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On-demand click functionalization of polyurethane films and foams

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ABSTRACT

A novel platform of side-chain functionalized crosslinked polyurethane (PU) films and foams has been used to afford new classes of PU materials. Indeed, alkyne pendant groups located along the polyurethane backbone have been modified via the copper catalyzed Huisgen 1,3-dipolar cycloaddition with various azide components. These cycloaddition reactions were carried out in water or in a mixture of water/acetone under mild conditions (room temperature to 50 °C) in the presence of low amounts of copper catalyst. The resulting functionalized films and foams were all characterized by FT-IR, contact angle measurements and confocal fluorescence microscopy. All these techniques successfully proved that the click chemistry process is valuable in functionalizing PU films and foams in an easy way. The post-functionalization of these alkyne-functionalized PUs afforded the creation of new classes of PU materials with easily adaptable physical properties by choosing the appropriate azide component.

1. Introduction

Step-growth polymerization is one of the oldest techniques to obtain polymers and is nowadays widely used in industry. Step-growth polymerization [1–3] consists of a series of successive reactions, in which at least two complementary compounds can react at any time, increasing the molecular weight of the obtained macromolecules. Among the different reaction types leading to step-growth polymers, polyurethanes (PU) began with the discovery of Bayer in the 40's [4], and many academic and industrial research groups have contributed to the knowledge of PU materials. PUs [5,6] are mostly, but not only, based on the reaction between diisocyanates, diols and polyols. Unique properties of PU materials can be reached as a result of the wide range of starting compounds. A lot of attention is also going to the degradability and the recycling of such polymers [7]. More recently, another promising topic is the functionalization of PU materials [8–11] either during the step-growth polymerization or afterwards, leading to highly functional materials.

Among PU materials, a great interest lies in the synthesis, functionalization and applications of PU films and foams [12,13]. Polymer films and foams are nowadays widely used since they offer good compromises such as mechanical, thermal, biodegradation or biocompatibility for instance, and many technical applications are involved among which automotive, sport, aeronautic applications as well as devices for electronic and medicinal applications [14]. Nevertheless, for many high-tech applications, PU materials and especially PU films and coatings need to bear functionalities to improve their intrinsic properties such as wettability, adhesion, biocompatibility, conductivity, cross-linking density and many others. Extensive work has focused to develop chemical and physical methods for surface modification and treatments of PU films. In practice, this can be achieved by plasma treatment, which involves difficult mechanisms inherent to the plasma nature. Depending on the conditions used, this technique allows for the modification of the surface properties of PU materials without altering the bulk properties since only the first nanometers of the surface can be reached. Plasma treatments are also known for improving the wettability, inducing cross-linking and chemical functionalization [15]. In addition to this physical treatment, ozone oxidation is being used to produce polymeric peroxides onto different materials able to initiate graft polymerization as an example [16]. Among these techniques, also treatments by corona, photons, electron beams, ion beams and X-rays exist [6,17–19]. Another known approach to modify the surface properties of PU films is the physical adsorption of another amine bearing polymer such as poly(ethyleneimine) [20,21]. Nevertheless, in most cases, only one specific functionality can be introduced to the material and the choice is limited to a few while the chemical structure of the materials may be affected by the above mentioned treatments.

To cope with this issue, we have developed a strategy based on the combination of step-growth polymerization and the copper catalyzed Huisgen 1,3-dipolar cycloaddition [22–25], which is

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nowadays accepted as a very useful and powerful method of polymer modification [9,26–30]. Previously, we proved that the synthesis of alkyne-based PUs using an interesting alkyne-based diol resulted in functionalized linear PUs, which were efficiently post-functionalized via click chemistry [9,31]. The obtained promising results convinced us to explore the click modification of crosslinked materials such as PU films and foams starting from alkyne-functionalized crosslinked PU materials. Several characterization techniques such as FT-IR, contact angle and confocal measurements were used to control the success of the cycloaddition reactions.

2. Experimental section

2.1. Materials

Copper(II) sulfate, $5H_2O$ (99+%, Acros) and L-ascorbic acid sodium salt ($Na_{asc.}$, 99%, Acros) were used as received. Compounds such as Zonyl-N_3 [9], azidopropanol (AzPOH) [32], 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-azidooctane (F13) [33], 4-azido-*N*-ethyl-1,8-naphthalimide (FGC-N_3, FGC standing for fluorogenic compound) [9,34], α-methoxy-ω-azido poly(ethylene glycol) (PEG-N_3, molecular weight of 1100 g/mol) [27] and 2,2-di(prop-2-ynyl)propane-1,3-diol (DPPD) [35] were synthesized according to the literature. Alkyne-functionalized PU films based on polyether diols were developed by Recticel (Wetteren, Belgium). The alkyne loading of different PU sample sheets is 1.19 mmol/g (Sample 1 or PU-S1), 2.31 mmol/g (Sample 2 or PU-S2) and 3.28 mmol/g (Sample 3 or PU-S3) and the thickness of the transparent material is about 1.5 mm. Alkyne-functionalized PU foam (open cell structure) was also synthesized by Recticel (density around 45.4 kg/m^3) with alkyne loading of 0.811 mmol/g.

2.2. Instrumentation

Infrared spectra were obtained from Perkin-Elmer Spectrum1000 FT-IR Infrared spectrometer equipped with PIKE Miracle HATR module. Static contact angle measurements on the PU films were performed using a OCA 20 from Dataphysics (distributed by Benelux Scientific) equipped with a 500 μl Hamilton syringe. For each measurement, 3 μl of milli-Q water was placed on the metal surface. The droplet was imaged using a video camera. The contact angle was determined on the screen of the monitor using the imaging software provided by the supplier (SCA 20). Three measurements were made on each sample. Confocal microscopy images were recorded on a Nikon EZ-C1 confocal microscope. For samples containing FGC, the excitation was performed at 488 nm and the emission recorded at 515 nm. Image analysis software (Image J) was used to quantitatively compare the fluorescence emission of materials.

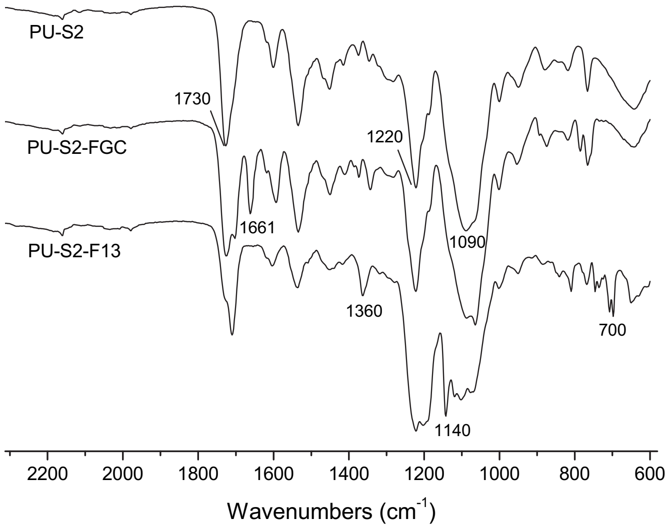
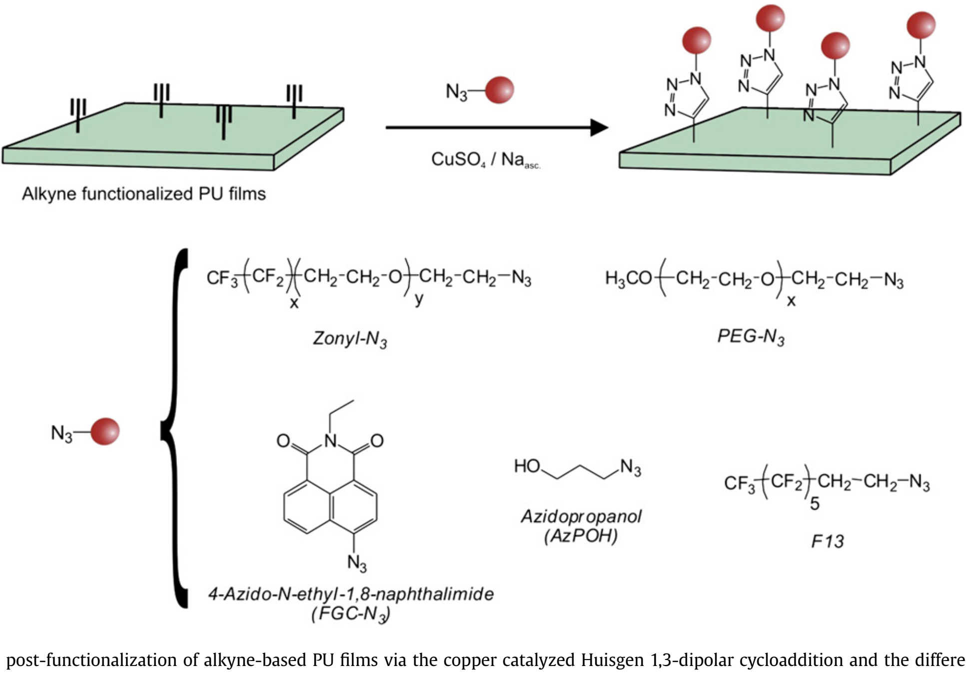


Fig. 1. FT-IR spectra of the starting PU film (PU-S2, top) and the modified PU films after 1,3-dipolar cycloaddition of FGC-N_3 (PU-S2-FGC, middle) and F13 (PU-S2-F13, bottom).

2.3. Typical Huisgen 1,3-dipolar cycloaddition onto PU films

In a round-bottom flask, the alkyne-functionalized PU film (1 equiv. of alkyne function, 1 cm × 1 cm) was charged with the azide compound (1.1 equiv.), the solvents (acetone and water in 1/1 volume ratio) and the copper catalyst based on $CuSO_4$, $5H_2O/Na_{asc.}$



Scheme 1. Scheme for the post-functionalization of alkyne-based PU films via the copper catalyzed Huisgen 1,3-dipolar cycloaddition and the different azide compounds used.

Table 1
Results of water contact angles before and after click reaction onto PU films.

Reference	Before modification	AzPOH	PEG-N_3	F13	Zonyl-N_3
PU-S1	86.9	61.9	–	98.1	111.6
PU-S2	89.1	75.8	–	97.2	105.4
PU-S3	81.7	68.3	64.1	93.0	109.8

Reaction conditions: PU sample (1 equiv.), azide component (2 equiv.), $CuSO_4$ (5 mol%), $Na_{asc.}$(10 mol%), solvents: water and acetone (1/1 volume ratio), room temperature.

(0.05 equiv. and 0.1 equiv. respectively). The reaction was performed overnight at room temperature. The resulting modified material was extracted with water and acetone, then dried prior to further characterizations.

2.3.1. Typical Huisgen 1,3-dipolar cycloaddition onto PU foam

In a round-bottom flask, the alkyne-functionalized PU film (1 equiv. of alkyne function) was charged with the azide compound (2 equiv.), acetone and the copper catalyst based on $CuSO_4$, $5H_2O$/$Na_{asc.}$ (0.05 equiv. and 0.1 equiv. respectively). The reaction was performed overnight at 50 °C. The resulting modified material was washed via Soxhlet extractions with acetone, then dried prior to further characterizations.

3. Results and discussion

In this study, the main aim of this work was to develop an efficient and easy route for tailoring PU film surfaces by grafting functional groups *via* the copper catalyzed Huisgen 1,3-dipolar cycloaddition using functional azide components (Scheme 1). The functional groups have been judiciously chosen in order to provide explicit results in case of successful modification such as fluorescence properties and tailored hydrophilic/hydrophobic properties.

PU films were immersed into a solution at room temperature containing a mixture of water and acetone (1/1 volume ratio), copper catalyst and the desired azide compound. The used copper catalyst is based on copper sulfate pentahydrate in combination with the reducing agent L(+)-ascorbic acid sodium salt also called sodium ascorbate ($CuSO_4$/$Na_{asc.}$). All functionalized PUs were characterized by FT-IR spectroscopy, contact angle measurements and confocal microscopy to follow the chemical modification of the materials.

3.1. Infrared spectroscopy

On Fig. 1, the IR spectra display the overlay of the starting PU film (PU-S2, top) and PU films modified with the azido-fluorinated compound F13 (PU-S2-F13, bottom) and 4-azido-*N*-ethyl-1,8-naphthalimide FGC-N_3 (PU-S2-FGC, middle).

The FT-IR spectrum corresponding to the starting PU film (PU-S2, upper spectrum, Fig. 1) shows typical bonds at 1730 cm^{-1}, 1220 cm^{-1} and 1090 cm^{-1}, belonging to urethane groups and the polyether diol used for the synthesis of the film. On the other hand, the spectrum of PU-S2-F13 (lower spectrum, Fig. 1) shows the appearance of typical bands at 1140 cm^{-1} and 700 cm^{-1} that belong to the grafted fluorinated compound F13. Also, the new absorption peak at 1360 cm^{-1} might be ascribed to the vibration of N=N from the formed triazole ring. Also, one band appeared on the spectrum of PU-S2-FGC (middle spectrum, Fig. 1) at 1661 cm^{-1}, ascribed to the vibration of C=O from the amide group of FGC-N_3. Additionally, on the spectra of the clicked PU films, no azide peak at approximately 2100 cm^{-1} could be observed, proving the absence of adsorption of the starting azide compounds (F13 and FGC-N_3) to the film. Additionally, the FT-IR spectra of materials functionalized with other components such as AzPOH and PEG-N_3 (data not shown) were not obvious enough to conclude about the grafting reaction since vibrations of the new chemical bonds are not sufficiently different from the ones of the starting material. Nevertheless, other characterization techniques were used to confirm the success of the cycloaddition reactions.

3.2. Contact angle measurements

Static contact angle measurements were performed by deposition of a drop of water on the surface of analyzed PU films (Table 1). This technique is one of the most common tools for analyzing, in a fast way, the surface properties of materials.

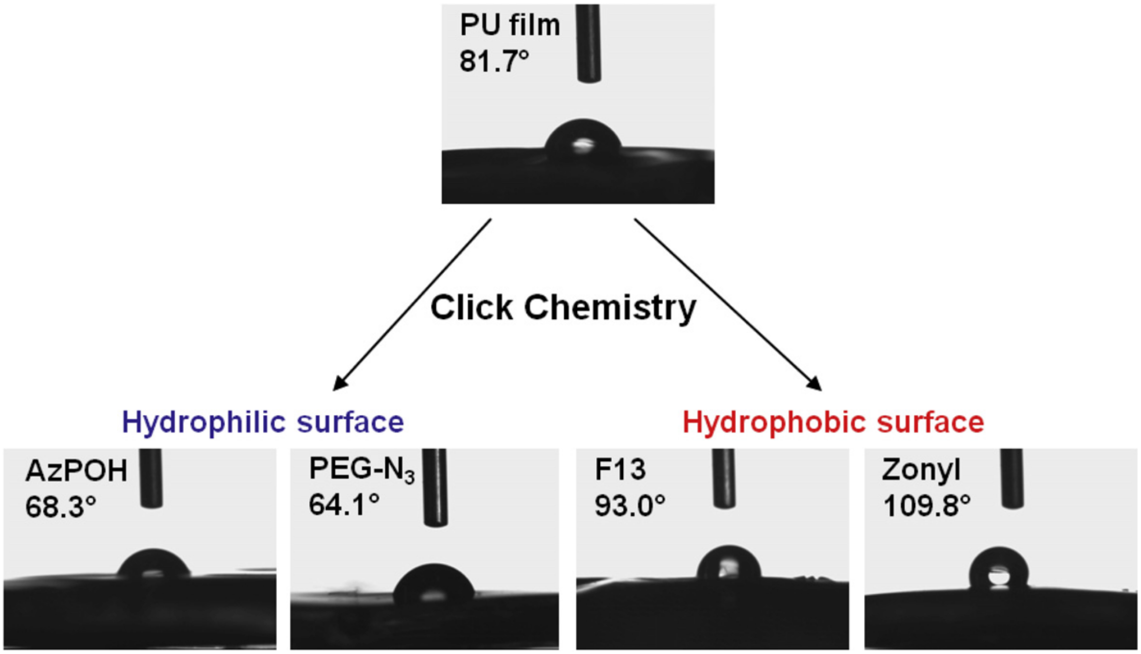


Fig. 2. Pictures from contact angle measurements of PU-S3 before and after click reactions with AzPOH, PEG-N_3, F13 and Zonyl-N_3.

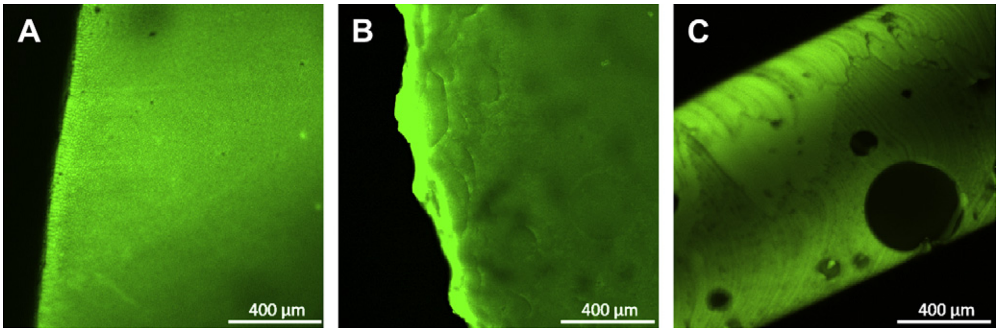


Fig. 3. Confocal transmission microscopy images of PU films after click reaction with FGC-N_3. (A) surface of PU-S2-FGC, (B) surface of PU-S3-FGC, C) cross-section of PU-S2-FGC.

The initial contact angle of the PU films (PU-S1, PU-S2 and PU-S3) is comprised between 80° and 90° (Table 1). The small differences between the contact angles of the three starting PU samples can be explained by the different ratio of components (polyols, diisocyanates,…) used during the elaboration of these PU materials. On the other hand, values resulting from the measurements of PU films after the copper catalyzed Huisgen 1,3-dipolar cycloaddition were much different in comparison to these initial values. Indeed, the wettability of PU films has improved by performing the click reaction with AzPOH, which is a hydrophilic compound. Also, the Huisgen cycloaddition between azido-functionalized PEG and PU-S3 was undertaken using the same reaction conditions, except that only water was used in this case instead of a water/acetone mixture. Also, in this case, the contact angle decreased, comparable to the decrease observed after the grafting reaction of azidopropanol.

On the other hand, when F13 was grafted to PU films *via* click chemistry, the surface became more hydrophobic and values can reach up to 98° for PU-S1 (Table 1), showing that the grafting process was effective. Finally, also another hydrophobic azide compound was used, namely Zonyl-N_3. This compound was synthesized from commercially available hydroxy-functionalized Zonyl FSO-100, which is a low molecular weight block copolymer having a first block based on a perfluoroalkyl chain followed by a second poly(ethylene glycol) block (Scheme 1). Zonyl FSO-100 is currently widely used in applications such as improved wetting agent, lubricant, antifogging and pigment compatibilizer in inks [36]. The obtained contact angles reached up to 110° (PU-S1 and PU-S3, Table 1), showing the significant increase of hydrophobicity after the click reaction with Zonyl-N_3. The pictures of the contact angle measurements (Fig. 2) confirm the change of the surface properties of the studied PU films. When hydrophilic treatment (AzPOH and PEG-N_3) was undertaken (pictures on the bottom left, Fig. 2), the drop of water spreads over the PU film due to a higher interaction between water and the newly modified PU material. On the contrary, when hydrophobic treatment (F13, Zonyl-N_3) was applied (pictures on the bottom right, Fig. 2), the water drop tends to minimize its interaction with the support.

3.3. *Confocal microscopy*

To further prove the efficiency of this surface click chemistry on polyurethanes, a clickable fluorogenic probe was synthesized, 4-azido-*N*-ethyl-1,8-naphthalimide (FGC-N_3, Scheme 1) according to a literature procedure [34]. This probe is non fluorescent in its starting form but it becomes highly fluorescent [34] when the click reaction occurs as a result of the presence of the triazole ring next to the aromatic system.

For this functionalization, PU films were introduced in a water/acetone mixture (1/1 v/v) containing 0.5 equivalent of FGC-N_3 toward the alkyne loading, $CuSO_4$, $5H_2O$ and $Na_{asc.}$ as reducing agent (Scheme 1). The click reaction was performed at room temperature, followed by extensive washing with water and acetone. A blank reaction, without adding copper catalyst, was also done under the same conditions.

Confocal microscopy was used to determine if the click reaction proceeds. First, the PU film from the blank reaction did not show any noticeable fluorescence. On the other hand, confocal microscopy images (Fig. 3) reveal the highly fluorescent character of PU films (PU-S2-FGC on image A; PU-S3-FGC on image B, Fig. 3) after the click reaction with FGC-N_3 when excited at 488 nm. The represented pictures were recorded on the border of the PU films to better see the contrast between the emitted fluorescent area (green color) corresponding to the PU films and the non fluorescent area (black

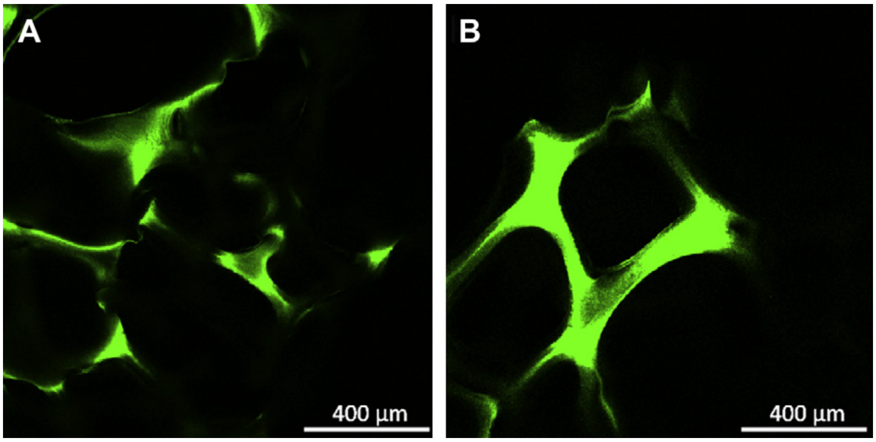


Fig. 4. Confocal microscopy images recorded at two different places (images A and B) of the resulting PU foam after click reaction with FGC-N_3 (green fluorescence channel).

color) corresponding to a place without any PU material. The intensity of the fluorescence detected on the surface seems to be qualitatively homogeneous along the PU film, showing that the click reaction occurred in the whole material. The black spots on the pictures are attributed to gas bubbles trapped inside the material during its synthesis. Sample PU-S2-FGC was also cut to further analyze the cross-section of the PU film (image C, Fig. 3). From this, it appears that the click reaction did not only occur on the surface but also inside the crosslinked material. This can be attributed to the good swelling behavior of the PU films in the solvent mixture.

The last part of this work was focused on the chemical modification of alkyne-functionalized PU foams via the copper catalyzed Huisgen 1,3-dipolar cycloaddition. Due to the facility of their synthesis and their broad application range, PU foams are important industrial polymer materials. Many possibilities have been explored to modify PU foam properties by varying the formulation or applying physical treatments (X-ray, electron beam, etc). In our work, such as for the PU films, alkyne-functionalized PU foams were reacted with various azide components in order to change the intrinsic properties of the polymer backbone and consequently to tune the final properties of the material. First attempts were successfully carried out with a common azide component such as benzyl azide of which the conversion for the cycloaddition was followed by studying the disappearance of the azide compound with GC. Then, the fluorogenic compound (FGC-N_3), previously used in the case of PU films, was reacted with the PU foam in acetone at 50 °C using $CuSO_4$, $5H_2O$/$Na_{asc.}$ (0.05 equiv. and 0.1 equiv. respectively) as copper catalyst. The resulting PU foam was submitted to confocal microscopy measurements in order to detect any fluorescence.

Fig. 4 represents the recorded pictures before and after laser excitation. It clearly proves the appearance of a strong fluorescence due to the cycloaddition of the fluorogenic compound to the PU foam (images A and B of Fig. 4). Moreover, the quite homogeneous fluorescence intensity may indicate a good distribution of the active sites in the PU foam and cells are clearly identifiable.

It is noteworthy that the recorded confocal microscopy image of the blank sample did not show any emission of noticeable fluorescence, although a very low intensity was detected (see further).

Image analysis software was used to quantitatively compare the fluorescence emission of FGC-N_3 clicked and unmodified foams (blank reaction). The corresponding confocal images were recorded using equal laser and detector intensity settings, followed by discertising the fluorescence intensity of every pixel between 0 (i.e. dark) and 255 (i.e. saturated fluorescence). Fig. 5 shows the obtained pixel intensities plotted as a histogram. The left distribution, corresponding to unmodified foams, exhibits a mean pixel fluorescence of 14.4 ± 3.7 while the right distribution, corresponding to FGC-N_3 clicked foams, exhibit a mean pixel fluorescence of 90.2 ± 7.9. These data clearly demonstrate the successful cycloaddition reaction via the use of the fluorogenic probe. Note that the low fluorescence of the unmodified foams is most likely due to auto-fluorescence of the foams or physically adsorbed FGC-N_3, despite extensive washing.

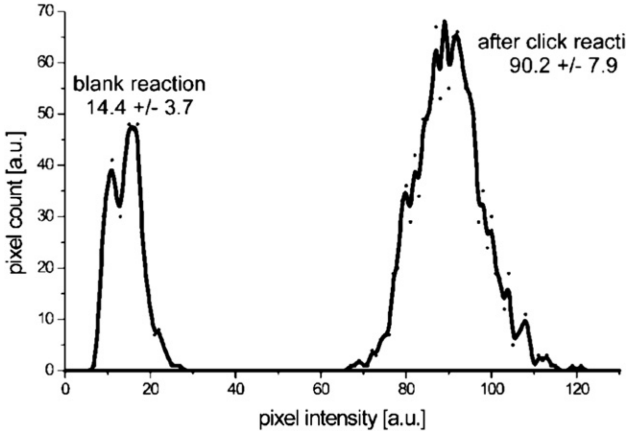


Fig. 5. Variation of the fluorescence recorded by confocal microscopy of the resulting foam after the reaction with FGC-N_3 without copper catalyst (blank reaction) and in the presence of copper catalyst (after click reaction).

4. Conclusion

In this contribution, the copper catalyzed Huisgen 1,3-dipolar cycloaddition was successfully applied to different PU materials such as films and foams. Alkyne-based PU films were functionalized with several azides allowing a total change of the surface properties, as demonstrated by contact angle measurements, only by changing the clickable azide compound. Confocal microscopy measurements could also prove the success of the cycloaddition reaction due to the emitted fluorescence of the modified PU film with the fluorogenic compound. The same strategy has been applied to alkyne-based PU foams and the detected fluorescence of the resulting PU foam proved that the click reaction occurred. This promising concept of the in-situ incorporation of alkyne functions creates a unique platform to obtain PU films and foams with easily adaptable physical properties, which is undoubtedly a major advantage in comparison to other conventional methods to functionalize PU materials.

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References

[1] Ebewele RO. Polymer science and technology. CRC Press; 2000.
[2] Rogers ME, Long TE, Turner SR. Chapter 1: introduction to synthetic methods in step-growth polymers. In: Rogers ME, Long TE, editors. Synthetic methods in step-growth polymers. Wiley; 2003. p. 1–16.
[3] Yokozawa T. Polycondensation. In: Matyjaszewski K, Gnanou Y, Leibler L, editors. Macromolecular engineering: precise synthesis, materials properties, applications, vol. 1. Wiley; 2007. p. 295–349.
[4] Bayer O. Angew Chem 1947;59(9):257–72.
[5] Backus JK, Blue CD, Boyd PM, Camm FJ, Chapman JH, Eakin JL, et al. Polym Sci Eng 1988;13:243.
[6] Randall D, Lee S. The polyurethanes book. John Wiley & Sons; 2002.
[7] Zia KM, Bhatti HN, Ahmada I. React Funct Polym 2007;67(8):675–92.
[8] Li Z, Zeng Q, Li Z, Dong S, Zhu Z, Li Q, et al. Macromolecules 2006;39(24):8544–6.
[9] Fournier D, Du Prez F. Macromolecules 2008;41(13):4622–30.
[10] Zhu ZC, Li QQ, Zeng Q, Li ZG, Li Z, Qin JG, et al. Dyes Pigm 2008;78(3):199–206.
[11] Li QQ, Li Z, Ye C, Qin JG. J Phys Chem B. 2008;112(16):4928–33.
[12] Thompson T. Design and applications of hydrophilic polyurethanes: medical, agricultural and other applications. Technomic; 2000.
[13] Thomson T. Polyurethanes as specialty chemicals: principles and applications. CRC Press; 2004.
[14] Friedman M, Walsh G. Polym Eng Sci. 2002;42(8):1756–88.
[15] Chan CM, Ko TM, Hiraoka H. Surf Sci Rep 1996;24(1–2):1–54.
[16] Yamauchi J, Yamaoka A, Ikemoto K, Matsui T. J Appl Polym Sci. 1991;43(6): 1197–203.
[17] Hirose M, Zhou J, Kadowaki F. Colloids Surf A 1999;153(1–3):481–5.
[18] Sanchis MR, Calvo O, Fenollar O, Garcia D, Balart R. Polym Test 2008;27(1):75–83.
[19] Pakula T, Minkin P, Beers KL, Matyjaszewski K. Polym Mater Sci Eng 2001;84:1006–7.
[20] Bruil A, Oosterom HA, ISteneker n, Al BJM, Beugeling T, Van Aken WG, et al. J Biomed Mater Res 1993;27(10):1253–68.
[21] Józwiak AB, Kielty CM, Black RA. J Mater Chem. 2008;18:2240–8.
[22] Kolb HC, Finn MG, Sharpless KB. Angew Chem Int Ed 2001;40(11):2004–21.

[23] Rostovtsev VV, Green LG, Fokin VV, Sharpless KB. Angew Chem Int Ed 2002; 41:2596–9.
[24] Wu P, Feldman AK, Nugent AK, Hawker CJ, Scheel A, Voit B, et al. Angew Chem Int Ed 2004;43(30):3928–32.
[25] Fournier D, Hoogenboom R, Schubert US. Chem Soc Rev 2007;36(8):1369–80.
[26] Lutz J- F. Angew Chem Int Ed Engl 2007;46(7):1018–25.
[27] Billiet L, Fournier D, Du Prez FE. J Polym Sci Part A Polym Chem 2008;46: 6552–64.
[28] Lecomte P, Riva R, Jérôme C, Jérôme R. Macromol Rapid Commun 2008;29(12–13):982–97.
[29] Binder WH, Sachsenhofer R. Macromol Rapid Commun 2008;29(12–13):952–81.
[30] Lutz JF, Schlaad H. Polymer 2008;49(4):817–24.
[31] Billiet L, Fournier D, Du Prez F. Polymer 2009;50(16):3877–86.
[32] Van Camp W, Germonpré V, Mespouille L, Dubois P, Goethals EJ, Du Prez FE. React Funct Polym 2007;67(11):1168–80.
[33] Szonyi F, Cambon AJ. J Fluor Chem 1989;42(1):59–68.
[34] Sawa M, Hsu TL, Itoh T, Sugiyama M, Hanson SR, Vogt PK, et al. Proc Natl Acad Sci USA 2006;103(33):12371–6.
[35] Eglinton G, Galbraith AR. J Chem Soc 1959:889–96.
[36] <www.dupont.com/zonyl>.