

Investigations on wood treatment by eco-friendly hydroxypolyurethanes

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Dimensional stabilisation is a crucial property for using wood in most applications. Therefore an isocyanate-free route is proposed, based on the reaction of various diamines with dicarbonates obtained by addition of two glycerol carbonates moieties on a linker. For the initial experiments, the mildest conditions to perform the reaction are researched with model mono- and polyamines without wood: solvent, temperature, number of equivalent and regioselectivity were investigated. Subsequently, beech wood blocks were impregnated by a double vacuum process involving cyclic carbonates and then polyamines. The key step was a polycondensation performed in the beech blocks after the monomers had been impregnated. Resistance of treatment to leaching, anti-swelling efficiency and decay durability versus *Poria placenta* were evaluated. Results were promising with ASE values of about 70% for a weight gain of approximately 30% after leaching. Biological tests indicated also an improvement of resistance to fungal decay of beech wood.

Keywords: Dimensional stabilisation, Anti-swelling effect, Wood preservation, Glycerol carbonate, Isocyanate-free polyurethanes, NIPU

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Introduction

Dimensional stabilisation is a crucial property for using wood in most structural applications. The wood polysaccharidic part is strongly hydrophilic and swelling effects occur by the intake or evaporation of water molecules when temperature and humidity are changing. In order to avoid these phenomena, a possible solution is to filling existing cavities and/or the withdrawal of water by hydrophilic polymers like the widely used PEGs. However, these are sensitive to oxidation and their leachability prevents them from being used in Use Class 3 for example. On the other hand, among numerous methods involving non-water soluble polymers, impregnation and polymerisation of polyurethanes is an interesting way to achieve this stabilisation. However the use of significant amounts of petrochemical compounds as well as the toxicity of isocyanates are a strong drawback to the development of this approach.

Therefore new approaches to preservation are proposed here based on the use of hydroxypolyurethanes obtained from very affordable starting compounds by an isocyanate-free route. Among an increasing number of possibilities involving various natural substrates (Benyahya *et al.* 2011; Bähr *et al.* 2012; Unverferth *et al.* 2013; Javni *et al.* 2013; Nohra *et al.* 2013) and thus, based on literature works (Rokicki *et al.* 2002; Webster 2003; Ochiai *et al.* 2005; Ubaghs *et al.* 2004), several ways were investigated involving either glycerol carbonate (GC) pro-

duced from a biodiesel plant by-product or carbonated polyglycerol (DCPG3), impregnated into the wood and reacting with primary diamines.

Initially, three pathways were investigated (Fig. 1) to evaluate their compatibility with some wood use prerequisites, particularly in terms of maximal reaction temperature and also of reactivity in the presence of water. Two of them were based on the use of glycerol carbonate (GC) which is a by-product of the diester industry, while the third implicated a dicarbonated polyglycerol easily obtained from bio-resourced polyol. The procedures were then applied to wood samples to check the efficiency of the treatments by measurement of ASE before and after leaching as well as the ability to improve the resistance of wood to fungal attack that could be expected because of the changes to the changes in chemical composition of the material.

Experimental methods

Materials

Dimethyl carbonate (DMC), the solvents and the di- and tri- amines were purchased from Fluka-Sigma-Aldrich Chimie SARL (St Quentin Fallavier, France). Glycerol carbonate was obtained from Novance (Compiègne, France); Polyglycerol was also obtained from Novance as a mixture of compounds with an average molecular weight of 242 ($n \sim 3$).

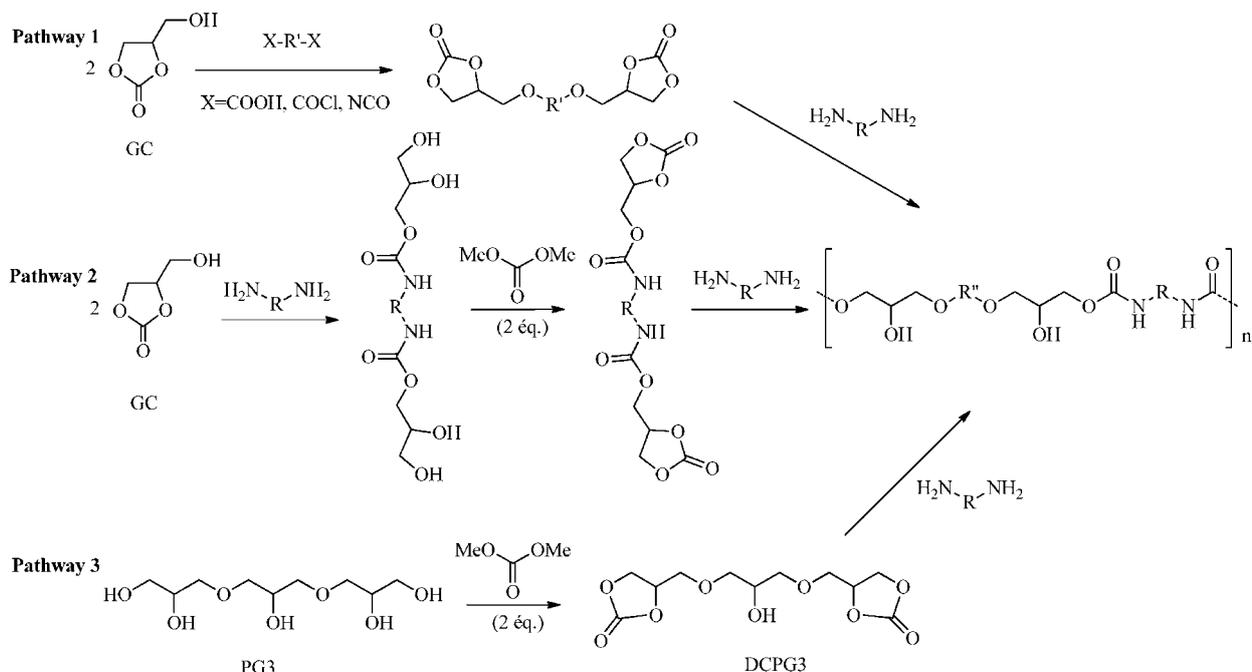
Instruments

¹H and ¹³C NMR spectra were recorded in water on a Bruker DRX 400 spectrometer. Chemical shifts are expressed in parts per million. FTIR spectra were recorded as thin films between NaCl plates on a Perkin Elmer FTIR spectrometer SPECTRUM 2000.

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1 Three investigated pathways to prepare hydroxypolyurethanes

Synthesis of polyglycerol carbonate (DCPG3)

In a 100 mL round bottomed flask equipped with a magnetic stirrer, a condenser and a thermometer, polyglycerol (2.10 g, 8.6 mmol), dimethyl carbonate (1.55 g, 17.2 mmol) and K_2CO_3 as catalyst (60 mg, 0.43 mmol) were placed. The reaction was carried out under reflux for 5 h. Methanol and residual DMC were then evaporated under reduced pressure.

1H NMR (400 MHz, $DMSO-d_6$), δ (ppm): 4.89 (m, 2H); 4.81–4.77 (broad s, OH); 4.51 (m, 2H); 4.28 (m, 2H); 3.78–3.16 (m, polyglycerol protons)

FTIR (NaCl film), ν (cm^{-1}): 3401, 2931, 1781, 1403, 1181, 1054

Reaction of carbonates with amines, general procedure

Five membered cyclic carbonate of polyglycerol was mixed with amine at room temperature in a round bottomed flask equipped with a magnetic stirrer. Progress of the reaction was monitored by FT-IR spectroscopy following the disappearance of the cyclic carbonyl band at 1781 cm^{-1} .

Impregnation procedure

Beech (*Fagus sylvatica*) heartwood was used for this study. Blocks of $15 \times 5 \times 25$ mm in radial, tangential and longitudinal directions respectively were dried at $50^\circ C$ for 48 h and weighed (m_0). Dried blocks (70 replicates) were placed in a 500 mL beaker inside a dessicator equipped with a two-way tap and subjected to a 5 mbar vacuum for 20 min. Blocks were then impregnated by suction with reagents solutions. The weight gain observed after drying was expressed according to the following formula

$$WG(\%) = [(m_1 - m_0) / m_0] \times 100$$

where m_0 is the initial dried mass and m_1 is the impregnated dried mass.

Decay studies

Decay resistance was studied using a malt agar plate decay test which is a modification of the standardised

EN 113 test involving the brown-rot basidiomycete *Poria placenta*. Sterile culture medium (20 mL), prepared from malt (30 g) and agar (40 g) in distilled water (1.0 L), were placed on 9.0 cm Petri dishes, inoculated with fungus and incubated for 1 week at $22^\circ C$ and relative humidity (RH) of 70% to allow colonisation of the medium by the mycelium. Three U.V. sterilised wood blocks (treated or untreated) were then placed in each Petri dish under sterile conditions. Incubation was carried out at $22^\circ C$ and 70% RH for 16 weeks. The weight loss (WL) due to fungal attack was expressed according to the following formula

$$WL(\%) = [(m_0 - m_1) / m_0] \times 100$$

where m_0 is the initial dried mass and m_1 is the dried mass after exposure to *P. placenta*.

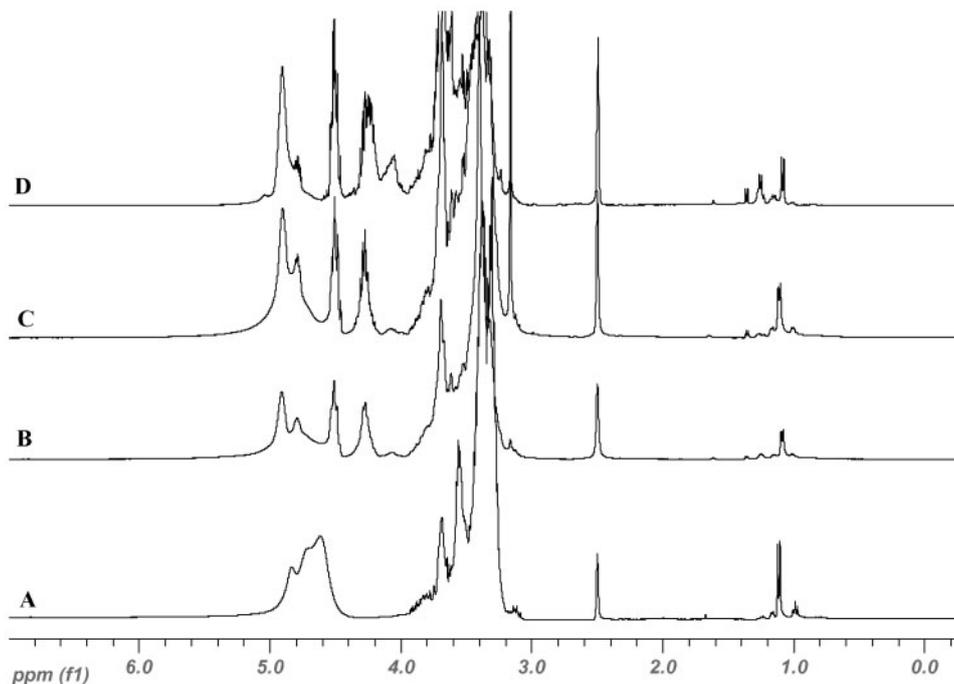
Results and discussion

Method development without wood

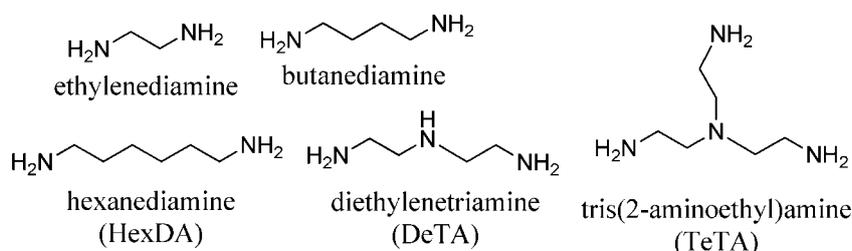
Dicarbonates preparation

A large combination of different dicarbonates was prepared according to three different synthesis pathways (Fig. 1) to get monomers with different solubilities that would give expected changes to leachability properties. Pathway 1 involved the use of diacyl chlorides, diacides or di-isocyanates to join two glycerol carbonate (GC) moieties (no more described in this paper). The key step of pathways 2 and 3 was the cyclic carbonate groups formation on polyols either obtained by a first condensation of diamines on GC or directly provided by an industrial source like the polyglycerol 3 (PG3). Formation of dicarbonates was studied and checked by FT-IR, 1H (Fig. 2) and ^{13}C NMR.

The best conditions were obtained by refluxing in methanol for 5 h with a catalytic amount of potassium carbonate and three equivalents of DMC. A higher quantity of DMC was not beneficial because it lead to an increased ratio of non-cyclic carbonate moiety which was obviously not suitable for the following polymerisation. This ratio between cyclic and non-cyclic carbonate groups was also



2 Effect of DMC equivalent number (0, 1, 3 and 10 from A to D) on cyclic carbonate formation with PG3



3 Di- and tri-amines used for polycondensation

easily monitored by FT-IR experiments since the first showed a vibration band at 1781 cm^{-1} while the second were detected at 1750 cm^{-1} .

Hydroxypolyurethanes formation

The reaction between dicarbonates and various diamines (Fig. 3) were investigated in order to find the best and mildest conditions compatible with a polycondensation step performable in the wood and taking account, as far as possible, a solvent free approach.

The development of the method conditions was carried out with a model monoamine, the *n*-butylamine, and mainly monitored by FT-IR by observing the disappearance of the cyclic carbonate carbonyl vibration and the appearance of the carbamate carbonyl at 1704 cm^{-1} (Table 1).

Occurring slowly at room temperature, the reaction can be performed in one hour at 50°C in methylene

chloride or water with slightly less than two equivalents (1.5) of mono-amine, meaning that the reaction of amine with cyclic carbonate prevails even in water where hydrolysis of cyclic carbonate may occur. At higher temperature, selectivity of the reaction in water was less important leading to higher amounts of hydrolysis.

These results were then applied to the di- and tri-amines to achieve polymerisations. The reaction effectiveness was evaluated by IR, NMR spectroscopy and also size exclusion chromatography (SEC), as illustrated hereafter (Fig. 4) with the SEC chromatogram obtained for the reaction product of DCPG3 with one equivalent of diethylenetriamine in water.

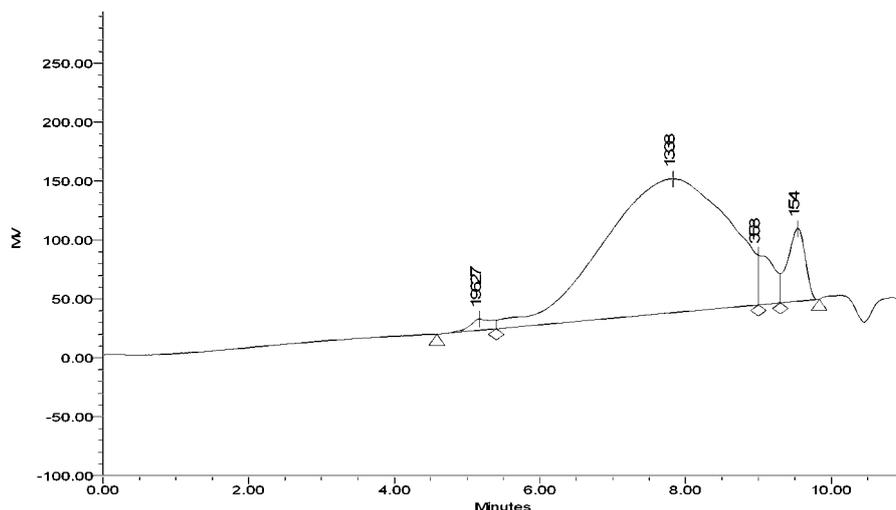
Wood treatment

Beech wood blocks were treated by a vacuum/pressure process in two steps:

Table 1 Reaction of polyglycerol carbonate with different amount of *n*-butylamine

Entry	<i>n</i> -Butylamine/eq*	Weight gain/%	Cyclic carbonate/meq g^{-1} of CPG3	$\nu_{\text{C=O}}\ 1781\text{ cm}^{-1}$	$\nu_{\text{C=O}}\ 1704\text{ cm}^{-1}$
a	0.5	12.5	1.7	Yes	Yes
b	1	21.5	3.0	Yes	Yes
c	1.25	33.5	4.7	Yes	Yes
d	1.5	37.5	5.3	No	Yes
e	2	43	6.1	No	Yes
f	4	42.5	6.0	No	Yes

*Calculated on the basis of a PG3 dicarbonate (DCPG3) with an average molecular weight of 294 g mol^{-1} .



4 Condensation product of DCPG3 and DeTA (1eq) SEC chromatogram

- (i) dicarbonates were impregnated with the appropriated solvent and dried
- (ii) diamines were then impregnated in a convenient solvent, the following drying period at 50°C allowing time for the polymerisation.

Each step was controlled by FT-IR experiment (Fig. 5).

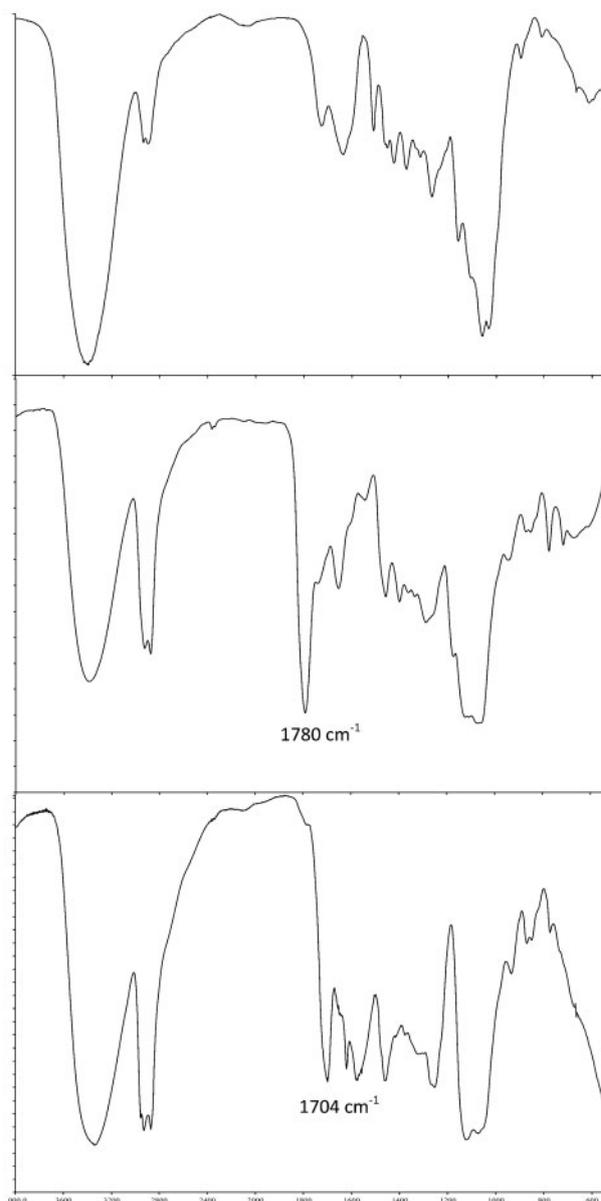
The presence of cyclic carbonate moieties can be attested by the 1780 cm^{-1} bond indicating the stability of this kind of chemical function during the first drying step. Its transformation during the second drying step into a 1704 cm^{-1} bond indicates the formation of carbamate groups by reaction with the polyamines.

The polymerisation of the product in wood was quantified by the weight gain of the blocks (WG) and the dimensional stabilisation by the Anti Swelling Efficiency (ASE). Some interesting results are summarised in Table 2.

The WG and ASE were measured before and after a leaching step in boiling water to characterise the treatment resistance to leachability, which is a crucial property for outdoor uses.

The effect as an antifungal treatment was also evaluated by an in vitro exposure of wood blocks for 16 weeks to *Poria placenta* colonies on the basis of weight losses (WL) due to fungal decay for both protected and unprotected samples. The results are presented in Table 2 as a ratio between the treated and untreated blocks to homogenise the values obtained with different experiments. Thus, the lowest ratio is obtained for the most efficient protective treatment. In any case, most of the WL absolute values obtained with the treated blocks were below the threshold usually considered as a significant complete protection.

For pathways 1 and 3, the measured weight gains after leaching showed good polyurethane retentions in the blocks. In addition, the values were not really different between diamines impregnated in dichloromethane and those used in water which is a very interesting point. The ASE measurements followed the same trend with better results for pathway 1 and particularly for pathway 3, in both cases by using the water soluble diamines. The good values as well as the small differences between ASE measurements, before and after leaching, in the case of the reaction of DCPG3 with DeTA/TeTA can probably be explained by the reticulation effect of TeTA.



5 Typical FT-IR monitoring of impregnation and drying/polymerisation two-step process with Untreated Beech wood spectrum (upper), Beechwood impregnated by DCPG3 spectrum (middle) and Beech wood impregnated by DCPG3 then DeTA and dried spectrum (lower)

Table 2 Characterisation of different pathways of hydroxypolyurethanes formation

Path-way	Dicarbonate (30% w/w)	Dicarbonate solvent	Amine (30% w/w)	Amine solvent	Before leaching		After water leaching		WL ratio*
					WG/%	ASE/%	WG/%	ASE/%	
1	GC with adipic linker	Acetone	HexDA	CH ₂ Cl ₂	31.8	22.3	25.8	18.2	0.175
				H ₂ O	35.2	30.1	28.7	25.2	0.073
2	GC with HexDA linker GC with DeTA linker	CH ₂ Cl ₂ H ₂ O	HexDA DeTA	CH ₂ Cl ₂	21.2	17.5	15.3	12.8	0.248
				H ₂ O	29.5	24.3	17.1	16.2	0.203
3	DCPG3	H ₂ O	HexDA	CH ₂ Cl ₂	39.8	47.2	25.0	33.0	Not done
				H ₂ O	30.7	62.3	20.0	37.2	0.128
				DeTA + TeTA	38.4	61.3	38.4	55.8	Not done

*Ratio between WL after fungal exposure of treated/leached and untreated blocks.

Pathway 2 led to worse results, particularly after leaching, and since it was the strategy involving the highest number of preparation steps, it no longer appeared to be a promising pathway.

In most of the cases, the hydroxypolyurethanes were efficient as antifungal treatment by providing a good protecting effect against the brown rot *Poria Placenta*. The best results were still obtained with the water soluble polyamines and for pathways 1 and 3.

Conclusion

Utilisation of hydroxypolyurethanes gives promising preliminary results for wood dimensional stabilisation and protection. They can be prepared from existing industrial by-products transformed in one step in reactive monomers, easily impregnatable into the wood with aqueous solution among various solvents. The versatility of their synthesis allows the preparation of a wide range of structures with a high modulation of their solubility and leachability properties. The polymerisation is carried out by a moderate heating step corresponding to the usual drying step of any wood treatment. The obtained anti-swelling effects are interesting and, moreover, the exhibited antifungal capability adds a supplementary advantage to this approach. Further experiments are however necessary to investigate more deeply the potential of such

approaches, particularly by evaluating the feasibility of the method with natural polyamines.

References

- Bähr, M., Bitto, A. and Mülhaupt R. 2012. Cyclic limonene dicarbonate as a new monomer for non-isocyanate oligo- and polyurethanes (NIPU) based upon terpenes. *Green Chem.*, 14, pp.1447–54.
- Benyahya, S. et al. 2011. Synthesis of glycerin carbonate-based intermediates using thiol-ene chemistry and isocyanate free polyhydroxyurethanes therefrom. *Polym. Chem.*, 2, pp.2661–67.
- Javni, I., Hong, D. P. and Petrovic, Z. S. 2013. Polyurethanes from soybean oil, aromatic, and cycloaliphatic diamines by non isocyanate route. *J. Appl. Polym. Sci.*, 128, pp.566–71.
- Nohra, B. et al. 2013. From petrochemical polyurethanes to biobased polyhydroxyurethanes. *Macromolecules*, 46, pp.3771–92.
- Ochiai, B., Satoh, Y. and Endo, T. 2005. Nucleophilic polyaddition in water based on chemo-selective reaction of cyclic carbonate with amine. *Green Chem.*, 7, pp.765–67.
- Rokicki, G. and Piotrowska, A. 2002. A new route to polyurethanes from ethylene carbonate, diamines and diols. *Polymer*, 43, pp.2927–35.
- Ubaghs, L., Fricke, N., Keul, H. and Höcker, H. 2004. Polyurethanes with pendant hydroxyl groups: synthesis and characterization. *Macromol. Rapid Commun.*, 25, pp.517–21.
- Unverferth, M., Kreye, O., Prohammer, A. and Meier, M. A. R. 2013. Renewable non-isocyanate based thermoplastic polyurethanes via polycondensation of dimethyl carbamate monomers with diols. *Macromol. Rapid Commun.*, 34, pp.1569–74.
- Webster, D. C. 2003. Cyclic carbonate functional polymers and their applications. *Prog. Org. Coat.*, 47, pp.77–86.