A sip of water in your thermoset: the role of H_2O as an accelerator of the crosslinking reaction of polyhydroxyurethane networks

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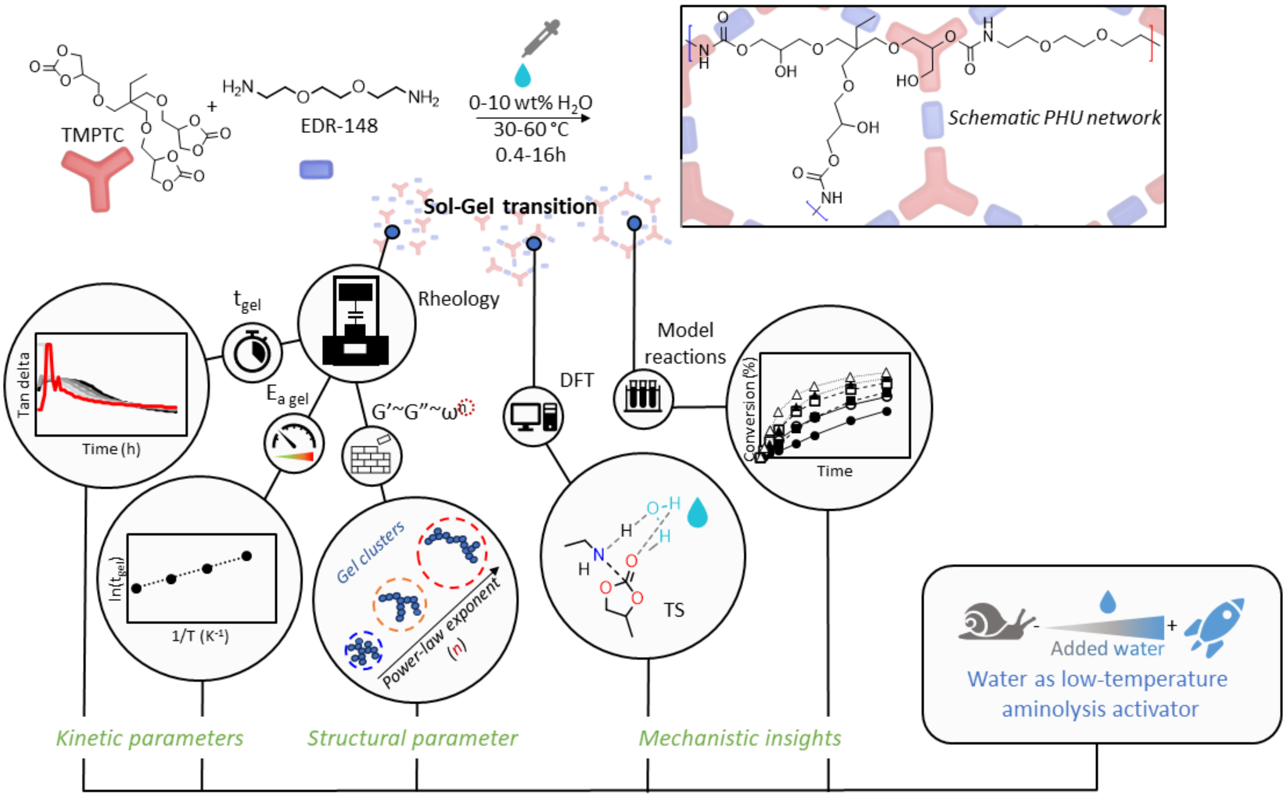
ABSTRACT: The impact of water, added as a diluent, on the sol-gel transition of a model polyhydroxyurethane (PHU) thermoset was investigated using multiwave rheology. An impressive 2 to 5 fold decrease in gel-time, t_{gel}, was observed for water content ranging from 2 wt% to 10 wt% at temperatures close to r.t. (30°C), indicating that water strongly accelerates the crosslinking process. Interestingly, multiwave rheology gives access to the power law exponent of the transition, *n*, a characteristic that has never been considered for PHU thermoset so far. In the frame of the percolation theory, the gradual increase of *n* with water content suggests an increase of the dimension of the PHU clusters at the sol-gel transition, likely due to the strong hydrogen bonding of water with the hydroxyl groups of the growing PHU. This is an unprecedented illustration of the specific interaction of water with the PHU during the crosslinking reaction, that is expected to contribute to an increase of the molecular mobility, and thus of the crosslinking rate. This is well supported by comparing water to other solvents with different hydrogen-bonding ability and polarity. On top of that, model reactions and DFT calculations were conducted to investigate the catalytic role of water on the aminolysis. For the first time, they indicate that water is an effective catalyst, acting as a proton shuttle during the ring opening of the 5cc, and provide an additional explanation for the tremendous impact of water on t_{gel}. In the end, this work introduces water as an accelerating agent for the curing of PHU thermosets at (near)-ambient temperatures, and suggests that multiple mechanisms – both physical and chemical – are at play during the crosslinking reaction.

Polyhydroxyurethanes (PHU) obtained by the aminolysis of CO_2-sourced 5-membered cyclic carbonates (5CC) are one of the most promising isocyanate-free alternatives to conventional polyurethanes (PU).[1] They are extensively investigated as PU substitutes for coating,[2,3] adhesive[4,5] and foam applications,[6–8] to name a few. However, one of their persisting limitations is their seemingly slower polymerization kinetics when compared to isocyanate-based PU, especially at (near)-room temperature (RT).[9] One of the main reasons for it is the progressive formation of a H-bonded network during PHU polymerization, due to their multiple pendant hydroxyl groups.[10,11] The intra- and inter-chains hydrogen bonds refrain the chains mobility and the diffusion of the monomers. Then, it is usually necessary to increase the polymerization temperature ($\gtrsim$ 80 °C) to observe the full conversion of the monomers over a reasonable period of time.[9] Unfortunately, this comes at the expense of side reactions.[12,13] Another alternative consists in the addition of a protic solvent to disrupt the H-bonded network and restore the chain mobility at low temperature. Alcohols, mostly methanol (MeOH), were described as excellent solvent for the synthesis of thermoplastic PHUs.[10,11]

When it comes to the synthesis of thermosets, the use of large amounts of solvent is poorly appropriate. Nevertheless, small additions of unreactive molecules, sometimes called plasticizers, are classically incorporated in thermosetting formulations to impart molecular mobility and to improve the diffusion of the monomers, especially when approaching the vitrification of the polymeric network.[10,14,15] In that case, an imperative prerequisite is to use innocuous compounds as they might leak out of the network and contribute to the emission of volatile organic compounds.

Interestingly, water (H_2O) is well known for its ability to accelerate the crosslinking reaction of epoxy-amine formulations.[16,17] Choi et al. demonstrated that small amounts of H_2O (1 to 3 wt%) are sufficient to significantly accelerate the curing reaction of conventional epoxy resins based on diglycidyl ether of bisphenol A.[16] In that case, a catalytic effect based on a hydrogen-bonded termolecular complex of epoxide-amine-water is suspected to be responsible for the acceleration of the reaction. This well-understood phenomenon is now of industrial importance and is used, for instance, to reduce the curing time of infusion epoxy-amine resins when repairing wind turbine blades.[18]



Scheme 1: General scheme of conducted study on the model PHU formulation composed of TMPTC and EDR148.

Surprisingly, even if the hydroplasticization of PHU thermosets by atmospheric moisture is a well-known phenomenon,[3,6,19,20] the impact of H_2O during the crosslinking reaction of 5CC-amine formulation has never been closely considered. It is likely that the risk to promote the undesired hydrolysis of 5CC has refrained this research axis.[21] However, recent studies demonstrated that, except at high temperatures (> 100 °C) or in the presence of specific catalyst,[22] 5CC are quite stable in aqueous media. For instance, using hydrophilic monomers, Bourguignon et al. recently reported the synthesis of PHU hydrogels at RT.[23–25] In contrast with

PHU thermosets synthesized in bulk, the crosslinking time of these hydrogels are extremely fast (gel time, t_{gel} < 10 min), thus suggesting that water helps in accelerating the polymerization reaction. During their investigation of a lignin-based poly-5CC, Salanti et al. observed that, when performed in water as a solvent, the aminolysis of the carbonates was much faster than in other conventional organic solvents.[26] The authors concluded on a catalytic effect of water, without further investigation of it.

Herein, the impact of water, introduced as an additive (2 to 10 wt%), was investigated for the crosslinking reaction of common thermosetting 5CC-amine formulations. An in-depth rheological study of the crosslinking reaction, using a multiwave methodology, reveals a tremendous decrease of the gel time, t_{gel}, when water is added. Moreover, for the first time, the frequency dependence of the mechanical response of the critical gel – i.e. the PHU at t_{gel} – is considered, illustrating that water strongly interact with the growing polymer network. Eventually, model reactions and computational calculations were used to rationalize the catalytic role of water during the aminolysis of 5CC.

Results and discussion

The experiments were performed on a formulation comprising trimethylolpropane triglycidylcarbonate (TMPTC) as a trifunctional cyclic carbonate, and 2-bis(2-aminoethoxy)ethane, *i.e.* Jeffamine EDR148, as a diamine. Structures of the precursors can be seen on Scheme 1. Both reactants were carefully dried before use (see ESI). They were first mixed in stoichiometric proportions (*i.e.* 5cc:NH_2 = 1:1), without any additives, before introduction in the rheometer (parallel plates, Ø 25 mm) preheated at 40°C. Their crosslinking reaction was investigated through *small amplitude oscillatory shear* (SAOS) experiments, using *Fourrier transform mechanical spectroscopy* (FTMS)[27] to record the storage (G'(ω)) and the loss (G''(ω)) moduli at different frequencies, ω, simultaneously (i.e. multiwave mode of the rheometer). In order to precisely identify the sol-gel transition, the gel time, t_{gel}, was determined using the Winter-Chambon criterion (detailed procedure in ESI).[8,13,28–30] According to this criterion, the relaxation modulus of the network at the gel point, also called the *critical gel*, follows a power law: G(t) ~ t^{-n}, where *t* is the time and *n* is called the critical exponent. Thus, G'(ω), and G''(ω) are expected to depend on frequency in an identical manner: G'(ω) ~ G''(ω) ~ ω^n. This means that, at t_{gel}, the loss factor Tanδ(ω) = G"(ω)/G'(ω) is independent of ω. In practice, G'(ω) and G''(ω) are monitored at different frequencies, ω, and Tanδ is plotted for all of them as a function of time. Then, t_{gel} corresponds to the intersection point of the different Tanδ(t) plots. This is well represented for the dry sample in Figure 1A. The storage and loss moduli were recorded at 5 different frequencies, ω = 1, 3, 10, 30 and 100 rad/s, and the plot of Tanδ(t) intersect for t_{gel} = 5.1 h. This experiment was repeated for the same system with the addition of 5 wt% (Figure 1B) and 10 wt% (Figure 1C) of water revealing the dramatic impact of the additive on the sol-gel transition. t_{gel} dropped from 5.1 h for the dry system to 1.6 h and 0.9 h for the systems containing 5 wt% and 10 wt% of water, respectively. This is well illustrated by plotting t_{gel} as a function of the water content in Figure 1D (black plot). It is worth mentioning that the addition of 2 wt% of water is already sufficient to observe a significant decrease of the gel time to t_{gel} = 2.9 h (Table S2). For this system, the limit of water solubility was determined to be between 10 and 15 wt%, beyond which the presence of 2 heterogeneous phases persist even after 2 minutes of mixing (at room temperature). 10 wt% was then the maximum water content considered in this study. For each experiment (curing at 40 °C with 0, 5 and 10 wt% of added water), triplicate measurements confirm their excellent reproducibility. The variation of t_{gel} was always within less than 4% of deviation.

Similarly, the effect of water was investigated at three other temperatures: 30°C, 50 °C and 60 °C (Figure S3, Table S2). The variation of t_{gel} as a function of the water content is represented in Figure 1D for all the temperatures. The addition of 5 wt% of water in a dry formulation leads to a 4 fold decrease of t_{gel} from 15.5 h to 3.93 h at 30 °C, against a 2 fold decrease from 0.91 h to 0.44 h at 60 °C. Clearly, the magnitude of the impact of water on t_{gel} decreases with increasing temperature. This temperature dependance was used to

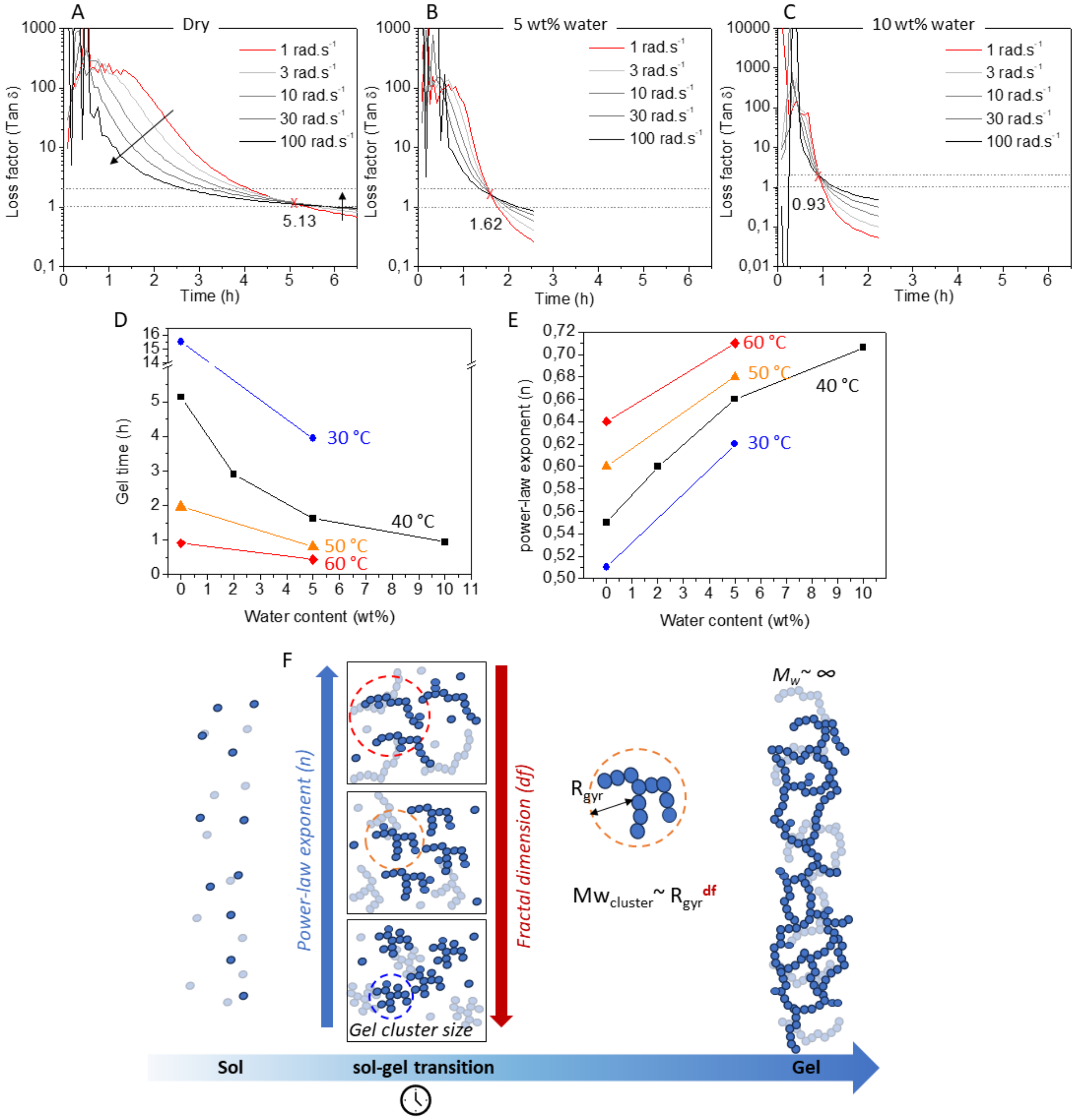


Figure 1: SAOS experiment in multiwave mode (FTMS), 1.9% global strain amplitude, 1-3-10-30-100 rad/s studied oscillation frequencies. Gelation timing at 40 °C are studied with 0 wt% (A), 5 wt% (B) and 10 wt% (C) of added water as the crossing point of the loss factor (Tan δ) at the various frequencies. Horizontal doted lines correspond to loss factor values of 1 and 2. Resulting gel time measured at various temperature according to the Winter-Chambon criterium (D). Corresponding values of the power-law exponents (E). Schematic relationship between the power-law exponent and the dimension of pre-gel clusters (F).

estimate the apparent gelation-energy, Ea_g, *via* a classical Arrhenius plot (Figure S4, more details in ESI).[31]A decrease of Ea_g from around 80 kJ mol^{-1} for the dry formulation to 61 kJ mol^{-1} for the formulation containing 5 wt% of water further illustrates the ability of water in accelerating the crosslinking process of the PHU system. This was further confirmed by monitoring the reaction through IR spectroscopy (ESI, Figure S5). The decrease (*resp.* the increase) of the intensity of the band at 1790 cm^{-1} (*resp.* at.1700 cm^{-1}) corresponding to the vibration of the C=O bond of the 5CC (*resp.* the urethanes) is much faster in the formulations containing water. Unfortunately, quantitative information cannot be extracted from these measurements due to the impossibility to measure the intensities of the bands at $t = 0$.

We first hypothesized that one of the underlying mechanism of the accelerating role of water is the well-known hydroplasticization of PHU resulting from the formation of hydrogen-bonds between water and the pendant hydroxyl groups of the polymer.[3,6,19] The specific interaction of water with the growing PHU network is expected to increase the polymer chain's mobility and the diffusion of the unreacted monomers, thus contributing to an acceleration of the crosslinking reaction and a decrease of t_{gel}. Conveniently, the multi-wave methodology used during the rheological monitoring provides an unprecedented illustration of this phenomenon. Indeed, in addition to the accurate determination of t_{gel}, the frequency dependence of the moduli in the vicinity of the sol-gel transition, $G'(\omega) \sim G''(\omega) \sim \omega^n$, gives access to the critical exponent, n (see ESI for details). In the frame of the percolation theory, that is conventionally used to describe the sol-gel transition of a thermoset, the formation of the *critical gel* – *i.e.* the polymer at t_{gel} – results from the interconnection of clusters of polymer that grow separately (Figure 1F). Right before gelation, it is demonstrated that the critical exponent, *n*, is related to the fractal dimension of the clusters, d_f. This exponent relates the mass of the objects, $Mw_{cluster}$, to their spatial size, R_{gyr}, *i.e.* their gyration radius: $R_{gyr}^{d_f} \sim Mw_{cluster}$.[32] Further elaborations of the percolation theory indicate that the critical exponent is proportional to the inverse of the fractal dimension: $n \sim 1/d_f$. With these considerations in hand, it is well accepted that clusters with poorly cross-linked structures and/or expanded by molecules of solvent (or unreacted monomers), will exhibit a small fractal dimension, d_f, and thus a large critical exponent, *n*.[33–35] Inversely, tightly crosslinked clusters will exhibit large d_f and small exponent *n* (Figure 1F).

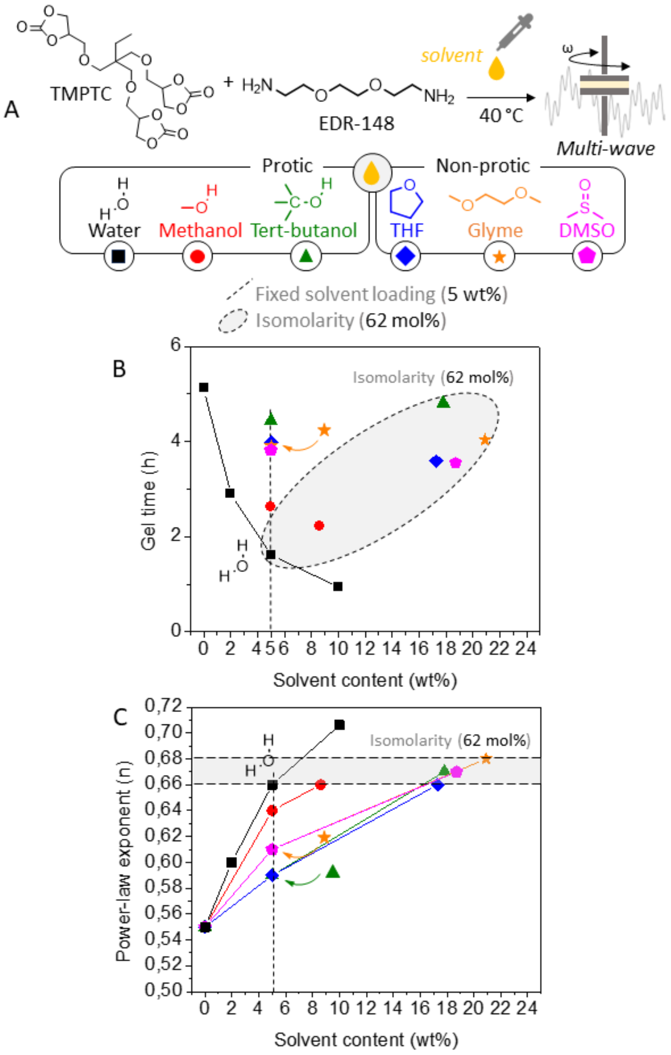


Figure 2: Measured gel-time for the model formulation (A) according to the Winter-Chambon criterium for various solvent species at both fixed solvent loading (5 wt%) and the same molar content (62 mol% by respect to 5cc) at 40 °C (B). Corresponding values of the power-law exponent (C).

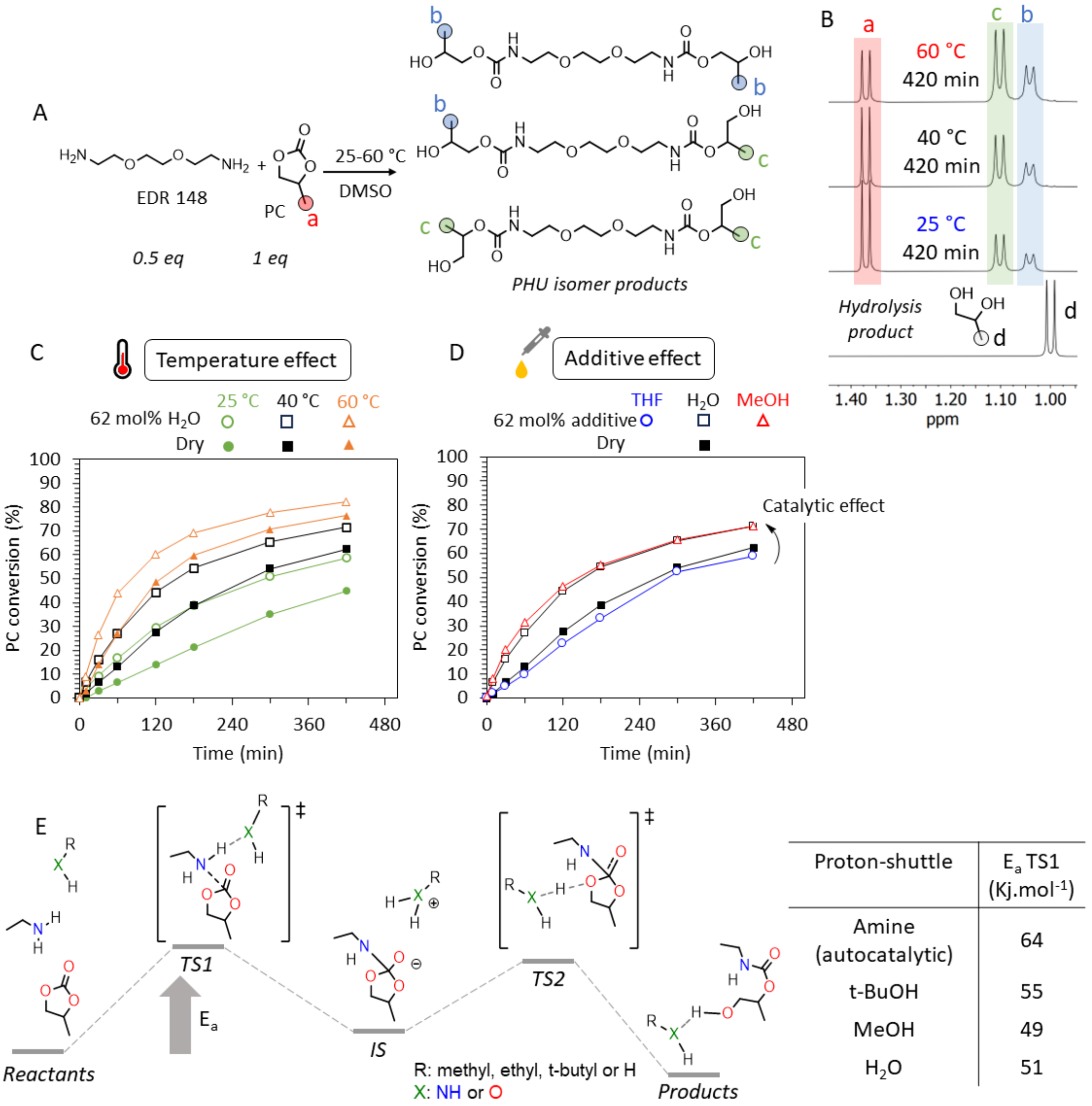
Using the preceding rheological measurements, the value of *n* was measured for the crosslinking reactions of TMPTC with EDR-148 in the presence of various amount of water, and at different temperatures (see ESI for the detailed procedure, Figure S5). For all temperatures, the evolution of *n* as a function of the water content is plotted in Figure 1E. Clearly, *n* is an increasing function of the water content in all cases. For instance, at 40 °C, *n* increases from 0.55 for the dry system to 0.71 for the system containing 10 wt% of water. Considering the scaling laws of the percolation theory, it can be concluded that water results in an expansion of the clusters before the gel points, which is consistent with its expected affinity for the hydroxyl functions of PHU and the hydroplasticization effect. Let's note that *n* variations of similar magnitude were reported for the crosslinking of PDMS gels with the additions of small amounts of good solvents of the polymer.[34] For a given water content, for instance 5 wt%, *n* increases from 0.61 at 30 °C to 0.71 at 60 °C. The temperature dependence of the critical exponent is classically explained due to variations of molecular mobility.[36,37] In the end, the multiwave investigation of the crosslinking reaction of the PHU confirms the strong interaction of water with the growing clusters of polymer. As expected, this will disrupt the intra/inter-chains hydrogen bonds of the clusters, improve their molecular mobility and, in return, accelerate their growing rate (Scheme S1).

To further test the validity of our experimental approach, water was compared to other solvents (Figure 2A). We selected two alcohols (protic solvents): methanol (MeOH) that was described as a good solvent for the synthesis of PHU due to its ability to decrease inter- and intra-molecular hydrogen-bonding, and tert-butanol (*t*-BuOH), a bulkier alcohol. Three non-protic polar solvents were also tested including dimethylsulfoxide (DMSO) and two ethers: tetrahydrofuran (THF) and Glyme. They are all good solvent of the precursors. They were first compared for a constant loading of 5 wt%. Rheology data are provided in ESI (Figure S6- S8). The gel times are reported in Figure 2A (points located on the same dashed line). All the non-protic solvents have a very similar impact on the crosslinking reaction, with t_{gel} ~ 4 h, *i.e.* a moderated acceleration as compared to the additive-free system (t_{gel} ~ 5 h), without common measure with water (t_{gel} ~ 1.6 h). For MeOH, t_{gel} ~ 2.6 h. This is the shortest gel time of all the tested solvents after water. Surprisingly, *t*-BuOH exhibit the longest gel time (t_{gel} ~ 4.4 h) of the series. Similarly, the critical exponent, *n*, are reported in Figure 2C (point located on the same dashed line). The use of all the solvents results in an increase of *n* as compared to the additive free system, but of smaller magnitude than water. Again, MeOH (*n* = 0.64) is responsible for the biggest increase after water (*n* = 0.66). Back to the percolation theory, this observation indicates that MeOH induces a substantial expansion of the pre-gel clusters, just like water and in good accordance with its ability to reduce t_{gel}. Once again, the protic-character of the two substances and their hydrogen-bonding capability with the growing PHU (both as donors and acceptors) seem to contribute to their ability to accelerate the crosslinking reaction. The contradictory performances of the other protic solvent, *t*-BuOH (*n* = 0.59), is likely due to its lower affinity with the PHU clusters, as compared to MeOH and water. This is well confirmed by the swelling experiments performed later in this study (Table 1).

It is worth noting that, by using a constant mass loading for all the solvents, their molar percentage as compared to the monomers is much smaller than water, the additive with the smaller molar mass. Thus, all the solvents were further compared by using the same molecular content. They were used at ~ 62 mol% by respect to 5CC moieties (this corresponds to the molar ratio of water when it is used at 5 wt%). The gel times, t_{gel}, and the critical exponent, *n*, are reported in Figure 2B and 2C, respectively (points located in the same grey area). Interestingly, at this molar ratio, all the solvents induce a similar, or even longer, gel time than previously reported at 5 wt% loading. The increase of the molar ratio does not improve their ability to accelerate the crosslinking reaction. However, for all of them, the critical exponent is now close to *n* ~ 0.67, *i.e.* the value reported for water. In reality, for these mass loadings (~ 18-20 wt%), it is likely that the excessive dilution of the monomers cancels the potential benefits of the increase of the molecular mobility of the clusters. For instance, Palmese et *al.* reported a decrease of the crosslinking kinetics of epoxy-amine formulations containing ≥ 20 wt% of THF.[38] When considering MeOH, the increase of its molar ratio results in further decrease of t_{gel} (~ 2.2 h), just like water. Contrarily to the other solvents, the corresponding increase of its mass loading is moderated (62 mol% = 8.6 wt%), thus limiting the risk of a dilution effect.

Eventually, these series of rheological experiments demonstrate that small protic molecules are excellent accelerating agents of the crosslinking reactions of PHU, and it illustrates that one of the underlying mechanisms is their expected ability to specifically interact with the PHU clusters of the critical gel, *via* hydrogen bonding, even at very small mass loading (~ 5wt%). Clearly, in all the tested conditions and within the limit of its solubility with the monomers, water always exhibit the shortest t_{gel}.

It led us to think that water might also play the role of a catalyst of the aminolysis reaction, just like it does for the addition of amine onto epoxides.[16,39] To test this hypothesis, a simple model reaction was performed by mixing propylene carbonate (PC) with our model diamine (EDR148) in dilute medium (DMSO, [PC] ~ 5 mol.L^{-1}), both in dry conditions and in the presence of a controlled amount of water (Figure 3A). Dried precursors were first mixed together, in a closed vial to prevent moisture uptake, and the reaction was performed at 40 °C under continuous stirring. The same reaction was then performed in the presence of 62 mol% of water as compared to PC, *i.e.* the H_2O:5CC ratio used in the thermosetting formulation containing 5 wt% of water. Both experiments were also performed at 25 °C and at 60 °C. Figure 3B displays the NMR spectra of the model reactions containing water, after 420 min, for the different temperatures (detailed NMR results in ESI, Figures S9-S20). The consumption of PC can be attested by the disappearance of the doublet **a** at 1.37 ppm while the concomitant formation of the two regioisomers of hydroxyurethane is confirmed by the appearance the doublets **b** and **c** at 1.05 ppm and 1.15 ppm, respectively. Importantly, these spectra were compared to that of propylene glycol, PG, the hydrolysis product of PC. The methyl protons of PG (doublet **d**, 1 ppm) are not quantifiable in the model reactions, thus confirming the very limited extent of hydrolysis in these conditions. The PC conversion as a function of time is plotted for the different model reactions in Figure 3C. Clearly, for all temperatures, the kinetics are faster in the presence of water. Triplicate of the reactions performed at 40 °C (Table S4), confirm the excellent repeatability and support the significance of our results. Thus, these



Proton-shuttle	E_a TS1 (Kj.mol^{-1})
Amine (autocatalytic)	64
t-BuOH	55
MeOH	49
H_2O	51

Figure 3: Model reaction has been performed between PC and EDR 148 in dry DMSO at various temperatures (A) both without and with added water. NMR monitoring of the reaction when water was added is given (B) with a spectrum of the not-observed product of PC hydrolysis (bottom spectrum). Following of the methyl groups signals between 1 and 1.4 ppm allowed to monitor the PC conversion over time at various temperatures (C). Working at the single temperature of 40 °C, the impact of added solvent nature was also studied (D). Catalytic effect was further confirmed by computing the energy profile of the reaction with various proton-shuttling species (E).

experiments reveal the catalytic ability of water for the aminolysis of 5cc. Water was then substituted by MeOH and THF in the same conditions. The conversion profiles of PC are plotted in Figure 3D. It indicates that MeOH displays a catalytic activity comparable to that of water, while THF has no impact on the kinetic (i.e. same conversion profile than the additive-free system). These results are in accordance with the trend observed in rheology. In reality, the catalytic activity of protic compounds such as H_2O and MeOH can be rationalized through a mechanism that was already described for amine R-NH_2. Indeed, it is well accepted that amine can accelerate their own addition on 5cc through an autocatalytic mechanism (Figure 3E, X = NH).[40,41] The catalytic amine acts as a proton shuttle, with an intermediary state, IS, corresponding to a cyclic amino alkoxide anion interacting with a NH_3^+ ammonium. H_2O or MeOH can play a similar role with an IS made of the same anion in interaction with a hydronium cation (H_3O^+, X = O, R = H) or a methoxonium cation ($MeOH_2^+$, X = O, R = Me), respectively. To test these hypotheses, DFT calculations were conducted to compare the catalytic activity of R-NH_2, MeOH and H_2O (Figure S21, S22). The energy of the first transition states (TS1) is reported in Figure 3E for the formation of primary hydroxyurethane. Clearly, for the rate determining step, TS1 is approximately 14 kJ mol^{-1} smaller in the case of MeOH and H_2O as compared to R-NH_2, thus suggesting that they are better catalysts. The same trend is confirmed for the formation of secondary hydroxyurethane (Figure S21B). In the end, these calculations are in good accordance with the results of both the rheological measurements and the model reactions.

Fully cured samples of PHU (TMPTC + EDR 148, 5cc/NH_2 = 1, 50 °C, 8h) were prepared to evaluate their affinity with some of the relevant solvents tested as additives. Vacuum dried samples (16h, 50 °C) were swollen in water, MeOH and *t*-BuOH as protic solvents, and in THF. Their swelling index (SI) as well as their linear swelling ratio (λ), were measured over a period of 48 h (ESI, Figure S23). The stabilized values of SI and λ are reported in Table 1, along the estimation of the gel content (GC). Clearly, water, MeOH and THF are good solvents of the PHU network with SI (resp. λ) comprised between 46% (resp. 1.15) for water and 91% (resp. 1.31) for MeOH. These results indicate that water is not the best swelling solvent. However, they reveal that its affinity with the PHU network is much bigger than its affinity with the starting monomers. Indeed, ~ 46 wt% of water can swell the PHU network, while no more than ~ 10-15 wt% of water can be added to the initial mixture of TMPTC + EDR 148. This observation correlates well with the results of rheology. They indicate that, during the crosslinking reaction, water will have much more affinity for the growing PHU clusters, than for the mixture of monomers. Water will greatly contribute to the expansion of the clusters, which is in accordance with the large increase of the critical exponent *n*. Inversly, *t*-BuOH affinity for the PHU network is significantly lower than the rest of the tested solvents, with SI ~ 11% (λ ~ 1.03). In comparison, we were able to add ~ 20 wt% of *t*-BuOH to the initial mixture of TMPTC + EDR 148 (Figure 2C), thus suggesting that it has a better affinity with the monomers. Again, this observation correlate well with the result of rheology, and with the very limited increase of the critical exponent *n* observed with *t*-BuOH as compared to the other protic solvents.

The thermal properties of the cured samples were measured in DSC (Table 1). The T_g increases from 0 °C to 13 °C before and after vacuum drying which is consistent with the usual hydroplasticization effect. It also validates that, for all the rheological measurements, the temperature of the experiment was ~ 20 °C above the T_g of the network, which is enough to guarantee that gelation and vitrification will not interfer. Finally, the porperties of a PHU network cured with 5 wt% of water were compared to those of the additive free sample (Table 1). Except for a significant decrease of T_g prior drying, they are essentially the same. The similarity of the two samples was further confirmed by comparing their IR spectra (Figure S25)., which are superimposable.

Finally, to further evaluate the role of water as an accelerating agent of the crosslinking reaction of PHU, we tested it for the reaction of TMPTC with another common diamine hardener, metaxylylene diamine (MXDA, Figure 4A). The crosslinking reaction was monitored through multiwave rheological measurements at 70 °C, for the dry system and for the system containing 5 wt% of water. The evolution of the Tan(δ) curves as a function of time are represented in Figure 4B and Figure 4C, respectively. A significant decrease of t_{gel} from 1.6 h to 0.5 h is observed thus confirming that water accelerates the crosslinking reaction of this system as well. It is worth noting that, for this system, the T_g of the dried and fully cured network is ~ 45 °C (Figure S28A). Thus, when monitoring the reaction in rheology for the dry system at lower temperatures than 70 °C, vitrification interferes with gelation. In particular, at 50 °C, multiwave rheology indicates that the system vitrifies before gelation (Figure S26B), such behavior is in agreement with other works on high T_g thermosets.[42] Conveniently, the addition of 5 wt% of water lower the T_g of the growing network (hydroplasticization) and the

Table 1: Characterization of model thermosets under dry and 5 wt% water loaded conditions

Sample	T_g (°C) of the *as-cured* sample[c]	T_g (°C) of the *dried* sample[d]	Swelling solvent[e]	Swelling index (SI, %)[f]	Linear swelling ratio (λ)[g]	Gel content (GC, %)[h]
No additive, Dry[a]	0	13	H_2O	47	1.15	91
			THF	66	1.21	98
			MeOH	92	1.31	90
			t-BuOH	11	1.03	> 99
H_2O, 5 wt%[b]	-7	10	H_2O	52	1.13	91
			THF	68	1.19	99
			MeOH	103	1.34	88
			t-BuOH	11	1.04	> 99

[a] Materials prepared from TMPTC and EDR148 (5CC:NH_2=1:1) after 8h of curing at 50 °C. [b] same as [a] with 5 wt% water. [c] Glass transition temperature from the cured sample on the 1st DSC cycle. [d] Glass-transition temperature of the cured material after drying at 50°C under vacuum for 16h on the 3rd DSC cycle. [e] The samples immersed in the swelling solvent were obtained from the model formulations cured for 8h at 50 °C + dried 16h at 50°C under vacuum.[f] Typical error barre is ±1%. [g] Typical error barre is ±0.03. [h] Typical error barre is ±1%.

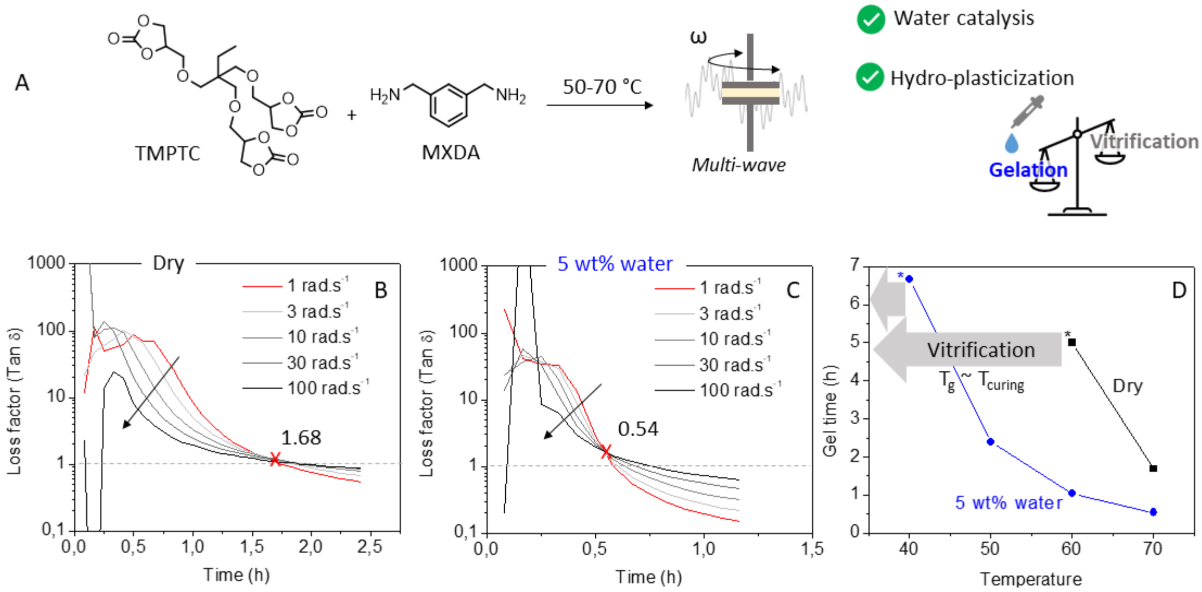


Figure 4: Preliminary test on a formulation comprising an aromatic diamine (MXDA) (A). Obtained SAOS Tanδ curves in FTMS modes at 70°C (B). Water addition led to faster gelation (C). Representation of the temperature range in which competition between gelation and vitrification is observed for both dry and 5 wt% water loaded formulations (D), datapoints with a star are points for which vitrification interferes with gelation despite a gel-point is present .

system can form a crosslinked gel (Figure S26C). Noteworthily, the power-law exponent was also affected by this vitrification interference (Figure S29, table S5 and related discussion).

To conclude, this work provides the first in-depth investigation of the role of water during the crosslinking reaction of PHU thermosets. Rheology measurements, using a multi-frequency approach, indicates that even very small amounts of water (< 5 wt%) can have a tremendous impact on t_{gel} (2 to 5 folds decrease). The multi-frequency methodology provides an unprecedented illustration of the strong interaction of water with the the critical PHU gel, which is expected to improve their molecular mobility and, in return, to accelerate their growing rate. Moreover, a combination of model reactions and DFT calculations reveals the catalytic role of water during the aminolysis of the 5CC and a mechanism is proposed for the first time.

Just like for epoxide resins, our results suggest that small amounts of water absorbed in the course of the curing reaction, or during the storage of the precursors, can significantly influence the crosslinking rate. While this might be of interest to accelerate some industrial processes (e.g. coatings, adhesion), PHU users must be well aware of potential repeatability issues if moisture uptake is neglected. By shedding light on this phenomenon, the present study underlines that it is of prime importance to fully understand the accelerating role of water, either to exploit or to prevent it.

AUTHOR INFORMATION

Author Contributions

FM: Conceptualization, methodology, validation, investigation, data curation, writing – original draft, TV: Conceptualization, methodology, validation, writing-review & editing, supervision. EG: Formal analysis, validation, investigation, resources, writing-review & editing.CD, HC: Conceptualization, validation, resources, writing-review & editing, supervision, project administration. BG: validation, resources, writing-review & editing, supervision, project administration.

Funding Sources

This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement no. 966700.

ACKNOWLEDGMENT

This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement no. 966700. Dr. Péroline Helbling is warmly acknowledged for discussions preliminary to the project.

ABBREVIATIONS

5CC, 5-membered cyclic carbonate; TMPTC, trimethylolpropanetriglycidyl-carbonate; EDR 148, 1,2-bis(2-aminoethoxyethane); THF, tetrahydrofuran; MeOH, methanol; DMSO, dimethyl sulfoxide; SAOS, small amplitude oscillatory shear experiment; FTMS, Fourrier transform mechanical spectroscopy; PC, propylene carbonate; MXDA, metaxylylene-diamine; Tg, glass-transition temperature; SI, swelling index; GC, gel content; DSC, differential scanning calorimetry

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