International Journal of Adhesion and Adhesives 92 (2019) 105–110

Contents lists available at ScienceDirect

International Journal of Adhesion and Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Improvement of storage stability of UF resins by adding caprolactam

P. Pereira[a], M. Almeida[b], J. Pereira[b], N.T. Paiva[a], J.M. Ferra[a], J. Martins[c,d], L. Carvalho[c,d], F.D. Magalhães[d,*]

[a] *EuroResinas – Indústrias Químicas, 7520-195, Sines, Portugal*
[b] *ARCP - Associação Rede de Competência Em Polímeros, Rua Dr. Júlio de Matos 828/882, Porto, Portugal*
[c] *DEMad - Instituto Politécnico de Viseu, Campus Politécnico de Repeses, 3504-510, Viseu, Portugal*
[d] *LEPABE-Faculdade de Engenharia da Universidade Do Porto, Rua Dr. Roberto Frias S/n, 4200-465, Porto, Portugal*

ARTICLE INFO

Keywords:
Adhesives for wood
Urea-formaldehyde resins
Aging
Reaction blocker

ABSTRACT

During storage, the structure of urea-formaldehyde (UF) resins suffers modifications due to reactions between monomers, oligomers, polymer and free formaldehyde, leading to increase in viscosity and decrease in pH. Eventually, viscosity reaches a value that renders the resin unusable, and it must be disposed off. This aging process is accelerated if storage temperature increases.

The aim of this work is to obtain UF resins with long storage stability, even when exposed to relatively high temperatures, such as 40 °C. The main strategy adopted was the addition of a chain growth blocker, caprolactam. This monofunctional compound reacts with end groups, blocking them and therefore reducing the polymer's reactivity. In addition, a weak base was added to adjust the pH value, instead of the traditional strong base, sodium hydroxide, therefore hindering the *Cannizzaro* reaction.

The storage stability of UF resins with formaldehyde to urea molar ratio of 1.6–2.0 was monitored by pH and viscosity measurements. Caprolactam was added in different amounts and at different reaction stages. It was found that 10% addition at the beginning of condensation led to the best results, giving a much higher storage stability at 40 °C (2 months when compared to 4 days for a commercial UF resin with low F/U molar ratio). As expected, the resin reactivity decreased with caprolactam addition, demanding for longer pressing times for wood-based panel manufacture. These verified the internal bond strength specification for EN 312 - P2 standard class. Formaldehyde content in the panels was above the E1 class limit when fresh or one month old modified resins were used, implying addition of formaldehyde scavengers. The resin stored for 2 months allowed producing panels within E1 limit. These preliminary results demonstrate the concept that addition of an end-group blocker during UF synthesis is an effective strategy for improving storage stability, encouraging future work on alternative compounds and synthesis conditions optimization.

1. Introduction

Urea-formaldehyde (UF) resins are synthetic thermosetting polymers obtained via condensation reaction of urea and formaldehyde. These resins are widely used as adhesives in wood-based panels, thanks to their low price, high reactivity and water dispersibility [1]. Their properties are influenced by different synthesis parameters, like the formaldehyde/urea molar ratio, the reaction temperature, and the pH values during each reaction step. Linear or branched polymer structures, for instance, may be preferentially formed depending on these reaction conditions [1–3].

Along with the resin storage, an increase in viscosity is usually observed due to physical or chemical interaction between the species present [4]. When it increases above a certain limit, the resin becomes unfit for practical use and has to be disposed off. Viscosity measurement is therefore the commonly used form of evaluation of resin storage stability.

Despite the practical relevance of the topic, very little information can be found in the literature concerning storage stability of these resins. Contrary to melamine-formaldehyde resins, in urea-formaldehyde resins the main process associated with resin ageing is considered to be chemical reaction progress, and not physical aggregation [5]. Degree of polymerization continues to increase due to condensation reactions between amino and hydroxymethyl groups, leading to the formation of methylene and methylene-ether linkages, therefore increasing resin viscosity [4,6–8]. Lee and co-workers studied UF resins behavior under

---

[*] Corresponding author.
E-mail address: fdmagalh@fe.up.pt (F.D. Magalhães).

https://doi.org/10.1016/j.ijadhadh.2019.04.005
Accepted 13 April 2019
Available online 16 May 2019

different storage temperatures, observing an expectable decrease in stability as temperature increases [9]. Kim and co-workers discussed the physico-chemical processes occurring during storage, and the influence of initial formaldehyde to urea (F/U) molar ratio. However, the authors did not present approaches for improving storage stability [10]. High F/U molar ratios at the end of synthesis have been seen to favor stability [11]. A recent patent describes the use of glycerin as a comonomer to increase UF storage stability [12]. In addition to polycondensations, another reaction should be taken into account during the storage period. Formaldehyde and the base commonly present, sodium hydroxide, may react according to the Cannizzaro reaction. This leads to a decrease in pH [13], which has a negative effect on storage stability, since the rate of condensation is promoted by low pH, resulting in faster polymer growth. Formation of methylolureas during storage also leads to a decrease in pH.

The strategy followed in the current work for improving storage stability of UF resins involves three simultaneous approaches:

1) Stabilizing the pH by using a weak base instead of the usual sodium hydroxide, avoiding the occurrence of Cannizzaro reaction.
2) Keeping F/U molar ratio high during storage, by adding the final urea only prior to mixing the resin with wood particles for particleboard production.
3) Adding a monofunctional comonomer (caprolactam) to block some of the polymer's reactive groups.

The major goal is to accomplish a resin formulation capable of remaining stable for two months at 40 °C, while maintaining appropriate performance for use as particleboard binder.

2. Materials and methods

2.1. Materials

The following industrial-grade reagents were supplied by Euroresinas S.A. (Sines, Portugal): commercial UF resin, urea, formaldehyde 55 wt%, caprolactam, sodium hydroxide 50%, ammonium sulphate and acetic acid 25%. Sodium bicarbonate was purchased from Sigma Aldrich. The chemicals were used as received without further purification.

Wood particles were provided by a particleboard manufacturer (Sonae Arauco Portugal, SA, Oliveira do Hospital).

2.2. Synthesis of UF resins

UF resins were synthesized according to the alkaline acid synthesis process, described elsewhere [14]. A round bottom flask (volume 2 L) was used, equipped with mechanical stirrer, water cooled condenser and a thermometer. Formaldehyde solution (55% wt. in H_2O) and sodium hydroxide (50% (m/m)) were added to adjust the pH for values between 8.0 and 9.0, followed by the addition of the first urea. After the methylolation step at 70–90 °C, the pH was once again adjusted to values between 5.0 and 6.5 to start the condensation step. Then, the second urea was added. When the viscosity reached the 200–350 mPa s, a base (sodium hydroxide or in the modified formulation, sodium bicarbonate) was added to stop the condensation step. Thethird amount of urea was added, either, in the conventional formulation, after base addition or, in the modified formulation, only at the end of storage time, before characterization analysis or mixing with wood particles. The amount of urea added was such as to lower the F/U molar ratio from a value between 1.6 and 2.0 to a final value between 1.10 and 1.15. The formulation neutralized with sodium bicarbonate and the third urea added at the end of storage was adopted as the reference resin for the caprolactam incorporation studies.

2.3. Incorporation of caprolactam

Caprolactam was alternatively added in different moments of the synthesis process: step 1 (addition at the beginning of condensation, before the second urea); step 2 (addition after the second urea, when viscosity reaches 100–200 mPa s); step 3 (addition at the end of the synthesis). In the two first cases the pH of the medium is acid and the temperature around 75–90 °C. In the third, the pH is basic and the temperature is 30–50 °C. The percentage of caprolactam added (5 or 10 wt%) is related to the total amount of resin solids, including the second urea.

2.4. Characterization

Viscosity, pH, gel time, and solids content were determined at the end of each synthesis. Viscosity was measured with a Brookfield viscometer. The resin pH was measured using a combined glass electrode. The resin gel time was determined by measuring the time needed for resin gelification at 100 °C, after addition of a cure catalyst (ammonium sulphate). The solid content was determined by evaporation of volatiles from 2 g of resin for 3 h at 120 °C. In order to evaluate the stability of the resins, they were stored in an incubator at 40 °C, and the viscosity was periodically measured with a Brookfield viscometer at the same temperature.

2.5. ABES

Two beech veneer strips were used, each measuring 0.5 mm thick, 20 mm wide and 117 mm in length. They were glued together with an overlap of 5 mm, using a resin amount of 6 mg. The trial conditions were 3% of catalyst and at a temperature of 105 °C.

2.6. Particleboard production

Production of particleboards is divided into four stages: preparation of raw materials, blending, mat formation, and pressing. Standard mixtures of wood particles were used for the core and face layers, which are composed of pine, eucalyptus, pine sawdust, and recycled wood. The moisture content of the standard mixtures was checked before blending to ensure that the mixing process was efficient. Wood particles were then blended with the resin, catalyst and paraffin in a laboratory glue blender. The glue content was 6% (resin solids to oven-dry weight of wood particles) in both layers. The cure catalyst, amount of ammonium sulphate, was 1% (based on solid resin) in the face layer and 3% in the core layer. The amount of paraffin was 2% (based on solid resin) in both layers. The glued particles mat was prepared in an aluminium container with $220 \times 220 \times 80\ \text{mm}^3$ and structured in three layers – upper face layer (20%), core layer (62%) and bottom face layer (18%). The mat was then pressed in a laboratory hot-press at 190 °C, with pressing times of 120 s and 150 s. The average density and thickness of the final boards were $658 \pm 8\ \text{kg m}^{-3}$ and 16 cm, respectively.

After pressing, the resulting boards were stored in a conditioned room (20 °C, 65% RH) before testing. The evaluated physico-mechanical properties, and respective standard tests, were: density (EN 323), moisture content (EN 322), internal bond strength (IB) (EN 319 - tensile strength perpendicular to the plane of the board), thickness swelling (EN 317). For each test, measurements were performed on three board replicates. The total extractable formaldehyde content was determined on only one board according to the perforator method (EN 120), which has an estimated error of 0.5 mg/100 g.

3. Results and discussion

3.1. Modification of type of base and F/U molar ratio

Fig. 1a) shows the evolution of viscosity in a commercial resin

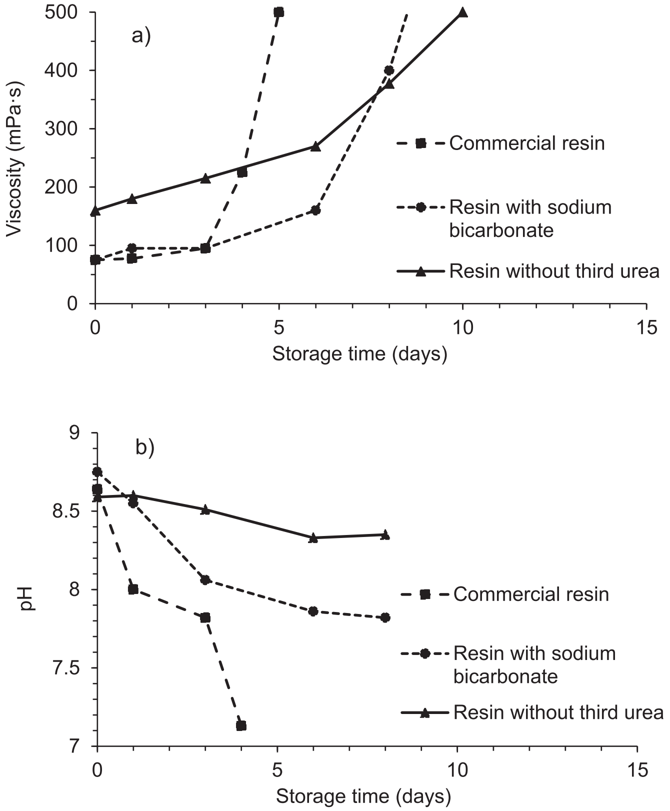

Fig. 1. Viscosity a) and pH b) as a function of storage time at 40 °C for commercial resin, resin with sodium bicarbonate and resin without 3rd urea addition.

stored at 40 °C. The common industrial practice is to adjust the final pH of UF resins using NaOH. Viscosity increases rapidly, showing the poor stability of commercial UF resins at 40 °C. The pH, shown in Fig. 1 b), also decreases quickly, achieving values around 7 in only 4 days. This decrease is probably associated with the well-known Cannizzaro reaction (Fig. 2), that involves sodium hydroxide and formaldehyde, consuming the strong base present in the resin [13,15].

$2HCOH + NaOH\ CH_3OH + HCOONa$

A laboratory synthesized resin, with the same formulation as the commercial version, was neutralized at the end of synthesis with a weak base, sodium bicarbonate, instead of NaOH. The viscosity increases slower than before, as seen in Fig. 1a), indicating a more stable resin. As expected, this is associated with a slower decrease in pH (Fig. 1b). In an attempt to improve pH stability further, another resin was synthesized and also neutralized with sodium bicarbonate, but the last urea addition was not performed. It must be noted that the resin without the last addition of urea has a higher initial viscosity, as seen in Fig. 1a). Nonetheless, this resin shows the most stable pH of the three (Fig. 1b)). When free urea is present, it reacts with formaldehyde forming monomethylolureas, which are slightly acidic. In addition, since urea has basic character, its consumption also contributes to decrease of pH. It seems therefore to be a good idea to add the third urea only after the end of storage, prior to the final application, since this contributes to a more stable pH during the storage period.

Nonetheless, as seen in Fig. 1a), the new formulation, using sodium bicarbonate and without addition of the last urea, is still not sufficiently stable in terms of viscosity, demanding for further modifications. The next approach, based on addition of a monofunctional comonomer, will be based on this formulation – resin with sodium bicarbonate and without the third urea. This will be designated as reference resin.

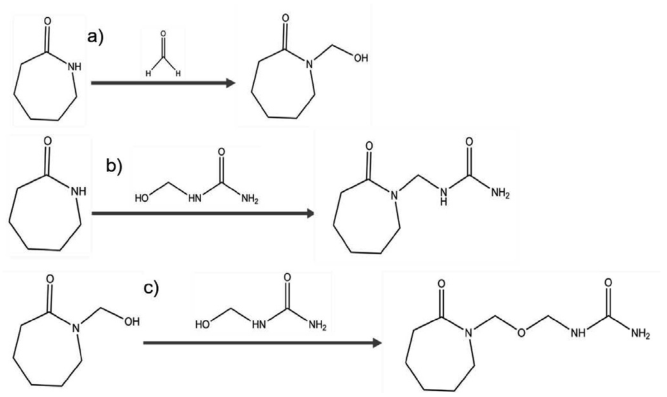

Fig. 3. Reaction schemes: a) caprolactam with formaldehyde; b) caprolactam with monomethylolurea and c) methylolcaprolactam with methylolurea.

3.2. Addition of caprolactam at different synthesis stages

A previous study demonstrated the reaction between caprolactam and formaldehyde, as well as the possibility of caprolactam participating in condensation reactions [16].

Fig. 3 shows the possible reactions between caprolactam and the monomers and oligomers present.

All these can occur during the condensation step. Since caprolactam has only one reactive group, the secondary amine, these reactions lead to partially blocked oligomers. Of course, caprolactam may also react with higher molecular weight species, if present. It must be noted that caprolactam's secondary amine is less reactive than the amino groups in urea.

In the current study, caprolactam was added at three different reaction stages. It is *a priori* expected that a more effective incorporation of this monomer in the polymer structure would be achieved in the beginning of condensation, before second urea addition (stage 1), since more free formaldehyde is present and only oligomeric species exist. At the middle of condensation (stage 2) larger polymer has already been formed, and the lower formaldehyde concentration may be disadvantageous for caprolactam incorporation. When caprolactam is added after the end of synthesis (stage 3), it is expected that it will not react with the polymer because pH is basic. However, this addition stage is relevant for comparison purposes, allowing to interpret whether reaction of caprolactam with the polymer is necessary for improving storage stability.

In all the synthesis the final condensation viscosity was set to 200–350 mPa s, which is lower than usual in this type of reaction, in order to allow a higher margin for the increase in viscosity during storage.

The characterization data for the reference resin and resins synthesized with addition of 10% caprolactam is presented in Table 1. All the resins were characterized after addition of the third urea.

Gel time of the resins increases with the addition of caprolactam, as shown in Table 1. . This is a consequence of caprolactam acting either as a blocker or as an inert compound.

In Fig. 4, the evolution of viscosity and pH during storage at 40 °C is presented for each resin. The limit value of viscosity that we consider to be acceptable for a stable resin without the addition of the last urea is 400 mPa s at 40 °C.

As shown in Fig. 4 a), the addition at different steps results in very different resin stabilities. Addition in stage 3 yields a behavior similar

$$2HCOH + NaOH \longrightarrow CH_3OH + HCOONa$$

Fig. 2. Reaction of formaldehyde with sodium hydroxide - Cannizzaro reaction.

Table 1
Characteristics of synthesized resins with 10% caprolactam, measured at 25 °C.

Resins/Properties	Solid Content (%)	Gel time (s)	Viscosity (mPa s)
Reference	63.2	72	240
Stage 1	63.4	90	250
Stage 2	64.4	94	280
Stage 3	62.7	102	270

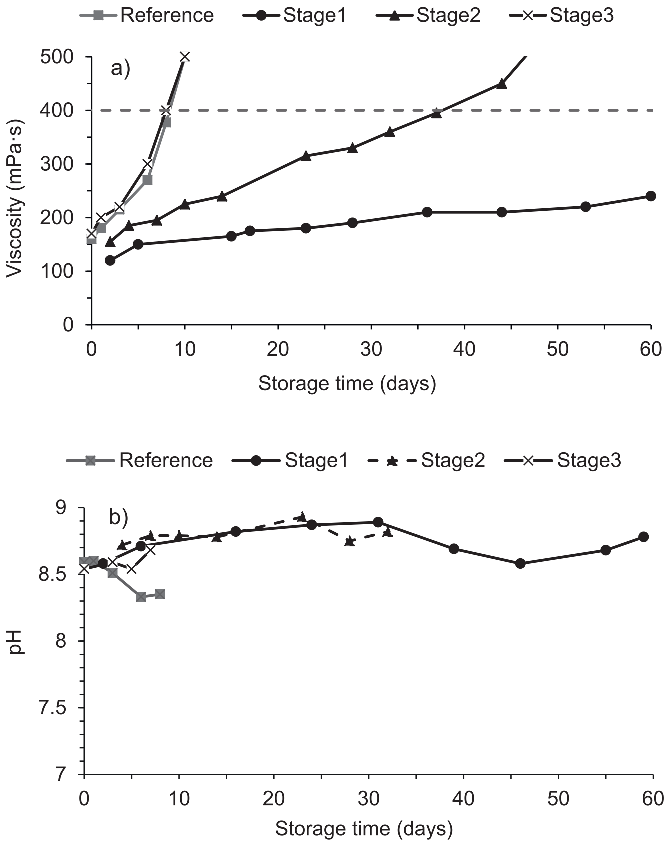

Fig. 4. Viscosity a) and pH b) as a function of storage time at 40 °C for reference resin and resins with caprolactam addition at different stages.

to the reference resin, which reaches the viscosity limit after 8 days. Caprolactam remains in solution, not reacting with the polymer, which does not contribute to improve stability. On the other hand, addition of caprolactam in stages 1 or 2 leads to very significant improvements in resin stability: more than 60 days and 37 days, respectively. The stability difference between additions in stages 1 and 2 may be related to the size of the polymer and the amount of free formaldehyde available to react with caprolactam. While in stage 1 monomers/oligomers and free formaldehyde are still available in solution for reaction with caprolactam, in stage 2 the content of free formaldehyde is lower and larger polymer chains are already formed.

Fig. 4 b) confirm that the pH is stable for all the resins without 3rd urea and with sodium bicarbonate even for 60 days at 40 °C.

3.3. Amount of caprolactam added

The reactivity of resin with 5% caprolactam is lower than that of the reference resin and similar to that of the resin with 10%, as seen in Table 2.

To better understand the effect of caprolactam concentration in the synthesis, samples of the reaction medium were taken along the condensation step and their viscosity measured. This provides a qualitative picture of how fast the condensation reaction is progressing.

Table 2
Characteristics of resins synthesized with different amounts of caprolactam added in step 1, measured at 25 °C.

Resins/Properties	Solid Content (%)	Gel time (s)	Viscosity (mPa s)
0% caprolactam (reference)	63.2	72	240
5% caprolactam	64.0	90	285
10% caprolactam	63.4	90	250

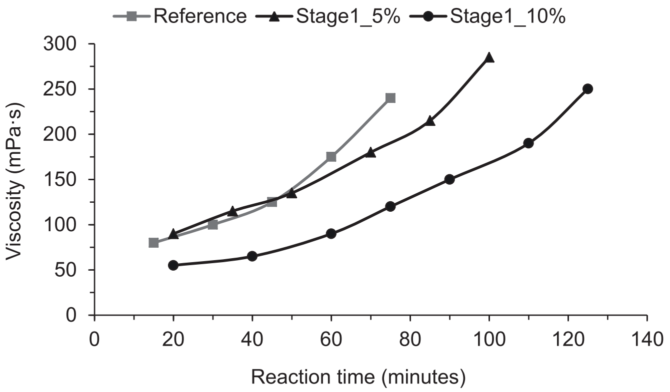

Fig. 5. Evolution of viscosity with time during the condensation reaction for different amounts of caprolactam added in step 1.

As shown in Fig. 5, there is a tendency for slower reaction progresses (slower viscosity increase) as the caprolactam amount increases. The reference resin takes 75 min to achieve the final condensation viscosity of 240 mPa s, while the resins with 5% and 10% of caprolactam take 100 min and 125 min, respectively. This is probably a consequence of the blocking effect promoted by caprolactam, which may react in two different ways when it is added to the resin. It can react with formaldehyde (Fig. 3 a)), forming a hydroxymethyl group in caprolactam that could be attacked by urea. The compound resultant from these reactions will be a urea linked to a caprolactam on one side and with an amino group on the other side. In other words, is a urea with only one reactive site, because the other side is blocked. The second reaction that could happen is the attack of the secondary amino group of caprolactam to a methylolated urea, giving the same final structure (Fig. 3 b)). Therefore, the blocking of these reactive sites will lower the availability of reactive groups and the rate of condensation. In addition, the blocking effect may result in a more branched polymer, which may contribute to the lower rate of viscosity increase.

In Fig. 6 it is possible to see that the stability of the resin with 5% caprolactam is much lower than the resin with 10%, even though it is still higher than for the reference resin. Such a large difference may indicate the need to surpass a threshold limit of blocked reactive sites to

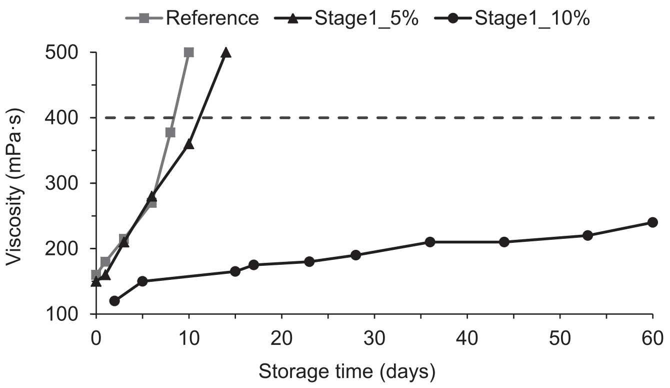

Fig. 6. Evolution of viscosity with analysis at 40 °C of resins with different percentages of caprolactam.

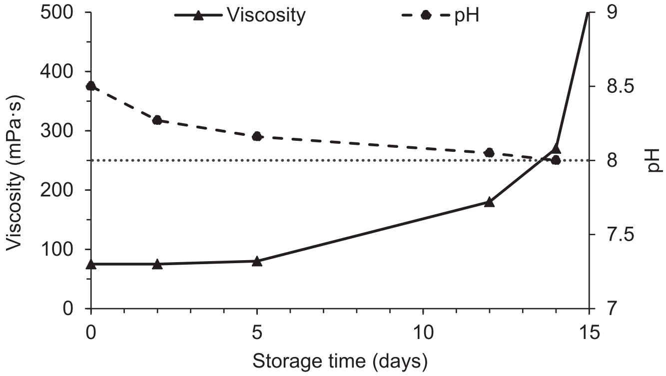

Fig. 7. Viscosity and pH as a function of storage time at 40 °C for resin with sodium bicarbonate, 10% caprolactam, and third urea addition after synthesis. The viscosity limit in these conditions is 250 mPa s.

ensure stability.

In order to clarify whether the stability of the formulation containing 10% caprolactam can still be accomplished if the third urea is added right after the synthesis, *i.e.* before the storage period, one last storage stability evaluation was performed.

As seen in Fig. 7, the viscosity increases sharply after 14 days of storage, which is significantly lower than the 60 days obtained previously (Fig. 6). This shows that the premature addition of the third urea has a negative influence on storage stability, and the blocking effect of caprolactam alone is not sufficient to counterbalance this. Urea may react with the polymer during storage, introducing more amino groups in its structure. This balance between amino and hydroxymethyl groups, makes the polymer more reactive, contributing to inter-chain condensation reactions during storage, and therefore to molecular weight increase. Fig. 7, also exhibit pH decrease due to the reactions of urea with formaldehyde and polymers.

3.4. Adhesive performance

The resin with best storage stability, containing 10% of caprolactam added in stage 1, was compared to the reference resin in terms of adhesive performance. Resins with different storage times were analyzed. An ABES equipment was used, which allows prediction of the mechanical performance of the resin during formation of wood-based particleboards [17]. The results are shown if Fig. 8.

ABES analysis shows significant differences in reactivity between the reference resin and the resin with 10% caprolactam. As predicted by the previous reactivity analysis, the reference resin achieves maximum bond strength, about 5 MPa, in 60 s. The fresh resin containing caprolactam took twice the time, 120 s, and the maximum strength value is only slightly lower. The resin with caprolactam stored for 1 month, on the other hand, reached a lower value of maximum tension, about 3.5 MPa, at 120 s. The same behavior is displayed by the resin stored for 2 months, with only a small decrease in the shear strength value at 120 s. These results indicate that particleboards produced with these resins should be pressed for 120 s, the usual time for the commercial resin and 150 s, in order to insure maximum bonding strength.

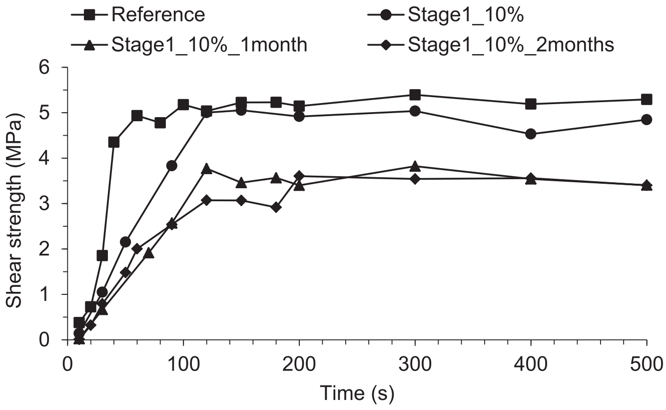

Fig. 8. Analysis with ABES technique at 105 °C of reference resin and resin with caprolactam (fresh and after 1 and 2 months of storage).

Table 3 presents the results of the physico-mechanical properties of the particleboards produced with the reference resin and the resin containing 10% caprolactam added in step 1, for different pressing times.

As predicted by ABES, internal bond strength is higher for the reference resin than for the resins with caprolactam, concluding that storage time is detrimental for the internal bong strength of the panels. The resins stored for 1 and 2 months present IB values at 120 s of 0.39 and 0.37 N mm^{-2}, respectively. When the pressing time is increased to 150 s, improves the IB values to 0.42 and 0.39 N mm^{-2}. It is important to note that all IB values verify the limit set by EN 312 for class P2 boards with thicknesses from 13 to 20 mm: IB ≥ 0.35 N mm^{-2}.

Concerning formaldehyde content, the reference resin has already relatively high values for a resin with molar ratio of 1.10–1.15, which is a consequence of the lower degree of condensation imposed, which leaves more free formaldehyde in the resin. Formaldehyde content increases when caprolactam is added, due to less effective curing of the resin during panel production, since less reactive groups are available. Interestingly, formaldehyde content decreases for the resins stored for 1 and 2 months, probably due to continuing reaction of the polymer with formaldehyde during this period. For the resins with caprolactam, only the one stored for 2 months shows formaldehyde contents within the limit set for E1 class particleboards, ≤ 8 mg/(100 g oven dry board), as defined in EN 13986.

4. Conclusions

Storage of UF resins is a relevant issue in industrial practice. Decrease of pH during storage was suggested as being a contributing factor. It is a consequence of two types of reaction:

1) The well-known Cannizzaro reaction that consumes the sodium hydroxide present in the aqueous medium due to reaction with formaldehyde.
2) Reaction between urea and free formaldehyde, giving origin to a slightly acidic compound, monomethylolurea, that together with the consumption of the basic compound, urea, leads to a decrease in pH.

In addition, the presence of free urea, typically added at the end of the synthesis to obtain the desired final formaldehyde/urea molar ratio, has an additional negative impact on stability, since it reacts with the polymer, promoting the inter-chain condensation reactions. Stability improvements could therefore be obtained by avoiding the Cannizzaro reaction, using sodium bicarbonate instead of sodium hydroxide for neutralization at the end of synthesis, and performing the third urea addition only after the storage time. However, it was observed that a significant stability improvement can only be obtained by combining this approach with introducing caprolactam as a reaction blocker at the beginning of the condensation synthesis step. The new formulation reached a storage stability of at least two months at 40 °C. This is a significant improvement when compared to the commercial resin, which is stable for only 4 days at this temperature.

Particleboards produced with the caprolactam-modified resins exhibited internal bond strength about 20% lower than the reference resin. However, the values were still acceptable according to EN 312 for class P2 boards (IB ≥ 0.35 N mm^{-2}), even after the resin was stored for 2 months at 40 °C were it presents an internal bound 36% lower. A negative aspect had to do with formaldehyde content, since panels produced with the new resin (fresh and after 1 month storage) showed

Table 3
Physico-mechanical analysis of the particleboard produced with resin step1_10% at different storage time and reference resin.

Resins/Properties	Reference		step1_10%		step1_10%_ 1 month		step1_10%_ 2 months	
Pressing Time (s)	120	150	120	150	120	150	120	150
Density (kg/m^3)	667 ± 6	673 ± 7	653 ± 7	658 ± 5	656 ± 2	653 ± 7	653 ± 1	651 ± 2
Internal Bond (N·mm^{-2})	0.62 ± 0.01	0.61 ± 0.02	0.48 ± 0.03	0.47 ± 0.02	0.39 ± 0.02	0.42 ± 0.02	0.37 ± 0.03	0.39 ± 0.04
Thickness swelling (%)	43.7 ± 0.9	41.5 ± 1.6	41.4 ± 1.4	44.2 ± 2.1	38.8 ± 3.5	36.7 ± 3.4	43.7 ± 1.4	41.5 ± 1.3
Moisture content (%)	6.5 ± 0.5	6.5 ± 0.2	5.8 ± 0.3	5.3 ± 0.2	6.9 ± 0.3	6.4 ± 0.1	6.5 ± 0.2	6.5 ± 0.1
Formaldehyde content (mg/100 g oven dry board)	7.9	–	10.9	–	9.2	–	7.6	–

values above the limit established for E1 class particleboards, ≤ 8 mg/100 g oven dry board (EN 13986). However, after 2 months storage the same resin allowed producing panels within this limit.

These results validate the concept that a reaction blocker contributes to prolong significantly the stability of a UF resin. The consequent decrease in reactivity insures that the reaction progresses sufficiently slow during storage, even at 40 °C, to allow usability after 2 months. Loss in performance does not impair use in particleboards. However, the formaldehyde content in the final panels increases, which may imply addition of formaldehyde scavengers to insure verifying the regulated limits. Use of other types of reaction blockers is under study, in an attempt to obtain equally good storage stability, but with less negative impact on particleboard production process, performance and emissions.

Acknowledgements

This work was financially supported by: project UID/EQU/00511/2019 - Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE funded by national funds through FCT/MCTES (PIDDAC), and by project 2GAR (SI I&DT - Projects in co-promotion) in the scope of Portugal 2020, co-funded by FEDER (Fundo Europeu de Desenvolvimento Regional) under the framework of POCI (Programa Operacional Competitividade e Internacionalização).

References

[1] Dunky M. Urea — formaldehyde (UF) adhesive resins for wood. Int J Adhesion Adhes 1998;18:95–107. June 1997.
[2] Siimer K. Study of the structural changes in urea-formaldehyde condensates during synthesis. Macromol Symp 1999;156:149–56.
[3] Ferra JM, Mendes AM, Costa MRN, Magalhães FD, Carvalho LH. Characterization of urea-formaldehyde resins by GPC/SEC and HPLC techniques: effect of ageing. J Adhes Sci Technol 2010;24:1535–51. https://doi.org/10.1163/016942410X501070.
[4] Siimer K, Kaljuvee T, Christjanson P, Pehk T. Changes in curing behaviour of aminoresins during storage. J Therm Anal Calorim 2005;80(1):123–30. https://doi.org/10.1007/s10973-005-0623-8.
[5] Jahromi S. The storage stability of melamine formaldehyde resin solutions: III. Storage at elevated temperatures. Polymer 1999;40(18):5103–9. https://doi.org/10.1016/S0032-3861(98)00724-1.
[6] Christjanson P, Siimer K, Pehk T, Lasn I. Structural changes in urea-formaldehyde resins during storage. Holz als Roh- Werkst 2002;60(6):379–84. https://doi.org/10.1007/s00107-002-0326-9.
[7] Kim MG. Examination of selected synthesis parameters for typical wood adhesive-type urea – formaldehyde resins by 13 C-NMR spectroscopy . II. J Appl Polym Sci 1999;37:997–1007.
[8] Kim MG, No BY, Lee SM, Nieh WL. Examination of selected synthesis and room-temperature storage parameters for wood adhesive-type urea – formaldehyde resins by 13 C-NMR spectroscopy. V. *J Appl Polym Sci.* 2003;89:1896–917.
[9] Lee S, Park J, Park S, Han S. Comparative study of the storage stability between a melamine-urea- formaldehyde and a urea- formaldehyde resin. For Prod J 2012;62(11):146–9.
[10] Kim MG, Wan H, No BY, Nieh WL. Examination of selected synthesis and room-temperature storage parameters for wood adhesive-type urea-formaldehyde resins by13C-NMR spectroscopy. IV. J Appl Polym Sci 2001;82(5):1155–69. https://doi.org/10.1002/app.1950.
[11] Józwiak M. Effect of molar ratio of melamine-urea-formaldehyde adhesive resins condensed no- waste method ' s on the selected properties of the polycondensates during storage time I . Basic physicochemical properties. Wood Technol 2015;171:168–71.
[12] No BY, Harmon DM, Todd R. Storage stable amino - formaldehyde resins and applications thereof. Patent 2014:1–9.
[13] Swain G, Powell A, Sheppard W. Mechanism of the cannizzaro reaction. Am Chem Soc 1979;1459:3576–83.
[14] Paiva NT, Pereira J, Ferra JM, Cruz P, Carvalho L, Magalhães FD. Study of influence of synthesis conditions on properties of melamine – urea formaldehyde resins. Int Wood Prod J 2013;3(1):51–7. https://doi.org/10.1179/2042645312Y.0000000009.
[15] Fry H, Uber J, Price J. Observations on a possible mechanism of the cannizzaro reaction with formaldehyde. Recl des Trav Chim des Pays-Bas. 1931;50(12):1060–5.
[16] Normand FC, Goodall DM, Duckett SB, van Tol MFH, Nusselder JJH. Separation and characterisation of caprolactam-formaldehyde reaction products. Analyst 2002;127(10):1312–7. https://doi.org/10.1039/b205438h.
[17] Ferra JM, Ohlmeyer M, Mendes AM, Costa MRN, Carvalho LH, Magalhães FD. Evaluation of urea-formaldehyde adhesives performance by recently developed mechanical tests. Int J Adhesion Adhes 2011;31:127–34. https://doi.org/10.1016/j.ijadhadh.2010.11.013.