

Deamination of Polyols from the Glycolysis of Polyurethane

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Methylenedianiline (MDA) is a secondary, undesired, product of the glycolysis process of polyurethane (PU) scraps due to hydrolysis and pyrolysis side reactions. As an aromatic and carcinogen amine, MDA poses different problems in handling, transporting, and labelling recycled polyols derived from glycolysis, hindering the closure of PU recycling loop. Aiming to provide a solution to this issue, in this work different deaminating agents (DAs) were investigated with the purpose of analyzing their reactivity with MDA. A first part of the study was devoted to the analysis of MDA formation as a function of reaction time and catalyst concentration (potassium acetate) during glycolysis. It was observed that the amount of MDA

increases almost linearly with the extent of PU depolymerization and catalyst content. Among the DAs analyzed 2-ethylhexyl glycidyl ether (2-EHGE), and acetic anhydride (Ac₂O) showed interesting performance, which allowed MDA content to be diminished below the limit for labelling prescription in 30 minutes. PU rigid foams were, therefore, synthesized from the corresponding recycled products and characterized in terms of thermal and mechanical performance. Ac₂O-deaminated polyols led to structurally unstable foams with poor compressive strength, while 2-EHGE-deaminated products allowed the production of foams with improved mechanical performance and unaltered thermal conductivity.

Introduction

Pure 4,4'-methylene dianiline is a crystalline white solid substance that melts at 90 °C and boils at 398 °C, at ambient pressure, it is a weak base, with a pK_a of 4.96 at 20 °C. According to the harmonized classification and labelling (CLP, Regulation EC 1272/2008^[1]) approved by the European Union (EU), this substance may cause cancer, damage to organs and it is suspected of causing genetic defects. Secondary effects due to contact are an allergic skin reaction, eye irritation it is harmful if swallowed, and very toxic to aquatic life with long-lasting effects^[2]. As well as in the EU, MDA appears in the NIOSH Occupational Cancer List^[3]. The presence of 4,4'-MDA in a polyol is theoretically not a problem, as during PU synthesis it reacts with isocyanate. However, according to the ECHA guidelines, its concentration in a polyol must be below 1000 ppm (or 0.1 % by weight) for health and labelling reasons. If MDA concentration into a polyol exceeds this limit, the polyol can still be used but labelled, handled and transported accordingly, increasing the degree of complexity for managing the supply chain of recycled polyols for PU production.^[1]

4,4'-MDA is naturally produced by PU products from to the scission of urethane and urea bonds by hydrolysis^[4] due to the

presence of microorganisms or atmospheric moisture^[5]. Hydrolysis and pyrolysis are also the main causes of MDA formation during the chemical recycling of polyurethanes via glycolysis; however, several solutions can be found.

Glycolysis is one of the most promising recycling routes for the recovering of rigid PU foam scraps^[6–8]: in this process, several chemical reactions are involved, yielding a polyol-like liquid product that can be used as a secondary raw material to produce new PU foams^[9,10]. A glycol is used to cleave the urethane group and release the original polyol and a lower molecular weight carbamate species. Hydrolysis and pyrolysis, however, may occur due to the humidity present in the reacting mixture and the high process temperature. These two reactions are the main cause of free aromatic amine production; according to the type of isocyanate used in the synthesis a specific aromatic amine is formed^[11]. Most frequently, diphenylmethane-4,4'-diisocyanate (pure MDI, or its polymeric forms, crude pMDI) is used, leading to the formation of 4,4'-MDA. Authors have studied a wide variety of PU waste, such as rigid^[12], flexible and viscoelastic^[13], polyisocyanurate foams^[14], adhesives and sealants^[15,16], microcellular PUs^[17], and RIM manufactures^[18].

Researchers are working in different directions in order to overcome this problem. On the one hand, there is an attention to identify an upstream solution by developing new safer isocyanates or non-isocyanate polyurethane materials (NIPUs)^[19–21]. On the other hand, researchers are developing strategies to minimize MDA formation during the recycling process, such as reducing the reaction time but still, ensuring a suitable viscosity of the glycolysis product, and using selective catalysts such as metalorganic compounds^[22]. Finally, strategies to reduce the MDA content after its formation in the recycling process can also be found. Datta *et al.*^[23] reviewed some of the purification steps for a glycolysis product and among them the deamination of the product with alkylene oxides and glycidol

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ethers. Lee *et al.*^[24] used butyl glycidyl ether, a suspect carcinogen substance^[25], in a concentration of 10% wt with 1% of N,N-dimethylcyclohexylamine (DMCHA) for 5 h at 150 °C to reduce the MDA content. They characterized the sample through NMR; however, they did not quantitate MDA before and after the deamination treatment. Shin *et al.*^[26] chemically modified the glycolysis product via addition polymerization of propylene oxide to deactivate aminic groups obtaining two different products with an amine value of 38.2 and 43.5 mg_{KOH}/g. Modesti *et al.*^[27] recycled a flexible water-blown polyurethane foam waste and converted the free aromatic amines into methylol end groups through formaldehyde. They used hexamethylenetetramine (HMTA) as source of formaldehyde that reacts with primary amines present in the split phase mixture. At the end of the deamination process, free amine content was lower than 100 ppm. Kim *et al.*^[28] led a deamination process with 2-EHGE under severe conditions at 200 °C for 1 h with a molar excess ratio of 3 and after 7 h of glycolysis. However, they did not reach the limit to avoid labelling prescription.

Instead of a glycolysis, in the case of a flexible PU waste, an acidolysis with a dicarboxylic acid can be applied. This process yields a product with a low aromatic amines content^[29,30]. Acidolysis is particularly convenient for obtaining a recycled polyol with very low hydroxyl value, suitable for flexible PU applications. For rigid PU applications, instead, a high hydroxyl value is needed, therefore, glycolysis is the most convenient choice.

Major chemical companies hold patents to reduce the MDA content in a recycled product. Air Products, Dow Chemical Company, and McDonnell Douglas diminished MDA content using alkylene oxides such as ethylene oxide (EO) and propylene oxide (PO)^[31–34]. Bayer AG employed low molecular weight urea or carbamic acid esters such as ethyl or methyl carbamate^[35], or hydrogen chloride^[36]. BASF reduced MDA with epoxidized native fatty oils such as soybean oil, linseed oil, rapeseed oil, and nut oils^[37], or adding stepwise small amounts of isocyanate^[38]. H&S Anlagentechnik GmbH developed an acidolysis process to recycle PU waste with aromatic amines content < 0.05 %wt^[39,40].

While a suitable solution to reduce the free aromatic amines content for flexible PU foam waste is available thanks to the implementation of an acidolysis process, for rigid PU waste the most effective solutions rely on the use of dangerous and explosive substances, such as alkylene oxides and at high pressure, that have limited applicability for smaller scale plants and companies. The use of safer chemicals is not sufficiently covered in literature, either because optimal conditions and quantification of MDA are not present, or due to the lack of studies related to the effects of deamination processes on the final performance of new foams. In this work we investigated new DAs to reduce the MDA content below the labelling prescription limit, selecting safer and easy to handle chemicals to obtain a simple and fast process to recover PU waste. We also deepened the study of a known deaminating agent to find optimal reaction parameters and investigated the effects of the

deamination processes on the mechanical and thermal properties of new synthesized rigid PU foams.

Results and Discussion

MDA formation

MDA formation and dynamic viscosity (μ) of the recycled product have been studied as a function of catalyst concentration and reaction time to analyze their dependence with such variables. Figure 1 shows how MDA concentration varies with time: MDA starts to increase linearly from a certain non-zero value according to the catalyst concentration employed. This is due to the PU loading step, as MDA is tracked only after the complete dissolution of the PU powder. During this time, a slight amount of MDA is formed as a consequence of the PU glycolysis inevitably produced before the end of the loading phase. As expected, the higher the KOAc concentration, the faster the growth of MDA in terms of weight percentage in the glycolysis product. MDA seems to reach a stable value at high reaction times. This is clear especially in the case of 50 mmol/100g_{PU} (5%wt). The initial value of MDA depends on the catalyst concentration. The effect of KOAc is made clearer in Figure 2: an increase of catalyst concentration leads to a non-linear increase of the MDA content. This is reasonable as a higher amount of catalyst gives higher rates for both wanted transesterification and unwanted hydrolysis. In both cases a nucleophilic attack by an alkoxide occurs^[41]. HPLC chromatograms at different reaction times are reported in Figure S12.

It is worthy to notice that the MDA concentration, in the case of 10 mmol/100g_{PU} (1%wt), is below the labelling limit threshold, however, MDA content is not the only parameter to look at to assess the quality of a glycolysis product as viscosity plays a significant role in the suitability and processability during the later foam synthesis step. Figure 3 highlights the opposite effect of KOAc concentration on the depolymerization degree of the product. The higher the concentration, the lower the viscosity and therefore the higher the depolymerization degree. Viscosity decreases exponentially with an increase of KOAc concentration, a reasonable target viscosity is around 6000 mPa·s to have a good workability during the foam synthesis phase. This again is reasonable, as a higher amount of catalyst increases the speed a transesterification, leading to the breakage of the thermosetting structure, freeing the original polyols. The suitability of a glycolysis product is determined by the MDA content and by its viscosity. Therefore, since the catalyst concentration has an opposite effect on these two, to obtain optimal polyol properties, KOAc concentration was set to 30 mmol/100g_{PU} (3%wt) allowing a good reaction control, acceptable viscosity, and limited MDA concentration. Reaction time was set to 4 h, a reasonable time for a further scale-up of the process.

Kinetics shown below are only related to the secondary reactions occurring during the recycling process (glycolysis itself is a transesterification, as a result no FTIR peaks' variation is expected). Full spectra are provided in the Supplementary

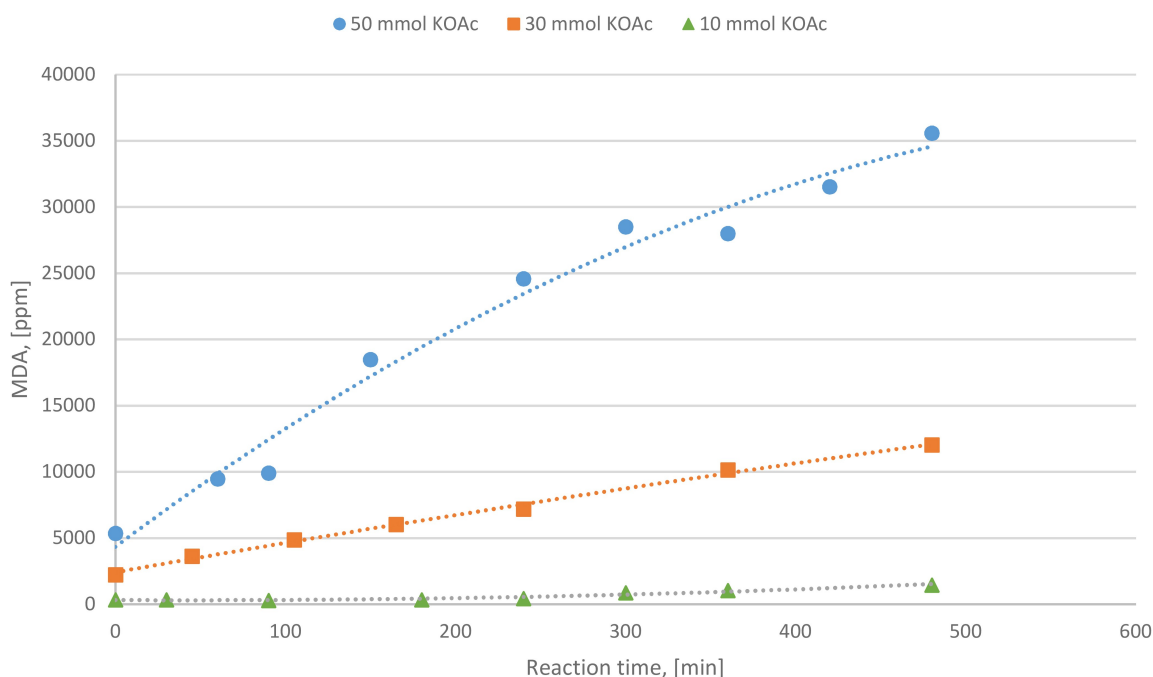


Figure 1. MDA formation kinetics as a function of reaction time and catalyst concentration during glycolysis at 200°C. Standard deviation on the measurement is $\pm 5\%$.

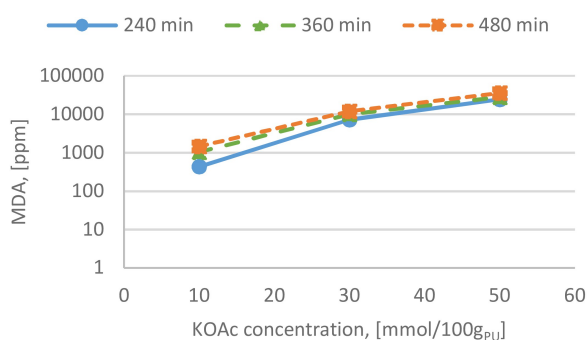


Figure 2. MDA formation as a function of catalyst concentration. Logarithmic y-axis.

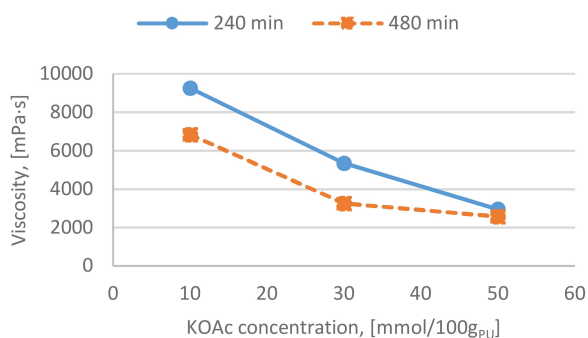


Figure 3. Viscosity of the glycolysis product as a function of KOAc concentration.

Material in Figures S3 and S4. Figure 4 shows the variation of relative absorbances of the peaks at 1723 cm^{-1} ($\nu(\text{C}=\text{O})$ urethane Amide I),^[42–45] 1538 cm^{-1} ($\delta(\text{N}-\text{H})$ urethane Amide II)

and 3354 cm^{-1} ($\nu(\text{N}-\text{H})$ nonbonded) with respect to a reference peak at 1120 cm^{-1} ($\nu(\text{C}-\text{O})$ symmetric aromatic ester), i.e. a group which is not involved in the reaction. Relative absorbance can be related to the concentration of a certain species according to Lambert-Beer's law (further information in the Supplementary Material).

Peaks at 1723 cm^{-1} and 1538 cm^{-1} are showing the same trends: this is due to the fact that they are referred to the same urethane bond, therefore their disappearance rate is very similar. They only differ in molar attenuation coefficient. Peak at 3354 cm^{-1} slightly increases along with the reaction time, reaching an equilibrium at around 7 h. This is in accordance with the trend of the MDA formation, shown in Figure 1.

The GPC chromatograms depicted in Figures S8–10 validate the conclusions concerning depolymerization degree and viscosity. The increased occurrence of overlapped peaks at shorter retention times suggests the existence of molecules with greater molecular weights. These peaks gradually diminish in magnitude over time. Figure 5 shows the evolution of M_w over time and in relation to catalyst concentration. It is observed that higher catalyst concentrations and longer reaction durations result in greater depolymerization degrees and a reduction in the ultimate molecular weight of the resulting product.

Final properties of the recycled polyol obtained are listed in Table 1. This recycled product underwent different deamination reactions as MDA content was far above the labelling limit of 1000 ppm to avoid expensive labelling procedures.

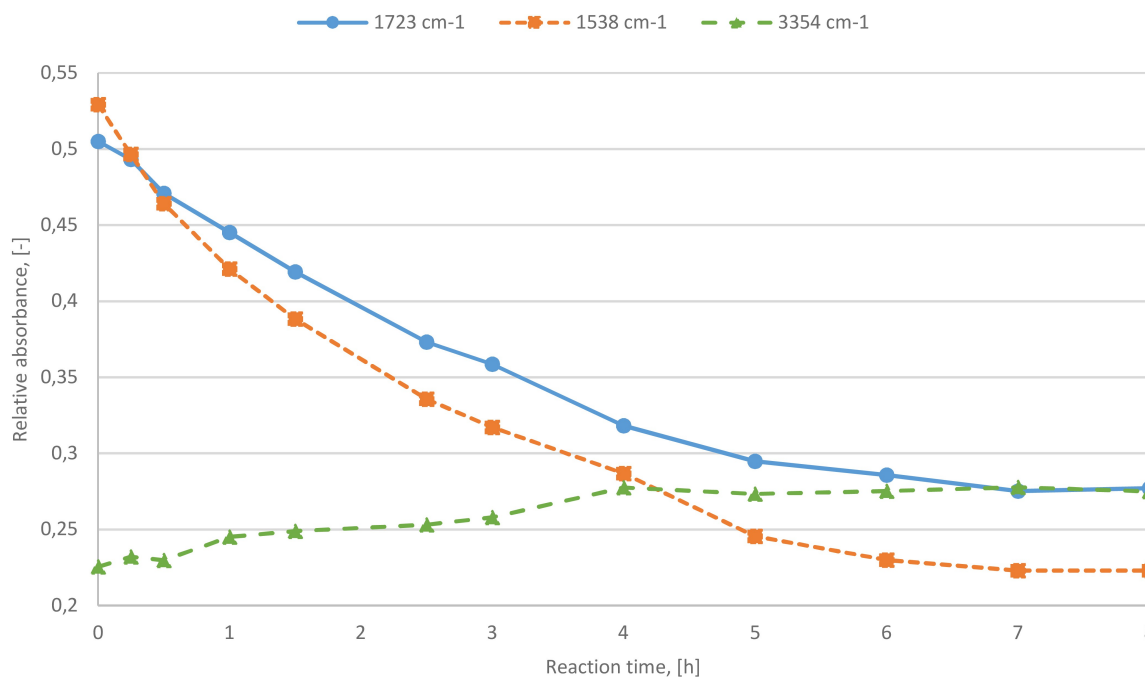


Figure 4. FTIR characteristic peaks' variation along with time. This trend is obtained with 50 mmol/100g_{PU} of KOAc.

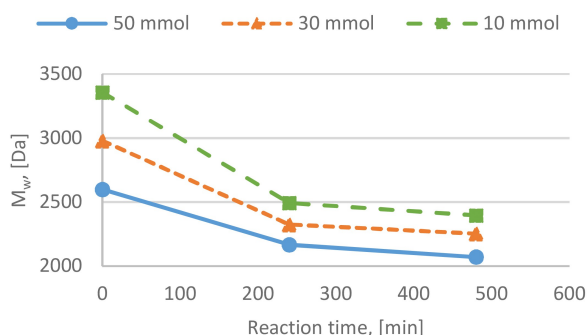


Figure 5. Averaged molecular weight of the glycolysis products at different catalyst concentration along with time.

Table 1. Glycolysis product properties before the deamination treatment. Maximum experimental error for the MDA content is $\pm 5\%$, for the viscosity is ± 140 mPa·s, for the hydroxyl value is ± 20 mg_{KOH}/g, and for the molecular weight it is ± 200 Da.

Property	Value
Viscosity	5500 mPa·s
MDA content	7000 ppm
HV	560 mg _{KOH} /g
M _w	2325 Da
\bar{D}	8.0

MDA abatement

Deamination reactions were run with the recycled product obtained from glycolysis with the properties listed in Table 1. The DA is added on a molar excess ratio basis, calculating the moles of MDA present in the reaction mixture. Reaction

schemes of 4,4'-MDA with different deaminating agents are shown in Scheme 1, a summary of the deaminating performances at 120 °C are shown in Table 2.

Deamination with 2-EHGE

2-EHGE is a good candidate as DA as it possesses an epoxy ring, known to be very reactive towards amines (Figure 12A). 2-EHGE deamination performances were studied at different concentrations and temperatures as, despite being tested in another work^[46], here the aim was to develop a process at lower temperature and DA concentration. Figure 6 shows the effect of 2-EHGE in molar excess of 5 and 3 as well as at stoichiometric concentration.

Working at 120 °C, the deamination kinetics is extremely fast: even though the deamination reaction is carried out for

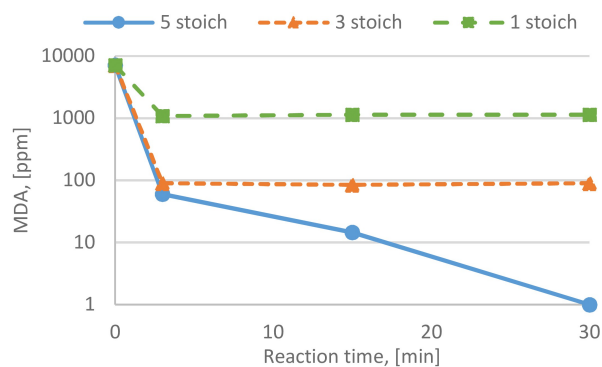
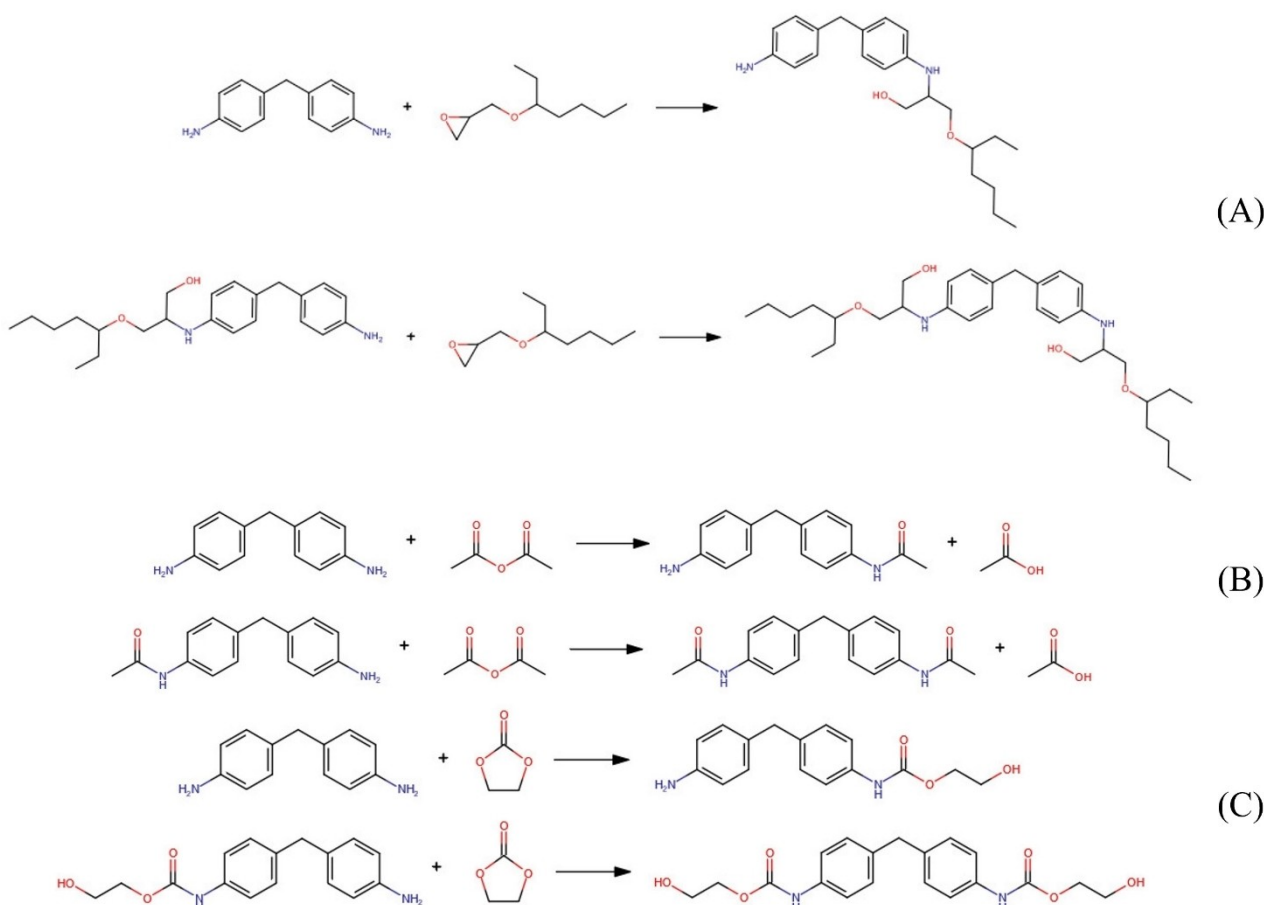


Figure 6. 2-EHGE deamination performances towards MDA at 120 °C. Logarithmic y-axis, standard deviation on the measurement is $\pm 5\%$.



Scheme 1. Reaction schemes of 4,4'-MDA with deaminating agents. (A) 2-EHGE, (B) Ac_2O , and (C) EC.

Table 2. Deamination performances summary after at 120 °C. Maximum experimental error for the MDA content is $\pm 5\%$, for the viscosity is ± 140 mPa-s, for the hydroxyl value is ± 20 $\text{mg}_{\text{KOH}}/\text{g}$, and for the M_w it is ± 200 Da.

DA	Molar excess	Time, [h]	c_{MDA} [ppm]	X_{MDA} [%]	μ , [mPa-s]	HV, [$\text{mg}_{\text{KOH}}/\text{g}$]	M_w [Da]	Φ , [-]
2-EHGE	3	0.5	100	99	5550	558	2108	8.3
Ac_2O	5	0.17	610	91	5670	512	2537	8.3
EC	5	2	1890	73	5890	563	2055	8.2

2 h, after 30 minutes MDA concentration settles to a constant value below the labelling requirements in all cases. In the stoichiometric case, MDA concentration settles close to 1000 ppm. After the very first minutes after the addition of 2-EHGE there is a sharp decrease in the MDA content and conversion reaches 85, 99 and 100% when increasing the excess of DA. With a 5-molar excess of DA a complete abatement is achieved, on the contrary, with a 3-molar excess, MDA settles around 100 ppm. This trend may be explained considering that in all three cases other reactions involving other less reactive N–H groups^[47,48] present in the recycled polyol occur, however the higher the molar excess, the higher the diminishing of MDA content. Diamines, indeed, present four reactive sites^[49] represented by each active hydrogen linked to the nitrogen. They are commonly used in the curing reactions of epoxy resins^[50]. In our case, however, we were not interested

in reacting all the active hydrogens but one was enough to decrease the concentration of pure MDA. Therefore, 5-molar excess is enough to avoid the settling of MDA concentration to a constant value, this is also the only value which is higher than the stoichiometric quantity in terms of equivalent of active hydrogens. Another benefit of 2-EHGE is that viscosity, molecular weight distribution (Figure S11), and hydroxyl value (HV) are unaltered by the deamination treatment (Table 2). Aiming to get the minimal temperature to obtain optimal deamination performances, tests with a 3-molar excess were carried out at a varying temperature, Figure 7 shows the results. Again, with this excess of 2-EHGE, temperature has a negligible effect on the kinetics as an almost complete conversion is obtained in around 15 minutes. FTIR spectra shown in Figure S5 confirm what abovesaid: the absorbance of the peak at 3354 cm^{-1} is diminishing in time and the peak is getting rounder, meaning

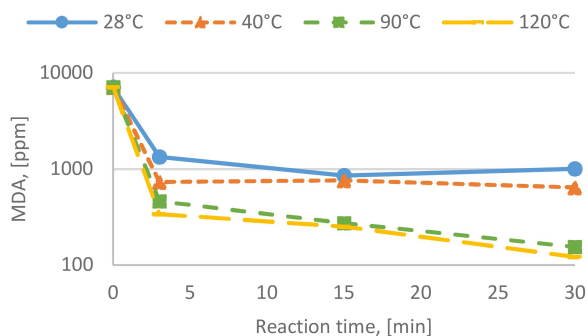


Figure 7. Effect of temperature on the performance of 2-EHGE (3-molar excess). Logarithmic y-axis. Standard deviation on the measurement is $\pm 5\%$.

that the amine-related peak in that region is disappearing, leaving the hydroxyl-associated broad peak. The specific reaction occurring can be written according to the structure of the substances involved as can be seen from Scheme 1A. 2-EHGE appears to be very reactive towards MDA independently on the reaction temperature, furthermore, the deamination occurs in less than 30 minutes. As a result, the deamination treatment does not significantly affect the overall process time and can be carried out close to ambient temperature. This product was used to produce new rigid foams. As previously mentioned, this DA was tested before^[28]. In that case, the deamination reaction was carried out in parallel with the glycolysis at 200 °C. We believe that this approach is counter-productive as from one side the depolymerization of the polymer continues at this temperature, yielding also new MDA; from the other side a high temperature increases the chance that side reactions occur during the process, reducing the one of the DA in reacting with the primary amine only. These two factors led to a product with a too high MDA content. Indeed, running a second deamination reaction in series rather than in parallel and at a much lower temperature led to a product with the desired properties.

Deamination with Ac_2O

Acetic anhydride, in Figure 12B, presents two acyl groups bonded to the same oxygen and this leads to its high reactivity. Deamination performances of Ac_2O are shown in Figure 8. At 120 °C, anhydride's abatement kinetics is slower than the 2-EHGE's one and it is strongly influenced by the molar excess ratio used. At stoichiometric conditions and excess 3, a conversion of 34% and 55% is reached after 10 minutes, respectively. After this time, conversion remains constant,

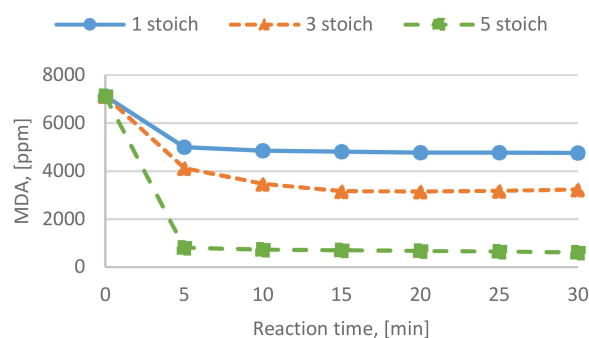


Figure 8. Deamination performances of Ac_2O at different excess ratios and at 120 °C. Standard deviation on the measurement is $\pm 5\%$.

without meeting the labelling limit of 1000 ppm. In the case of 5-molar excess, 91% conversion is reached in 10 minutes and labelling requirements are met. An example of the FTIR spectra are shown in Figure S6, in which the hydroxyl-associated peak is getting rounder, therefore the underneath one at 3354 cm^{-1} is disappearing. Viscosity and the molecular weight distribution, shown in Figure S11, are not affected by the presence of the anhydride (Table 2). Possible reaction scheme is shown in Scheme 1B. The drawback of this DA is that a 5-molar excess is needed to reach the necessary MDA content that suggests the occurrence of side reactions such as the esterification of the residual cleavage agent, DEG, also due to the formation of acetic acid, as shown in Scheme 2. This was also verified by the measurement of the hydroxyl value of the product: a slight decrease in this value indicates the consumption of hydroxyl groups.

However, since the labelling limit was met under certain conditions, this product was used to produce new rigid foams.

Deamination with EC

EC is the last DA tested as the carbonate group might be reactive to MDA (Figure 12C). Deamination tests were performed at the same conditions cited before, with a 5-molar excess with respect to MDA (Figure 9), 1000 ppm limit is almost reached after 2 h of reaction with a slow reaction rate. Also in this case, viscosity, molecular weight distribution (Figure S11), and hydroxyl value are not affected by the DA (Table 2). Scheme 1C shows the possible reaction scheme involving the carbonate substance. This reaction scheme is confirmed by studying FTIR spectra along with reaction time in Figure S7. Characteristic peaks of $EC^{[51,52]}$ at 1805 and 1775 cm^{-1} are exponentially decreasing, while peaks related to the urethane



Scheme 2. DEG esterification through Ac_2O .

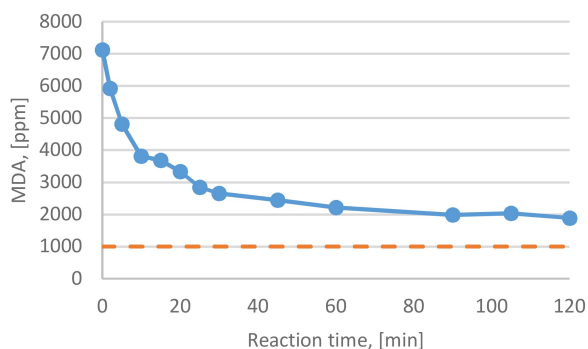


Figure 9. Deamination performance with EC at 120 °C. Orange dotted line is the labelling limit. Standard deviation on the measurement is $\pm 5\%$.

structure (1726 and 1540 cm^{-1}) are increasing, as seen from Figure 10. As the labelling limit was not met with this substance, EC was discarded as possible deaminating agent.

New rigid foam synthesis

New foams were synthesized with glycolysis products, before and after the deamination process, with products meeting the labelling threshold, therefore the ones with 3-molar excess of 2-EHGE and 5-molar excess of Ac_2O . Formulation used was the original one in which the recycled product was added in substitution with the polyol with the closer hydroxyl value, namely Alcupol® C-5710. Substitution percentages went from 25 to 50% by weight. Target density was set to $40 \pm 5\text{ kg/m}^3$. Results are listed in Table 3. Compressive strengths along

Table 3. New rigid foam performances in terms of apparent density, ρ , normalized compressive strength, $\sigma_{c, \text{norm}}$ and thermal conductivity, λ . Maximum standard deviation for σ_c is $\pm 14\text{ kPa}$, for λ is $\pm 0.2\text{ mW}/(\text{m}\cdot\text{K})$.

Foam	ρ , [kg/m^3]	$\sigma_{c, \text{norm}}$ [kPa]	λ , [$\text{mW}/(\text{m}\cdot\text{K})$]
Reference	44	227	25.4
25% pre-treat	43	244	25.3
50% pre-treat	44	252	26.1
25% post-treat with 2-EHGE	41	297	24.7
50% post-treat with 2-EHGE	38	335	25.9
25% post-treat with Ac_2O	38	192	28.8
50% post-treat with Ac_2O	39	121	28.9

growth direction are normalized according to Gibson *et al.*^[53] with the Equation S3^[26] shown in the Supplementary Material. It results that glycolysis product, without deamination step, has a beneficial effect on mechanical properties of the foams as the compressive strength increases with the substitution percentage. This effect has already been noticed^[14] and might be due to the isocyanic moieties present in the recycled product that increase the affinity and miscibility with the isocyanate part of the formulation, leading to finer morphology^[54] and higher mechanical performances. Thermal conductivity seems not to be affected by the presence of the recycled product. In the same way, the deamination treatment with 2-EHGE is not affecting the thermal conductivity. On the contrary, 2-EHGE presence increases the compressive strength of the foam. It is increased by roughly 30% in the case of 25% substitution and nearly 50% in the case of 50% substitution. This result is

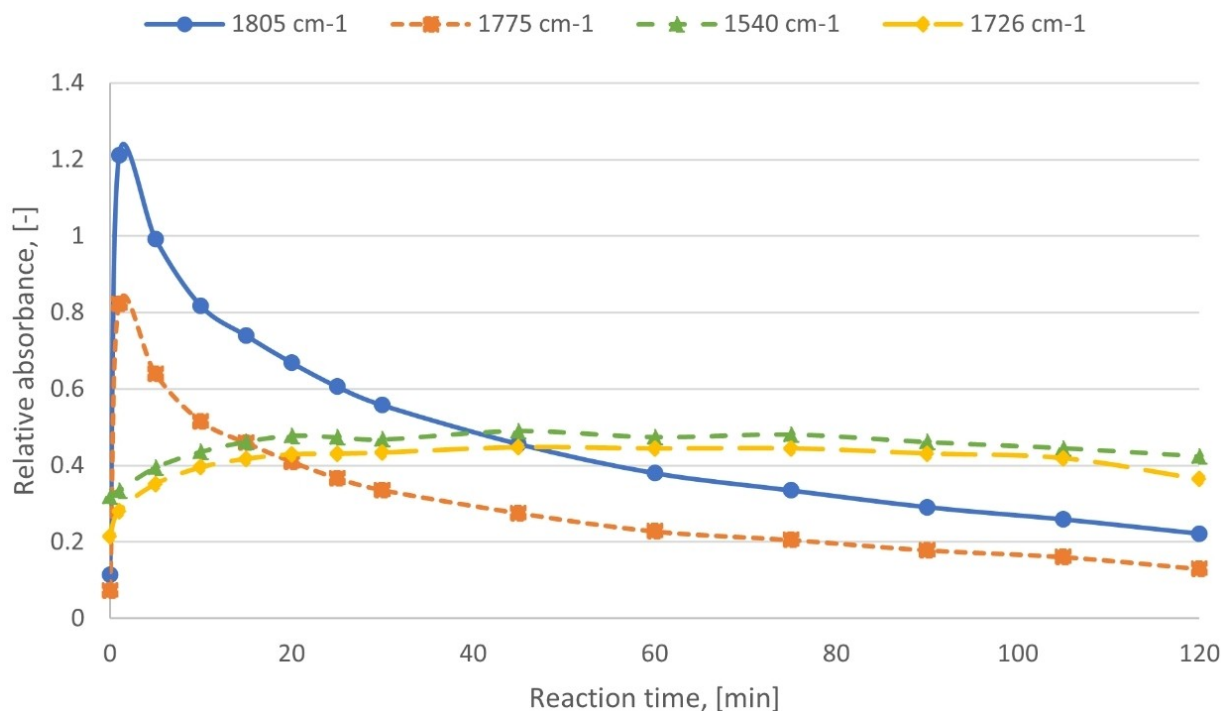


Figure 10. FTIR peaks' trend of the deamination with EC at 120 °C along with reaction time.

particularly interesting and might be explained by the presence of oxazolidinone moieties^[55] formed by the reaction of isocyanate and residual excess of 2-EHGE present in the recycled product.

Ac₂O deamination treatment, instead, leads to a decrease in the mechanical and thermal performance of the foams. The higher the substitution percentage of recycled product, the lower the compressive strength and the higher the thermal conductivity. Structural stability was not guaranteed anymore as foam collapsed after few hours after the cut. This effect can be explained by the fact that the use of an acidic DA in large excess may salify the base catalysts used during the PU synthesis. This may also lead to a higher content of open cells^[56].

This is verified by looking at synthesis characteristic times shown in Table S2 in the Supplementary Material. Gel and tack-free times are greater than the reference ones as the residual excess of acetic anhydride and acetic acid may interfere with the catalysis of the PU synthesis. SEM micrographs confirmed the above. Figure 11 shows the x200 magnification of the reference foam, the foam 25RP, 25RPE, and 25RPA foams, whereas in Table 4 there is the average cell diameter of four foams.

Conclusions

In this work we assessed the performances of three deaminating agents (DAs) to diminish the MDA content of a glycolysis

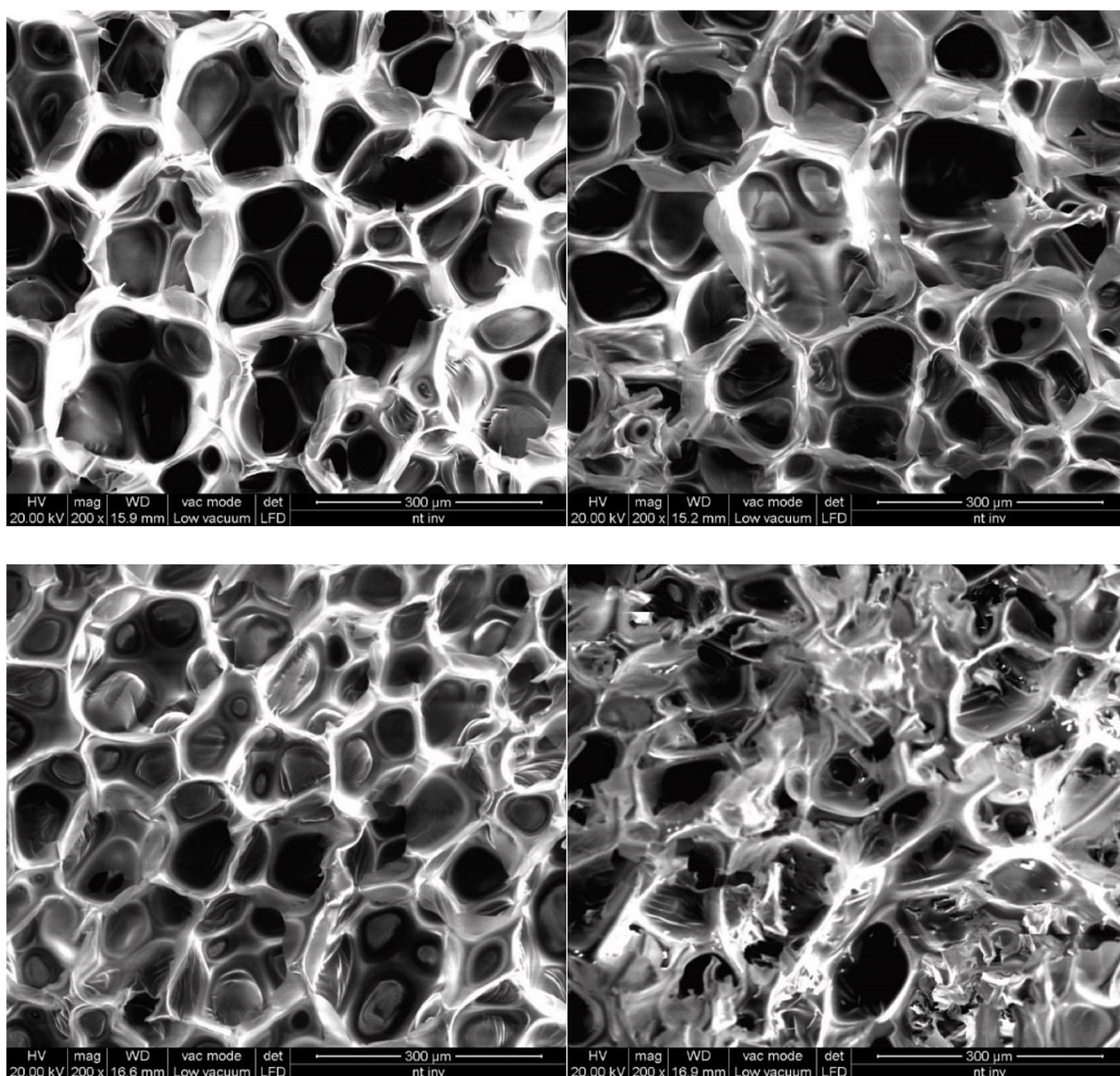


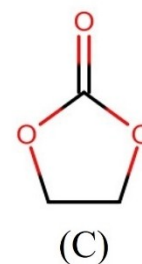
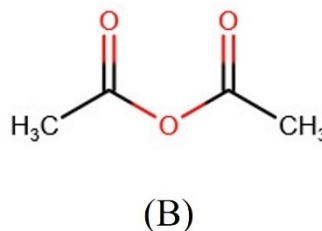
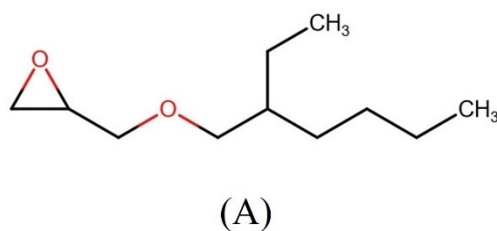
Figure 11. SEM micrographs of the reference foam (top left), 25RP (top right), 25RPE (bottom left), and 25RPA (bottom right). Magnification $\times 200$.

Table 4. Average cell diameter of Ref, 25RP, 25RPE, and 25RPA foams.

Foam	d, [μm]
Ref	154
25RP	148
25RPE	127
25RPA	136

product. MDA is a carcinogenic substance which is produced during side reactions of the chemical recycling of polyurethane (PU) via glycolysis. Rigid PU foam waste was subjected to glycolysis with diethylene glycol (DEG) and potassium acetate (KOAc) as a catalyst. During this process, we discovered that MDA content increased almost linearly with the reaction time and its formation is exponentially related to the KOAc concentration. An optimal KOAc concentration of 30 mmol/100 g of polyurethane (3%wt with respect to the polymer) was identified as a good trade-off between reduced MDA concentration and sufficient depolymerization degree to produce a recycled polyol with suitable viscosity. After the glycolysis process, a deamination treatment was carried out by comparing the performance of different DAs in order to get rid of the excess MDA in the product. 2-EHGE was proved to be extremely reactive to MDA with a slight molar excess of 3, providing an almost complete conversion of MDA in less than 15 minutes, independently on the reaction temperature. As well as 2-EHGE, acetic anhydride has been demonstrated very reactive towards the deamination reaction; however, a large molar excess of 5 was needed to decrease the MDA concentration below 1000 ppm. Finally, EC was used with a 5-molar excess at a glycolysis temperature of 120 °C. A conversion of 79% was reached in 2 h, leading to a product with MDA content close to the labelling limit. In all the last three cases, viscosity was not affected by the deamination treatment.

New PU rigid foams are synthesized by starting from deaminated products in a substitution of 25% and 50% by weight to a virgin polyol. Ac_2O -deaminated products lead to structurally unstable and low performing foams due to the high acidity of the recycled polyol, while 2-EHGE-deaminated products allowed the production of foams with improved (up to 50% higher than the reference) mechanical performance and unaltered thermal conductivity enabling to close the loop of polyurethane recycling problem.

**Figure 12.** DAs' structure, 2-EHGE (A), Ac_2O (B), EC (C).

Experimental Section

Materials

Glycolysis products were obtained from PU waste gently supplied by an external company, in the form of powder. The pristine foam has an apparent density of 40 kg/m³ and it has been obtained by using pMDI and three different polyols, the same used later in the foam synthesis part. Diethylene glycol (DEG) was used as cleavage agent, whereas potassium acetate (KOAc) was used as glycolysis catalyst at different concentrations. Cleavage agent and catalyst were both supplied by Sigma-Aldrich. 4,4'-MDA standard was purchased from Sigma-Aldrich and employed to calibrate the reversed-phase liquid chromatography (HPLC) analysis used to quantify MDA content in the reaction products. The calibration procedure is described in the Supplementary Material.

DAs tested in this work were an epoxy (2-(2-ethylhexoxymethyl)oxirane aka 2-ethylhexyl glycidyl ether (2-EHGE)), an anhydride (acetic anhydride (Ac_2O)), and (1,3-dioxolan-2-one aka ethylene carbonate (EC)), they are shown in Figure 12.

During the characterization of the reaction products, HPLC-grade acetonitrile and MilliQ ultrapure water were employed as eluents for the analytical techniques and samples preparation. N-methyl-2-pyrrolidone, acetic anhydride and 4-dimethylaminopyridine were used in hydroxyl value measurement. These were all supplied by Sigma-Aldrich.

Raw materials used during the foam synthesis were:

- Isocyanate: Desmodur® 44 V20 L (pMDI, Covestro AG, Leverkusen, Germany), %NCO = 30.5–32.5, viscosity at 25 °C = 160–240 mPa·s
- Polyols: a non-disclosable mixture of three polyols, Alcupol® C-5710 (polyether triol, Repsol S.A., Madrid, Spain), hydroxyl value, HV = 570 mg_{KOH}/g, viscosity at 25 °C = 700 mPa·s, Alcupol® R-3810 (polyether triol, Repsol S.A., Madrid, Spain), HV = 380 mg_{KOH}/g, viscosity at 25 °C = 350 mPa·s, and Adicrol FD 315 (aromatic DEG-based, Nord Composites UK Ltd, Wednesbury, UK), HV = 300–330 mg_{KOH}/g, viscosity at 25 °C = 2000–3000 mPa·s
- Catalysts: Niax™ A1 (bis(2-dimethylaminoethyl)ether, Momentive, Waterford (NY), USA) and N,N-dimethylcyclohexylamine (Sigma-Aldrich, St. Louis (MO), USA), respectively as, gel and blow catalysts while Kosmos® 45 (potassium acetate, Evonik industries AG, Essen, Germany) as trimerization catalyst
- Surfactant: Tegostab® B8460 (polyether polydimethylsiloxane, Evonik Industries AG, Essen, Germany)
- Blowing agent: deionized water

Methods

Glycolysis and deamination processes

The glycolysis of PU waste was carried out on a 1 L round-bottom flask heated through a MR Hei-Tec isomantle (Heidolph Instruments, Schwabach, Germany). The system was equipped with a reflux condenser, a mechanical overhead stirrer with a glass shaft and a PTFE blade end and a Pt1000 temperature sensor. The cleavage agent and the catalyst, DEG and KOAc, respectively, were loaded into the reactor and heated to the working temperature, namely 200 °C. The use of a basic catalyst prevents the dehydration of the glycol yielding 1,4-dioxane. This substance would indeed be formed under similar conditions of temperature but with the presence of strong acid catalysts, such as sulfuric or hydrochloric acid^[57,58]. Once the setpoint temperature was reached, PU powder was loaded stepwise into the reactive mixture according to its dissolution rate in the glycol and on the amount to be treated, generally within 30–40 minutes time interval. The waste-to-solvent ratio was set to 1.5 kg_{PU}/kg_{DEG}, loading typically 200 g of PU in 133 g of DEG, to allow a final recycled product with a hydroxyl value suitable for new rigid applications although at the expense of a high amount of catalyst to obtain a proper viscosity (see Figure 3). Reaction time started after the loading and dissolution of PU waste. The reaction was stopped after 4 h (in some cases the reaction was made last longer, 8 h, to get an MDA formation profile along with time).

Deamination reactions were run after the characterization of the glycolysis product. Deamination reactions were carried out with the same equipment abovementioned but in this case the glycolized product was heated to the desired temperature and then the DA was added. The reaction time was set to 2 h to avoid too long overall process times.

Characterization of the glycolysis and deamination products

4,4'-MDA content was measured through a reversed-phase liquid chromatography (HPLC) analysis. In order to get a calibration line, an HPLC method was developed. A Waters e2695 separation model coupled with a Waters 2489 UV detector (Waters Corporation, Milford (MA), USA) with double wavelength was employed. A hydrophobic C18 with hydrophilic-endcap column (pore diameter 300 Å, particle size 5 µm, diameter×length 4.6×250 mm) kept at 40 °C was used. Milli-Q ultrapure water (acidified with 0.05% of difluoroacetic acid) and HPLC-grade acetonitrile were used as eluents starting from 97% of water with a 1%/min gradient and run time of 10 minutes. The 4,4'-MDA was dissolved in acetonitrile. 10 µL were injected in the HPLC at different dilution factors. Samples coming from the glycolysis and deamination reactions were prepared seemingly; after 1 h sonication and a filtration with 0.2 µm PTFE filters, samples were injected. Calibration line information are reported in the Supplementary Material.

MDA conversion was calculated as:

$$X_{MDA}(t) = \left(1 - \frac{c_{MDA}(t)}{c_{MDA}^0}\right) \cdot 100 \quad (1)$$

In which c_{MDA} is the concentration in ppm of MDA at different sampling times, superscript 0 stands for initial concentration of MDA.

Qualitative analysis of the glycolysis products was carried out by Fourier-transform infrared spectroscopy (FTIR) monitoring urethane, hydroxyl and amine peaks' variations. Spectra were obtained with a

Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific, Waltham (MA), USA) using a Smart iTR Attenuated Total Reflectance sampling accessory equipped with a diamond crystal. Wavenumber range for all spectra is 4000–720 cm⁻¹.

Hydroxyl value of the reaction products was measured according to the ASTM D4274-11^[59] using a Mettler Toledo G20S Compact Titrator (Mettler Toledo Columbus (OH), USA). Finally, dynamic viscosity was measured at 25.0 ± 0.5 °C with a Brookfield viscometer (AMETEL, Brookfield, Middleboro (MA), USA) according to ASTM D4878-15^[60].

Gel permeation chromatography (GPC) was utilized to assess the distribution of molecular weights in the glycolysis products both before and after deamination. In this analysis, we employed a Jasco PU-980 pump model (Jasco, Easton, MD, USA) equipped with three Phenogel size exclusion columns (Phenomenex, Torrance, CA, USA) with particle diameters of 5 µm and pore diameters of 1000 Å, 100 Å, and 50 Å, along with a Jasco RI-830 refractive index detector. Prior to injection, the glycolysis samples were dissolved in tetrahydrofuran (THF) at a concentration of 0.04% w/w and filtered using a 0.1 µm PTFE filter. The samples were eluted at a temperature of 40 °C with a flow rate of 0.35 mL/min. Calibration of the system was achieved using polystyrene standards (Fluka Analytical, Charlotte, NC, USA).

Synthesis of new foams

Reaction products obtained before and after the deamination process were used to produce new PU rigid foams to assess their suitability and performance. Foams were produced with an increasing amount of recycled product and performances evaluated with respect to an equivalent foam obtained with virgin polyols. The synthesis was a one-shot method: isocyanate was added to a premix obtained from polyols, catalysts, surfactants and blowing agents. After a strong mechanical agitation (10 s) the mixture was poured into a pre-heated mold to allow the foam expansion. Foams were cured at 70 °C for 24 h to complete the crosslinking reactions before their characterization. The isocyanate index used was 110.

Characterization of new PU foams

Produced foams were characterized in terms density according to standard ASTM D1622-20^[61], the target density was fixed to 40 ± 5 kg/m³. Dynamometer Galdabini Sun2500 (Galdabini, Cardano al Campo, Italy) was used to measure the compression resistance according to ASTM D1621-16^[62] along the growth direction of the foam. Thermal conductivity was measured through a Holometrix Micromet Lambda 2300 V heat flow meter apparatus (Netzsch, Selb, Germany) according to ASTM C177-19^[63], at mean temperature of 10 °C with a temperature difference of 20 °C between the plates. Scanning electron microscopy (SEM) was employed for the analysis of foams morphology and to measure average cell diameter according to the ASTM D3576-20^[64]. SEM micrographs were collected with a Jeol 6490 SEM (Jeol Ltd., Tokyo, Japan) on gold sputtered samples with an accelerating voltage of 20 kV. All foams were tested one day after their production to prevent any effect related to ageing.

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Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

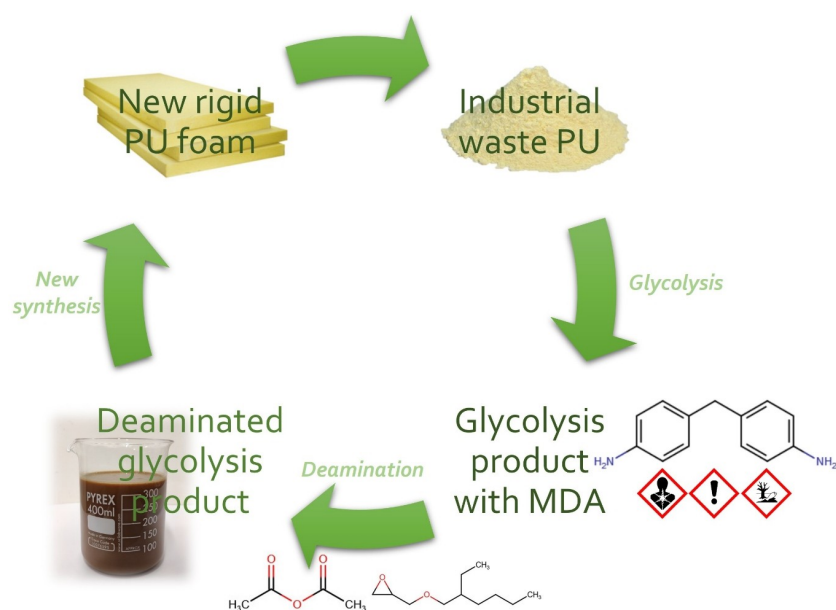
The data that support the findings of this study are available in the supplementary material of this article.

Keywords: aromatic amines · chemical recycling · circular economy · glycolysis · polyurethane foam

- [1] *Official Journal of the European Union* **2008**, 2007/0121/COD, 1–1355.
- [2] ECHA, “4,4'-Methylene dianiline – Substance Infocard,” can be found under <https://echa.europa.eu/it/substance-information/-/substanceinfo/100.002.705>, n.d.
- [3] NIOSH, “4,4'-methylene dianiline – Carcinogen List,” can be found under <http://www.cdc.gov/niosh/topics/cancer/npotocca.html#d>, n.d.
- [4] R. Tillotson, T. E. Crumplin, G. J. Jones, G. Marshall, J. Dawson, *Herit Sci* **2019**, *7*, 5–9.
- [5] T. Nakajima-Kambe, Y. Shigeno-Akutsu, N. Nomura, F. Onuma, T. Nakahara, *Appl. Microbiol. Biotechnol.* **1999**, *51*, 134–140.
- [6] A. Kemono, M. Piotrowska, *Polymers (Basel)*. **2020**, *12*.
- [7] J. Chen, J. Wu, P. C. Sherrell, J. Chen, H. Wang, W. X. Zhang, J. Yang, *Adv. Sci.* **2022**, *9*, 2103764.
- [8] J. A. Chiong, H. Tran, Y. Lin, Y. Zheng, Z. Bao, *Adv. Sci.* **2021**, *8*, 2101233.
- [9] W. R. White, D. T. Durocher, *J. Cell. Plast.* **1997**, *33*, 477–486.
- [10] F. Simioni, M. Modesti, *Mater. Eng.* **1991**, *2*, 127–144.
- [11] D. Simón, A. M. Borreguero, A. de Lucas, J. F. Rodríguez, *Waste Manage.* **2018**, *76*, 147–171.
- [12] C. H. Wu, C. Y. Chang, J. K. Li, *Polym. Degrad. Stab.* **2002**, *75*, 413–421.
- [13] F. Simioni, M. Modesti, *Cell. Polym.* **1993**, *12*, 337–348.
- [14] M. Modesti, F. Costantini, E. dal Lago, F. Piovesan, M. Roso, C. Boaretti, A. Lorenzetti, *Polym. Degrad. Stab.* **2018**, *156*, 151–160.
- [15] B. Godinho, N. Gama, A. Barros-Timmons, A. Ferreira, *J. Polym. Sci.* **2021**, *59*, 697–705.
- [16] Z. Liu, F. Yan, *Adv. Sci.* **2022**, *9*, 2200264.
- [17] M. Modesti, F. Simioni, S. A. Rienzi, *J. Elastomers Plast.* **1992**, *24*, 288–305.
- [18] M. Modesti, F. Simioni, *Polym. Eng. Sci.* **1996**, *36*, 2173–2178.
- [19] A. Gomez-Lopez, F. Elizalde, I. Calvo, H. Sardon, *Chem. Commun.* **2021**, 57, 12254–12265.
- [20] P. Parcheta-Szwindowska, K. Rohde, J. Datta, *J. Therm. Anal. Calorim.* **2022**, *147*, 13329–13339.
- [21] P. Stachak, I. Łukaszewska, E. Hebda, K. Pielichowski, *Materials* **2021**, *14*, DOI 10.3390/MA14133497.
- [22] C. Molero, A. de Lucas, J. F. Rodríguez, *Polym. Degrad. Stab.* **2009**, *94*, 533–539.
- [23] J. Datta, J. T. Haponiuk, *J. Elastomers Plast.* **2011**, *43*, 529–541.
- [24] J. Y. Lee, D. Kim, *J. Appl. Polym. Sci.* **2000**, *77*, 2646–2656.
- [25] “Butyl 2,3-epoxypropyl ether – Substance Information – ECHA,” can be found under <https://echa.europa.eu/it/substance-information/-/substanceinfo/100.017.616>, n.d.
- [26] S. R. Shin, H. N. Kim, J. Y. Liang, S. H. Lee, D. S. Lee, *J. Appl. Polym. Sci.* **2019**, *136*, 1–9.
- [27] M. Modesti, F. Simioni, R. Munari, N. Baldoin, *React. Funct. Polym.* **1995**, *26*, 157–165.
- [28] M.-G. S.-H. J.-H. L.-Y. Kim, *Int. J. Saf.* **2005**, *4*, 14–17.
- [29] N. Gama, B. Godinho, G. Marques, R. Silva, A. Barros-Timmons, A. Ferreira, *Chem. Eng. J.* **2020**, *395*.
- [30] N. Gama, B. Godinho, G. Marques, R. Silva, A. Barros-Timmons, A. Ferreira, *Polymer (Guildf)* **2021**, *219*, 123561.
- [31] R. M. Machado, B. E. Farrell, Air Products and Chemicals Inc., *Process for Modifying the Glycolysis Reaction Product of the Polyurethane Scrap – US005300530*, **1994**.
- [32] R. M. Machado, J. W. Mitchell, J. P. Bullock, B. E. Farrell, *Thermochim. Acta* **1996**, *289*, 177–187.
- [33] H. R. van der Val, The Dow Chemical Company, *Process for Conversion of Polyurethane Polymer to Polyol and Fresh Polyurethane Polymer Therefrom – US005274004 A*, **1993**.
- [34] M. B. Sheratte, McDonnell Douglas Corporation, *Process for Converting the Decomposition Products of Polyurethane and Novel Composition Thereby Obtained – US004110266*, **1978**.
- [35] T. Munzmay, W. Raschofer, W. Meckel, Bayer Aktiengesellschaft, *Process for the Production of Hydroxyl-Group-Containing Compounds from Polyurethane Polyurea and/or Polyurea Wastes – US005635542 A*, **1997**.
- [36] G. Niederdelmann, N. Roemer, J. Schenk, H. Hetzel, E. Grigat, Bayer Aktiengesellschaft, *Process for Separating Polyurethane Hydrolyzates into Polyether and Diamine – US004399236*, **1983**.
- [37] B. Naber, M. Lezius, BASF, *Preparation of Recyclate Polyols – US005556889 A*, **1996**.
- [38] B. Naber, M. Gassan, T. Schupp, S. Chakrabarti, BASF, *Reduction of the Amine Content of Recycled Polyols – US005968992*, **1999**.
- [39] S. Fulev, V. Stoychev, M. Boyadzhiev, H&S Anlagentechnik GmbH, *Method for Producing Polyol Dispersions from Polyurethane Waste and Use Thereof – US20210017*, **2021**.
- [40] V. Stoychev, M. Boyadzhiev, H&S Anlagentechnik GmbH, *Recyclingpolyol – DE102016122276 A1*, **2018**.
- [41] M. Murai, M. Sanou, T. Fujimoto, F. Baba, *J. Cell. Plast.* **2003**, *39*, 15–27.
- [42] H. Lobo, J. V. Bonilla, *Handbook of Plastics Analysis (Plastics Engineering 68)*, CRC Press, **2003**.
- [43] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley & Sons, Ltd, **2004**.
- [44] B. K. Sharma, *Infrared Spectroscopy. Instrumental Methods of Chemical Analysis*, Goel Publishing House, **2005**.
- [45] J. S. Dillon, *Infrared Spectroscopic Atlas of Polyurethanes*, Lancaster, **1991**.
- [46] M.-G. Kim, S.-H. Kim, J.-H. Chun, L.-Y. Soon, *Int. J. Saf.* **2005**, *4*, 14–17.
- [47] C. Huang, X. Sun, H. Yuan, C. Song, Y. Meng, X. Li, **2019**, DOI 10.1016/j.vibspec.2019.102993.
- [48] B. Francis, *Handbook of Epoxy Blends*, Springer Cham, **2016**, 1–27.
- [49] Z. Qiu, K. Wang, Z. Li, T. Li, J. Bai, C. Yin, X. Ye, H. Liu, *J. Chem.* **2018**, *2018*, DOI 10.1155/2018/4627903.
- [50] J. L. Massingill, R. S. Bauer, *Applied Polymer Science: 21st Century*, Elsevier Science, **2000**, 393–424.
- [51] K. Bžáček, H. Beneš, Z. Walterová, S. Abbrent, A. Eceiza, T. Calvo-Correas, J. Datta, *Polym. Chem.* **2021**, *12*, 1643–1652.
- [52] A. Bukowczan, P. Stachak, I. Łukaszewska, T. M. Majka, E. Hebda, K. Pielichowski, *Thermochim. Acta* **2023**, *723*, 179484.
- [53] L. J. Gibson, M. F. Ashby, *Cellular Solids: Structure and Properties, Second Edition*, Cambridge University Press, **2014**, 1–510.
- [54] D. Randall, S. Lee, *The Polyurethanes Book*, Chichester, **2002**.
- [55] P. R. Nair, C. P. Reghunadhan Nair, D. J. Francis, *J. Appl. Polym. Sci.* **1999**, *71*, 1731–1738.
- [56] K. Kamińska, M. Barczewski, M. Kurańska, E. Malewska, K. Polaczek, A. Prociak, *Materials* **2022**, *15*, DOI 10.3390/MA15176087.
- [57] “EPA – Preliminary Information on Manufacturing, Processing, Distribution, Use, and Disposal: 1,4-Dioxane,” **2017**.
- [58] “PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL – Toxicological Profile for 1,4-Dioxane – NCBI Bookshelf,” can be found under <http://www.ncbi.nlm.nih.gov/books/NBK153680/>, n.d.
- [59] ASTM D4274-16, **2016**, 1–10.
- [60] ASTM D4878-15, **2015**, 1–4.
- [61] ASTM D1622-20, **2020**, 1–5.
- [62] ASTM D1621-16, **2016**, 1–5.
- [63] ASTM C177-19, **2019**, 1–23.
- [64] ASTM D3576-04, **2010**, *14*, 1–5.

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RESEARCH ARTICLE



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Deamination of Polyols from the Glycolysis of Polyurethane 

Phasing out of landfilling is inevitable, chemical recycling allows the consideration of plastic waste as a resource

to get the most out of it to produce new valuable materials.