications like pillows, mattresses etc. [2,3].

The production of PU foams with controlled and tailored properties involves the use of many additives, such as a UV stabilizer, flame retardants, silicones, catalysts, and chain extenders. Many studies highlighted the importance of these additives on the final properties of the PU materials [4-6]. PU are segmented polymers that comprise hard and soft segments and the use of chain extenders deeply modifies the organization of both domains [7]. However, very few molecules have been investigated as chain extenders, primarily glycols such as diethylene glycol, butanediol or small diamines such as putrescine, ethylene diamine [8,9]. Aminoalcohols (AA) are a class of molecules containing both hydroxyl and amino (primary, secondary, tertiary) groups around an alkane backbone. They are widely used in many industries and find applications in chemical manufacturing, paints, coatings, and personal care. Their diverse structures as well as physical and chemical properties may provide new features to PU materials. The primary amines of AA are more reactive with isocyanates than alcohol groups and lead to the formation of urea bonds. Urea bonds are tougher and less flexible than urethane bonds because of the higher density of the hydrogen bonds that can be built. Hence, a new material can be obtained based on a mixed poly(urethane-urea) network with a controlled density of urea bonds. Polyurea are materials with interesting properties but are generally more expensive to produce than PU. Adding urea bonds in PU through the chain extenders is thus very promising. In this paper, several AA were studied, and their reactivity with isocyanates, their behavior as potential catalysts in standard PU mixtures, and the consequences of their addition in a standard flexible PU foam formulation were specifically researched.

Materials and Methods

All AA were obtained from Advancion Sciences company. They are defined by their molecular weight (MW) and their number of functional groups (f) (the sum of alcohol and primary amine groups). Those molecules are: 2-amino-2-methyl-1-propanol (AMP, MW=89.1 g/mol, f=2), 2-amino-2-ethyl-1,3-propanediol (AEPD, MW= 119.2 g/mol, f=3), Tris(hydroxymethyl)-aminomethane (Tris, MW=121.1 g/mol, f=4), 2-dimethylamino-2-methylpropanol (DMAMP, MW=117.2 g/mol, f=1), *N,N*-dimethyl-3-methoxypropylamine (DMMOPA, MW= 117.2 g/mol, f=0). Their structure is detailed in Table S1. Polyols Alcupol F-2832, C-5571, X-7510, R-3810 were obtained from Repsol. Silicone and catalyst agents Tegostab® B8724 LF2, B8737 LF2, DABCO 33LV and DABCO BL11 were acquired from Evonik. 1,2-diamino-2-methylpropane (DMP), 1,3-propanediol (1,3-PD) and 1,3-butanediol were purchased from Sigma-Aldrich.

AMP was distilled under low pressure to remove excessive water content. The water content of all aminoalcohols was measured by the Karl-Fisher method before any use.

FTIR spectroscopy:

The IR data were acquired using the transmission method. Demountable Omni-cell Specac liquid cell with NaCl windows were used. Infrared spectra were collected at 4 cm^{-1} resolution with a Brucker Vertex 70 apparatus equipped with a DTGS detector, a KBr beam splitter and a blackbody source.

Exothermicity measurements:

Temperature probes (thermocouples) connected to a cDAQ-T1101 Bundle from National Instruments and linked to the computer were used to monitor the temperature changes inside the reactive mixture. SignalExpress software was used to acquire the signals from the thermocouples with a time interval of 200 ms. The reaction tube was covered with a block of PE foam to increase the insulation of the system and be as close as possible to an adiabatic system.

Gel times:

Alcupol X-7510, a triol, was added to a 10 mL polypropylene tube followed by the addition of a defined amount of AA. The amount of AA (called %mol cat) corresponds to a molar fraction of the total OH functions coming from the triol. The correct concentration of AA is obtained by diluting a concentrated mixture of 8 %mol cat. Typically, 8 %mol cat. mixture is prepared as follows: Alcupol X-7510 is added to a tube (5 g, 7.46 mmol, 100 eq) as well as the studied catalyst (0.60 mmol, 8 eq). The mixture is mixed well by strong manual shaking. The mixtures are then heated to 60°C. TDI (118 eq) is quickly added, and the tube is shaken for 10 s. The timer is started and the tube is kept at 60°C. The time necessary until no more flowing of the system is observed is noted as the gel time.

Stress-strain measurements:

Compression tests were performed on a INSTRON ElectroPuls E300 testing machine. A 100N load cell has been used and measurements were performed at room temperature and ambient humidity. The curves were acquired on cubic samples (3 cm x 3 cm x 3 cm) of the synthesized PU foams, cut with a hot wire. The strain rate was 0.04 s-1 and the maximum strain (end of loading) was set at 80%.

X-Ray tomography:

PU foams were imaged with a micro-CT scan (RXSolutions EasyTom 150-160). A microfocus X-Ray source (Hamamatsu L12161-07) was used and acquisitions were carried out at 70 kV tube

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voltage and 142 µA tube current for voxel dimensions of 0.010x0.010x0.010 mm^3 (distance source-detector 398.9 mm and source-sample 31.4 mm). The detector was a VARIANT PaxScan 2520DX (1920x1536 pixels on 127 µm pixel pitch, 16-bit). Each saved projection is an average of 20 frames captured at 5 frames per second.

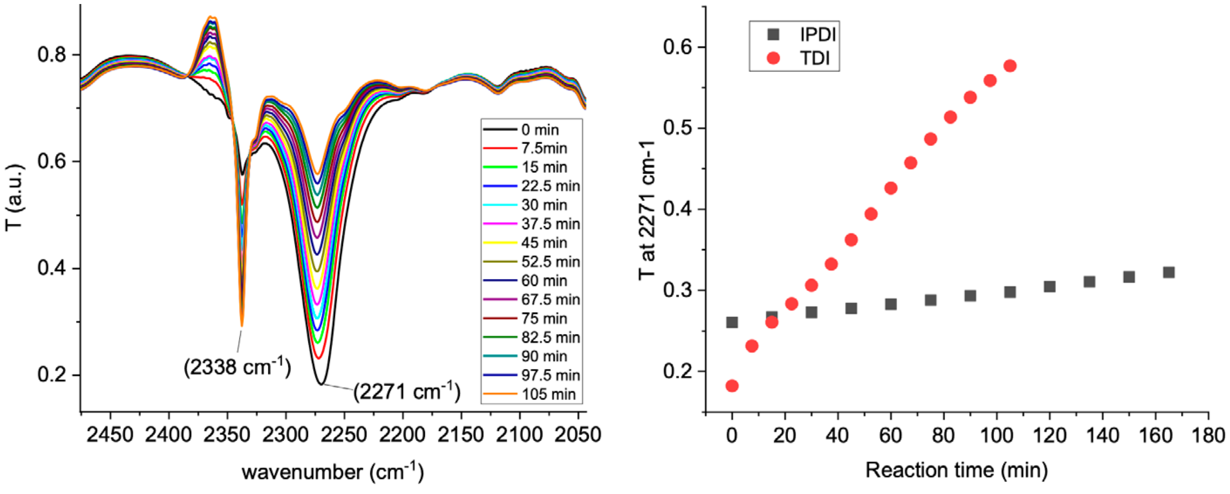
Results and Discussion

Reactivity of AA with Isocyanates

To produce homogeneous PU foams, the kinetic parameters of the reaction are crucial. Because the isocyanate (NCO) functional group strongly absorbs infrared light (around 2700 cm^{-1}), FTIR spectroscopy is the technique of choice to monitor the reactivity of isocyanate functions with different AA molecules. By following the change of transmittance of each sample, we can establish the main reactivity trends. The change of intensity directly indicates the conversion of the isocyanate functions:

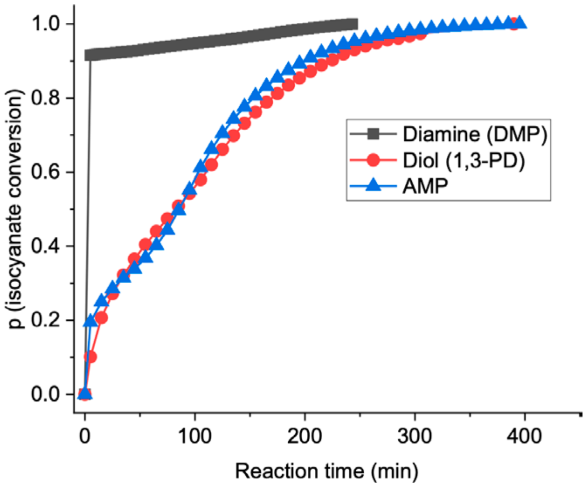
$$p(t) = 1 - \frac{A_t - A_\infty}{A_0 - A_\infty}$$

where p(t) is the isocyanate conversion and A_0, A_t and A_∞ are the initial absorbance, the absorbance at a reaction time t, and the absorbance at equilibrium after an infinite reaction time, respectively.



a)

b)



c)

Figure 1. (a) Evolution of the transmittance as a function of reaction time for a system containing AMP and TDI, (b) comparison of the reaction kinetics of TDI and IPDI with AMP, (c) isocyanate conversion as a function of reaction time for DMP, 1,3-PD and AMP.

Figure 1(a) illustrates the decrease of the intensity of the NCO band as a function of time and the conversion of isocyanate. To decide between which isocyanate was the best suited for evaluating the reaction kinetics of AA, AMP was first allowed to react with IPDI and TDI, two different diisocyanates. As expected, TDI reacts much faster than IPDI due to the aromaticity of TDI that activates the isocyanates groups by mesomeric effect (Figure 1[b]). TDI was thus used for the following experiments because a high reactivity is needed to build PU foams. Then, several reactants were tested to evaluate and compare the reactivity towards TDI of one AMP and model molecules, a diol 1,3-PD and a diamine DMP, chosen for their structure close to the AMP (Figure 1[c]). The diamine reacts much faster with NCO than AMP and the diol 1,3-PD. Indeed, most of the NCO groups were already consumed by the beginning of the measurement. The fast reaction takes place in the very first moment after mixing the chemicals. It was possible to confirm that aminoalcohols molecules bearing amine and alcohol groups have an intermediate reactivity between the corresponding diamine (DMP) and diol (1,3-PD).

Another way to evaluate the relative reactivity between different samples consisted in measuring the exothermicity of the reaction, i.e. the temperature elevation to determine the heat released. The method has been previously theorized and explained. For example, Li et al. employed this method to evaluate the isocyanate conversion as a function of reaction time [6]. Different AA were tested: DMP, 1,3-PD, AMP, AEPD, DMAMP, and DMMOPA. The concentration of active chemical functions (OH+NH_2) was kept constant between the different samples (Figure 2).

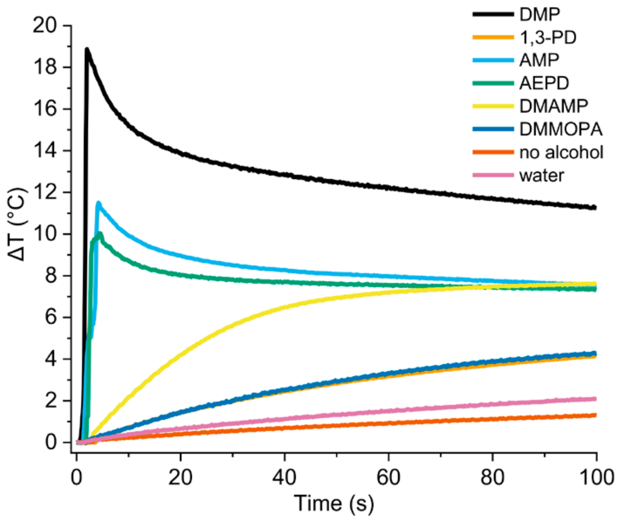


Figure 2. Temperature profile of dilute systems when different AA are used; the amount of reactive chemical functions from AA is kept constant.

It can be observed that for every product containing a primary amine function, i.e. DMP, AMP, and AEPD, there is a temperature peak at the first moment of the reaction, immediately after the addition of TDI (less than 2 s after addition), most certainly due to the rapid formation of urea bonds. On the other hand, for AA bearing only OH groups and/or a tertiary amine (DMAMP, 1,3-PD), the temperature increase is exponential and reaches a plateau after few minutes. It can be noted that the temperature elevation is more significant in the solution containing DMAMP than 1,3-PD, which tends to confirm the catalytic activity of the tertiary amine on the formation of the urethane bond of this molecule.

When introducing DMMOPA without other reactive molecules, the temperature elevation profile is equivalent to the one obtained for 1,3-PD, even if there are no OH or NH_2 functions. The temperature increase was also recorded when adding TDI in a solution containing nothing more than solvent and catalyst (no alcohol) and in a solution that also contains water, always with the same total number of functions. The temperature rises only very slightly, less than 2°C, which is far less than what is obtained when DMMOPA is added in the solution, confirming the catalytic properties of this molecule that has no alcohol nor primary amine.

Influence of AA on PU Polymerization – Catalytic Potential of AA

The chemical structure of some AA is very close to the structure of the amine-catalysts used in the PU industry. Thus, the catalytic properties of AA were investigated to reveal any potential interesting properties by measuring the gel time of a mixture of TDI and a triol, Alcupol X-7510, in the presence of either AA, diol, diamine or DABCO BL11 and DABCO 33 LV, which are catalysts widely used to produce PU foams (Figure 3[a] and 3[b]).

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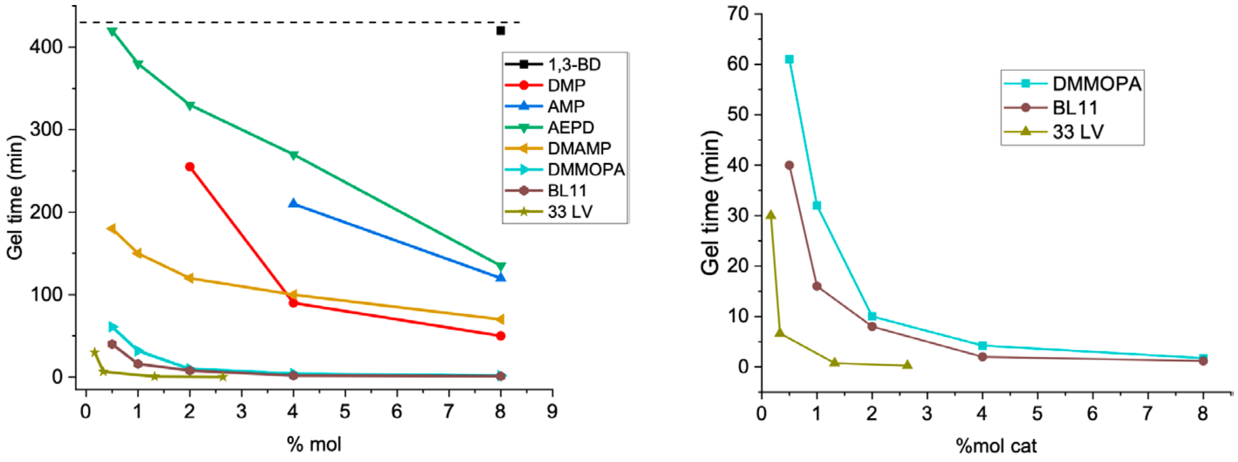

a)

b)

Figure 3. (a) Gel times of TDI and Alcupol X-7510 in the presence of increasing amounts of different potential catalysts, (b) zoom on the results obtained after the addition of DMMOPA, BL11 and 33LV.

For mixtures without any catalyst (i.e. without AA, diol, diamine), the gel time is over 400 min. Approximately the same gel time is obtained with an addition of 1,3-BD, which confirms that it has no catalytic activity towards the formation of the PU network. However, the gel times are systematically shorter for any other added molecules, confirming the catalytic activity of all AA. The more AA or standard catalysts are added, the lower the gel times, which means that the polymerization is speeded up. AMP have the smallest effect of all the AA. This can be explained by the fact that the reactive primary amines groups will quickly react and immobilize these molecules in the PU/PUrea network, preventing them from later helping the bond formation. DMP, the diamine, has a similar behavior. DMAMP is more interesting from a catalytic point of view. The gel times are clearly reduced compared to the reference system. The DMAMP structure possesses one tertiary amine and one alcohol group. The presence of this tertiary amine certainly explains this behavior, efficiently catalyzing the formation of the polyurethane/polyurea network. During polymerization, the presence of the alcohol group also contributes to the integration of DMAMP into the polymer network. It can thus be classified as a reactive catalyst.

Non-reactive catalysts are obviously more efficient due to their mobility in the reactive mixture. Common commercial amine catalysts, DABCO BL11 and 33LV, are also very efficient for catalyzing the formation of urethane/urea bonds. 33LV, which is specially designed and recommended for this application, is the most efficient. But DMMOPA, which has a chemical structure very close to BL11, also shows a very good catalytic activity, confirming that the structure directly impacts the catalytic behavior.

Influence of AA in PU Foams

PU foams represent a very large part of the total PU market. Here we have already shown that AA react with isocyanates and can also act as polymerization catalysts. So, after confirming the possibility of including AA in PU systems, the influence of AA on PU foam production was studied. By comparing the mechanical properties of foams built with and without AA, it is possible to determine the main trends of the influence of AA. This consisted in measuring the impact of increasing amounts of AMP, AEPD, and Tris on the stiffness and pore morphology.

A standard formulation of TDI-based flexible foams was chosen as a reference for comparison. Then the amounts of polyol and all the additives (Tegostab 8727, 8737, Dabco, and water) were kept constant in the whole study. TDI was adjusted accordingly to compensate the excess of alcohol and primary amine functions coming from the addition of AA. Typical foam formulations used for this study are reported in Table 1 and pictures are shown in Figure 4(a). The amount of functional groups (OH+NH2) coming from a specific added AA is expressed as a ratio of the number of functions from the AA ($n_{OH,AA}$) to the number of functions from the polyol ($n_{OH,polyol}$). X is defined as:

$$X = \frac{n_{OH,AA}}{n_{OH,polyol}} \qquad 1)$$

Table 1. Details of the PU Foam Formulations.

Component	Reference	AMP X=1	AMP X=4	AEPD X=1
Alcupol F2832	15 g	15 g	15 g	15 g
Tegostab 8724	112.5 μL	112.5 μL	112.5 μL	112.5 μL
Tegostab 8737	37.5 μL	37.5 μL	37.5 μL	37.5 μL
Dabco 33LV	44.1 μL	44.1 μL	44.1 μL	44.1 μL
Dabco BL11	13.5 μL	13.5 μL	13.5 μL	13.5 μL
Water	525 μL	525 μL	525 μL	525 μL
AA		0.33 g	2.67 g	0.29 g
TDI	4.96 mL	5.52 mL	9.48 mL	5.52 mL

The structural analysis was done using X-ray tomography and the mechanical properties were evaluated by density and compression tests. Compression testing is the most classic way of evaluating the flexibility and recovery of a foam. Different information can be obtained from these curves, in particular the slope of the linear elastic region which corresponds to the apparent modulus E of the material (Figure 4[b]).

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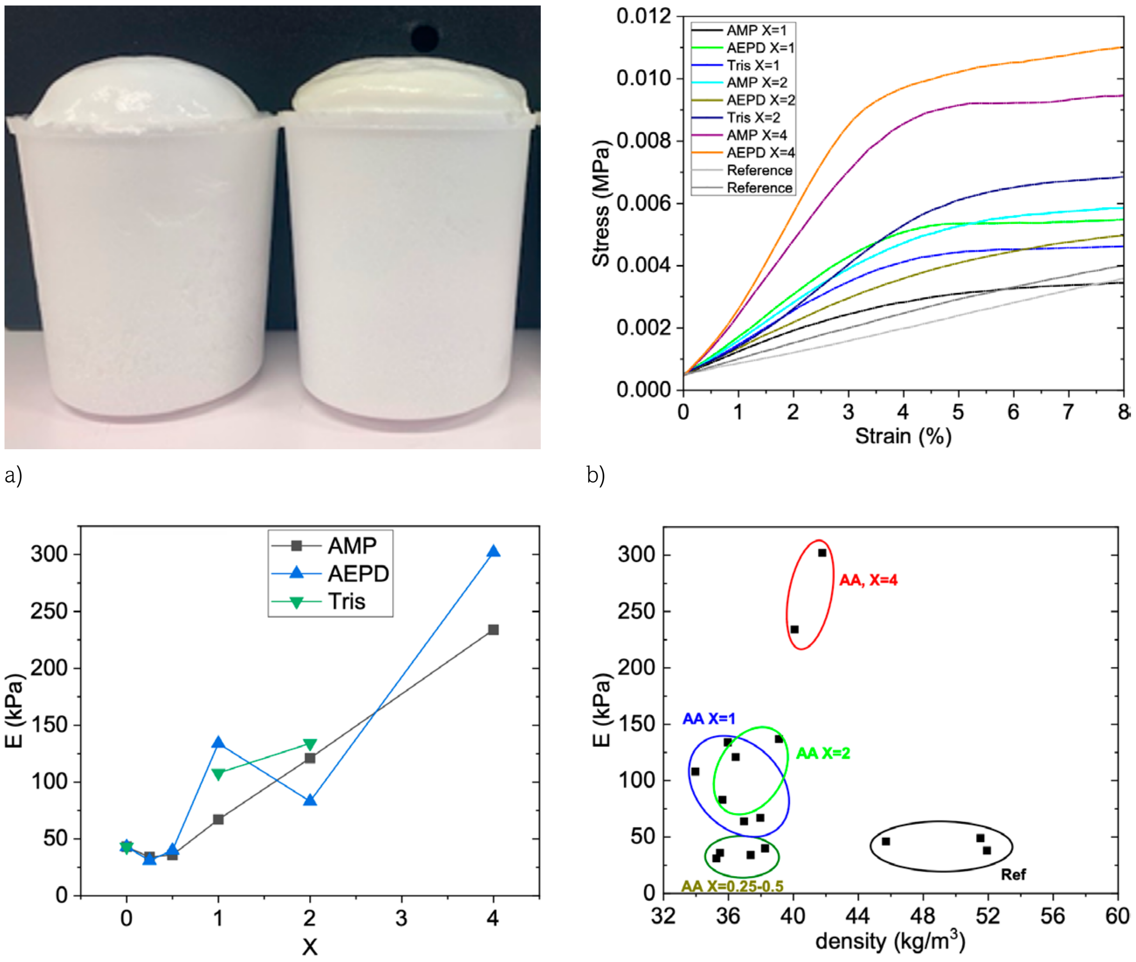

a) b)

a) b)

Figure 4. (a) Photograph of two foams obtained with the reference formulation (left) and with AMP X=1 (right), (b) Compression curves between 0 and 8 % strain, (c) Young's moduli vs density plot, and (d) Young's moduli as a function of the amount of AA added.

The reference samples have an average modulus of E = 43.5 ± 8 kPa for an average density of d = 51.7 ± 0.3 kg/m^3. From Figure 4(b) and 4(c), a clear tendency of the modulus E to increase when adding an increasing amount of AA can be observed. This means that AA introduce rigidity in the material. This is typically what is expected with the addition of small molecules, with a functionality above 2, that can act as crosslinking points. Small diols and diamines are also typically used in the PU synthesis to act as chain extenders to promote phase segregation between the apolar and soft domains of the polyol and the polar and rigid domains rich in urea and urethane bonds.

To sort the data obtained and distinguish the main effect of adding AA, the results were sorted according to a modulus-density plot (Figure 4[d]). This plot reveals the main trends of the influence of AA in a PU formulation. Compared to the reference samples (black circle), it is clear that the addition of AA increases the apparent elastic moduli of the obtained foams. The more AA is added,

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the tougher the foams are. At the same time, we can also notice a decrease in density even when very low amounts of AA were added (small X values). These observations suggest that the addition of AA results in a lower degree of cell opening. The closer the cells are, the tougher the foams are and the more CO_2 gas is trapped within the foam cells. This would explain the two observed phenomena: decrease in density and increase of Young's moduli. Structural analyses were then performed by X-ray tomography to visualize the cells in the foam.

X-ray tomography is a powerful technique that allows scanning of the internal structure of a variety of samples. It can reconstruct the porous structure of foam material, making it possible to identify the size and distribution of the porosities.

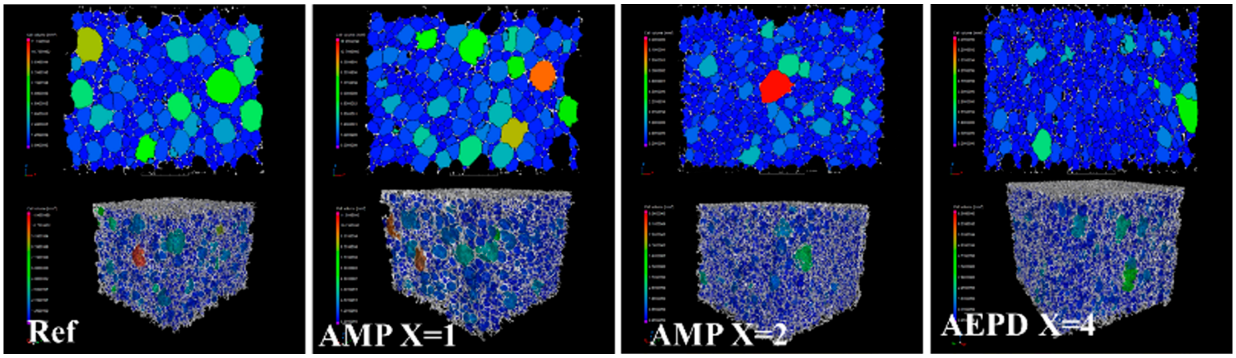

Figure 5. Pictures obtained from X-ray tomography of 4 foam cubes: a reference sample (Ref), a foam with addition of AMP (X=1 and X=2) and AEPD (X=4).

Figure 5 shows an example of the detailed structure that can be obtained using this technique. The figures obtained for all the samples are presented in Figure S4. First, it appears that the structure of all the foams produced with comparable amounts of AA is very close. There is no significant divergence in the pore size, wall thickness, and pore morphology. For all samples, the pores are of various sizes, between 1 and 0.1 mm. The pores are slightly anisotropic, oval-shaped, due to the compression exerted by the sides of the beaker during the blowing of the material. Foams produced with the reference formulation exhibit the same morphology as the foams produced by adding AA.

However, the addition of increasing amounts of AA resulted in the formation of smaller pores, which greatly contribute to stiffening of the material. PU are segmented polymers with hard and soft domains. Hard segments form hydrogen bonds and crystallize to create hard domains. The hard domains, linked by strong hydrogen bonds, are dispersed within the soft domain matrix. The dispersion and morphology of these hard domains determine the final properties of PUs. In the PU foam formation, AA act as chain extenders and build urea and urethane groups by reacting with isocyanates. Thus, AA integrate the hard segments and alter the organization of the hydrogen bonding. The microphase separation between hard and soft domains is thus less pronounced. By increasing the compatibility of the hard and soft domains, the microphase separation, which leads to cell rupture, is delayed and thus more closed cells are produced [6,10] and tougher material is obtained.

Conclusion and Perspectives

The aim of this study was to investigate: (i) the reactivity of AA in PU formulations and (ii) the effect of these molecules on flexible cold-cure PU foams. For this purpose, different AA with different structures, molecular weights, and functionality numbers were tested. Among the reactive molecules tested, AMP, AEPD, and Tris are di-, tri-, and quadrifunctional, respectively, while DMAMP contains one tertiary amine and one hydroxyl group. DMMOPA with no alcohol and a tertiary amine was considered as non-reactive. Results showed that the reactivity of AA with isocyanates is adapted to play the role of chain extenders, and that AA are catalyzing the formation of the PU network. Thus, they could partially replace classic tertiary amine-based catalysts in industrial PU foams. Finally, AA were added to PU foams and the structure and mechanical properties were examined. By increasing the apparent Young's modulus, AA stiffen the PU foams while increasing the number of closed cells. Consequently, AA could be used to finely tune the properties of PU foams. Detailed structural analyses of the produced PU materials will be done to understand the influence of AA on the ordering of the hard versus soft domains that leads to the observed mechanical properties.

Acknowledgements

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