

ASSESSMENT OF UREA BASED VITRIMERS AS A NEW MATRIX MATERIAL FOR FIBRE REINFORCED POLYMERS

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Abstract

Vitrimer are covalently cross-linked polymeric materials which can be thermally processed in a liquid like state without losing their network integrity. In this work, composites using novel vitrimers based on the dynamic amine exchange reaction of vinylogous urea as matrix material, are assessed. First, the production process, based prepregging followed by either hot pressing or autoclaving, is discussed. Then, a mechanical characterization of both $[0^\circ/90^\circ]_{2S}$ and $[\pm 45^\circ]_{2S}$ by quasi-static testing is conducted. Furthermore, both thermoforming capabilities of the composite, as well as fibre recycling by a simple chemical treatment is demonstrated. It could be concluded that vitrimers prove to be a promising material for future fibre reinforced polymers.

1 Introduction

For fibre reinforced polymers, usually only thermosetting or thermoplastic polymer materials are considered. However, a new type of polymer, the so called 'vitrimers' have recently been developed [1, 2]. Vitrimer are covalently cross-linked polymeric materials which can be thermally processed in a liquid state without losing their network integrity, hence trying to combine the best of both worlds. Indeed, theoretically they should combine the thermal processing capabilities of thermoplastics with the excellent mechanical properties of thermoset polymers.

There are two types of cross-link mobility, dissociative and associative. For the dissociative mobility, the cross-links completely disappear, thus having a complete loss of network integrity. This should make them the easier to process, but usually yielding a lower T_v , the temperature at which mobility occurs. For the associative mobility, a bond can only shift from a first molecule to neighbor molecule after another molecule has bonded to the first molecule, hence maintaining network integrity. The latter is harder to process, but yields a higher T_v . Both principles are illustrated in Figure 1.

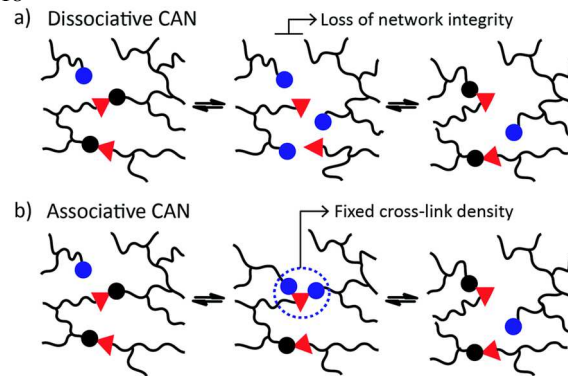


Figure 1: illustration of associative and dissociative covalent adaptable networks [3]

In this work, novel vitrimers based on the dynamic amine exchange reaction of vinylogous urea (vurea) moieties are introduced. After a preliminary assessment on the polymer level, vinylogous urea clearly emerge as the most promising material. Of all the considered combinations (urethanes, amides and urea), it showed the fastest intrinsic exchange kinetics in combination with promising mechanical properties ($T_g \sim 110^\circ\text{C}$, $E \sim 2.2 \text{ GPa}$) and remarkably short relaxation times above T_g , in the order of a few seconds when heated. The latter are promising for the thermoforming capabilities of the composite.

In the next paragraph, the used materials, equipment and processing is discussed. This is followed by an overview of the conducted mechanical characterization, as well as a preliminary assessment of the thermoforming capabilities. Also, the potential recyclability is looked upon. Finally, some conclusions are drawn.

2 Materials and methods

2.1 Materials

For the matrix, vurea were produced by mixing 1,4-(piperazine)bis(acetoacetamide) (PIP-AA) with hydrogenated methylenedianiline (hMDA) and tris(2-aminoethyl)amine (TAEA). This leads to a polycondensation reaction between acetoacetamide functional groups with the amines to produce the characteristic vinylogous urea group, whereas network formation is ensured by the addition of the trifunctional TAEA. Figure 2 represents these monomers with the added mole equivalents used in the production. It can be readily seen that 3 out of 5 amine groups belong to the TAEA monomers thus leading to a very densely crosslinked network. Furthermore, these equivalents lead to a 5% excess of amines. Upon complete reaction, this leads to the presence of free amines, necessary for further exchange reactions upon shaping the material. 0,5mol% pTsoH is added as a catalyst

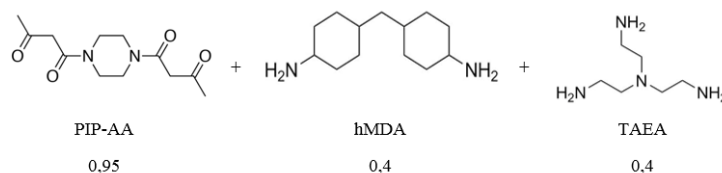


Figure 2: Monomers and their mol equivalents used for the production of a vurea

For the fibre reinforcement, a plain weave glass fabric from interglass was chosen (ref 92146), with a density of 425g/m^2 . The ratio warp to weft yarns is 13,03.

2.2 Methods

To produce the prepreges, a hand lay-up process was considered. In this process, the fibre reinforcement is placed on a Teflon coated glass plate. The resin is then applied by pouring it on the fibres and a roller is used for a homogeneous distribution over the entire sample. Knowing the density of glass fibres, the volume of the fabric can be calculated from its weight. In this way, using the density of the polymer, the amount of needed monomer can be calculated according to a predetermined volume percentage of fibre. For underlying research, a fibre volume fraction of 50% was aimed for. Due to the fast reaction, viscosity increases rapidly. In order to get sufficient time at lower viscosity to ensure a homogeneous distribution of the polymer over the fabric, a sufficient amount of methanol is added to get a more dilute system. After the hand lay-up process, a drying cycle has to be done. The first step takes place in a convection oven at 90°C for 1 hour. The main purpose is to remove the added methanol. A second step takes place in a vacuum oven for 1 hour where the temperature is chosen sufficiently high to get a complete curing and removal of the released water due to the condensation reaction. A representation of the prepreg production process can be seen in Figure 3

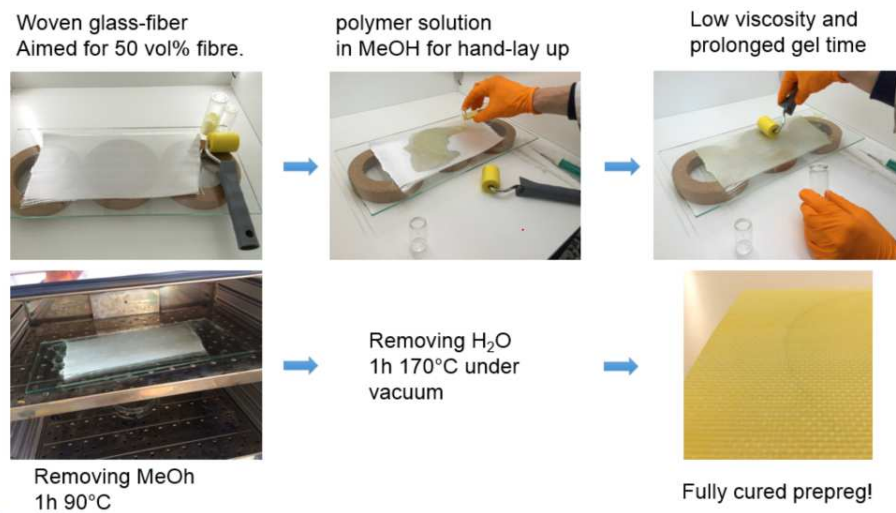


Figure 3: Illustration of the prepregging principle by hand layup

For hot pressing, a Fontijne press with maximum load capability of 450kN and two flat heated plates of 300mm x 300mm was used. The produced prepregs were stacked according to the desired stacking sequence and placed between two aluminium plates, each having a PI film attached to it, to facilitate removal of the composite afterwards. After a parameter optimization, the plates were pressed for 1h at 150°C and 7MPa and were then allowed to cool down to room temperature. These process parameters yielded the best quality plates, meaning no voids could be detected under microscopic observation of the polished sides and only limited push out of the polymer was present, thus maintaining the desired fibre volume fraction.

For the autoclave process, an in-house developed autoclave was used. The maximum temperature achievable is 200°C and the maximum pressure outside the vacuum bag is 8 bar. Again, a parameter optimization was performed and the plates were manufactured by heating till 200°C, which is then kept constant for 20 minutes, after which the autoclave is allowed to cool down till room temperature. An internal pressure of -85kPa (vacuum) and an outer pressure of 7,8 bar was maintained for 8h, which was long enough for the autoclave to cool till room temperature. It should be noted that this pressure is significantly lower than the one used for hot pressing. However, this was compensated by the higher processing temperature of 200°C which, in combination with the applied vacuum on the prepreg

stacking, resulted in high quality composite plates, again with no voids visible under microscopic observation of the polished sides and no push out. As such, the fibre volume fraction of the autoclaved plates will be a bit lower than the hot pressed samples.

Mechanical properties were derived by performing tensile tests on rectangular specimens of 30mm x 250mm; the thickness varied between 2mm and 3mm, depending on the used process. The specimens were equipped with a longitudinal and a transverse strain gauge. All tensile tests were performed on a servo-hydraulic INSTRON 8801 tensile testing machine with a FastTrack 8800 digital controller and a load cell of ± 100 kN. The quasi-static tests were displacement-controlled at a displacement speed of 2mm/min. For the registration of the tensile data, a combination of a National Instruments C-series DAQ chassis, NI 9215 and NI 9237 measurement cards was used. The load, displacement and strain data were sampled on the same time basis.

3 Results and Discussion

3.1 $[0^\circ/90^\circ]_{2s}$ stacking sequence

After optimization of the process, a number of plates were pressed, all with similar results; Figure 4 illustrates the results of one of those hot pressed plates; An average Young's modulus of 33200 MPa and an average Poisson's ratio of 0,163 were found for all the successful tests.

All specimens showed a similar failure behaviour: already quite early in the test, small delaminations initiated. More severe delaminations occurred later on, which resulted in the stepwise load drops as can be seen in Figure 4 (a). The average failure stress was 336MPa.

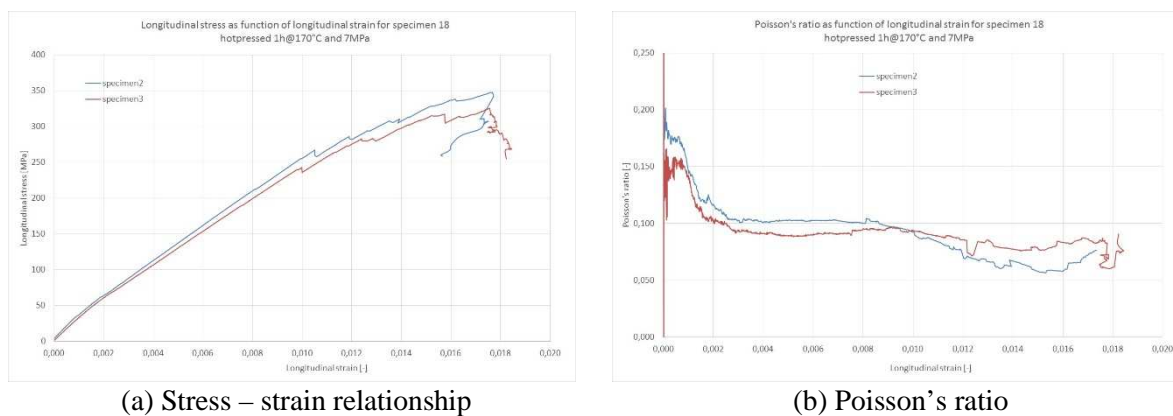


Figure 4: Mechanical properties of a hot pressed $[0^\circ/90^\circ]_{2s}$ plate.

The results of one of the autoclaved plates are shown Figure 5. Again, other plates have been produced and tested to assess reproducibility, which was higher than for the hot pressed plates. A similar failure mechanism was present, although the delaminations initiated later and were less severe compared to the hot pressed samples. Hence, there are no load drops visible in Figure 5 (a) and this resulted in a higher average failure stress of 367MPa; an average Young's modulus of 28464 MPa and an average Poisson's ratio of 0,135 were found. It should be noted that specimen2 failed in the grips, thus yielding an underestimation of the failure load; such specimens were not taken into account when calculating the average failure load.

The Young's modulus is slightly lower compared to the hot pressed samples, but this is due to the fact that the fibre volume fraction is also lower. Indeed, for both processes, the same prepregs with the same fibre volume fraction were used, but in the hot press, there was always pushout of neat resin, which was not the case for the autoclave process, as mentioned earlier.

Although the values mentioned above are quite promising and comparable to other thermoset materials, the load is mainly carried by the fibres in a $[0^\circ/90^\circ]_{2s}$ stacking sequence. As such, a $[\pm 45^\circ]_{2s}$ stacking sequence was chosen, to assess the behaviour of the vitrimer under in-plane shear. Given the fact that the autoclave yielded more reproducible results, a higher strength and less delaminations, only the autoclave process was considered.

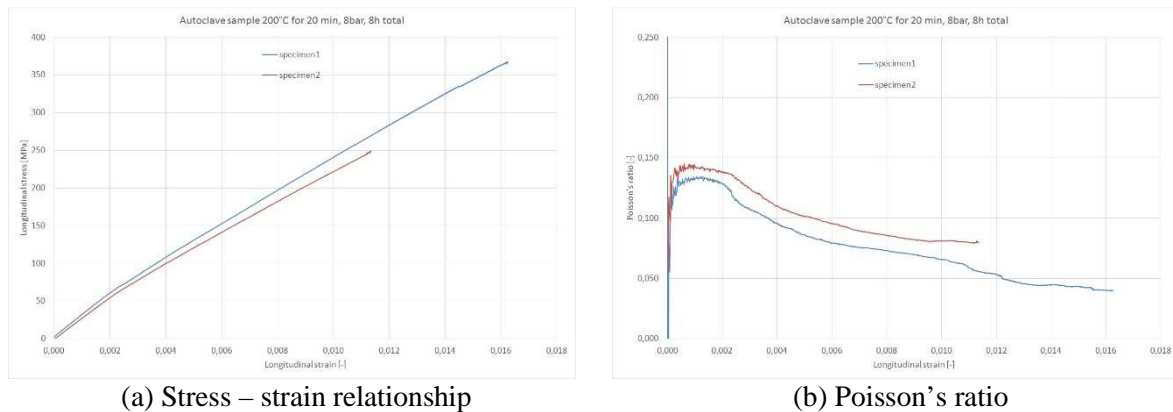


Figure 5: Mechanical properties of an autoclaved $[0^\circ/90^\circ]_{2s}$ plate.

3.2 $[\pm 45^\circ]_{2s}$ stacking sequence

Figure 6 illustrates the in-plane shear behaviour of an autoclaved plate. Figure 6 (a) shows shear stress as function of the shear strain until the strain gauge debonded. This was due to a large delamination and failure of 2 of the 8 layers. The remaining layers were still capable of carrying load, as can be seen in the force-displacement curve in Figure 6 (b).

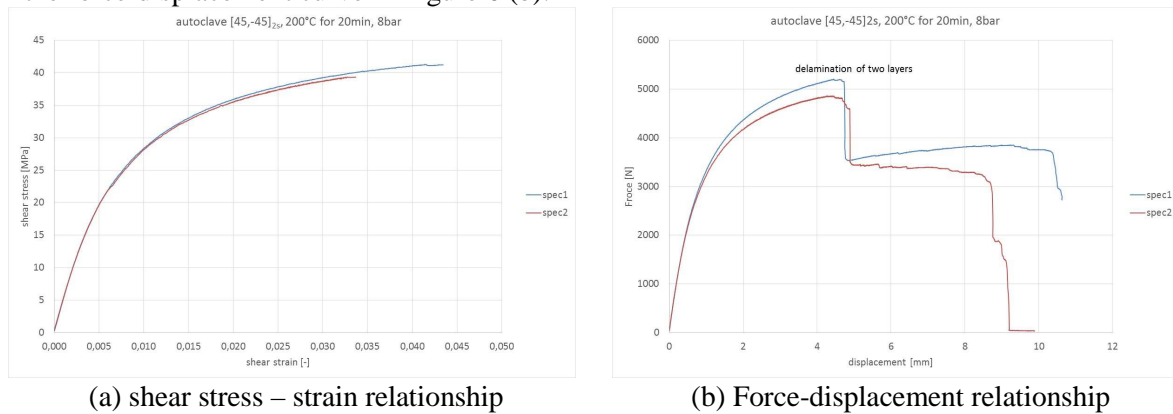


Figure 6: Mechanical properties of an autoclaved $[\pm 45^\circ]_{2s}$ plate

The shear stiffness has an average value of 4728MPa, which is acceptable, but the failure stress of 41MPa is fairly low compared to common epoxy systems [4]. A similar delamination behaviour was also seen in other plates, hinting for a low interlaminar strength. As such, more research on improving the interlaminar strength is necessary.

3.3 Thermoformability

Given the nature of the polymer, it is definitely worth assessing the thermoforming capabilities. Two layers of prepreg were first consolidated into a composite plate by hot pressing and then placed over a

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pre-heated mould with a triangular shaped cavity; next the pre-heated counter mould was placed on top of this. Using a manual hydraulic press, light pressure was applied to close the mould without breaking the fibres. After 10 minutes, the mould was opened and the successfully thermoformed specimen was removed, as shown in Figure 7.

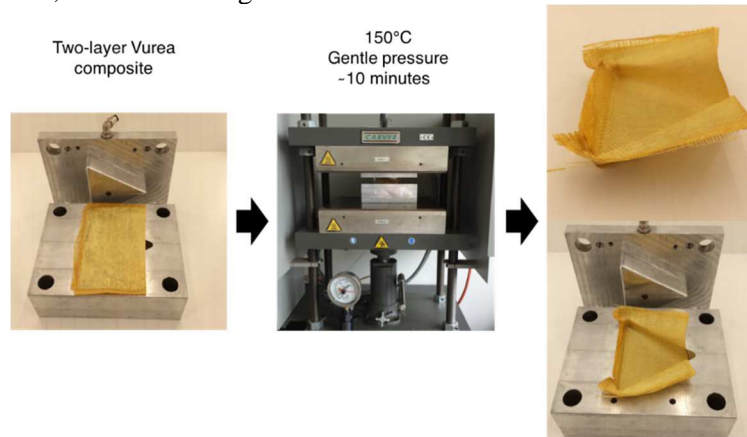


Figure 7: illustration of the thermoforming capabilities of a glass fibre reinforced vitrimer

Although further optimization is necessary, this already is a promising result.

3.4 Recyclability

Finally, because of the chemical nature of the polymer, an attempt was made to recycle the composite by submerging it into a solution of N-methylpyrrolidone (NMP) with a primary amine. As a reference, a sample was also submerged in pure NMP without primary amine. As can be seen in Figure 8, for the NMP-amine solution, it was possible to fully remove the vitrimer matrix, leaving only the glass fabric behind after only 15 minutes at 100°C, whereas after 20h in the reference NMP, nothing really happened except a discoloration due to oxidation, thus illustrating that the presence of the amine, rather than the NMP caused the recycling event.

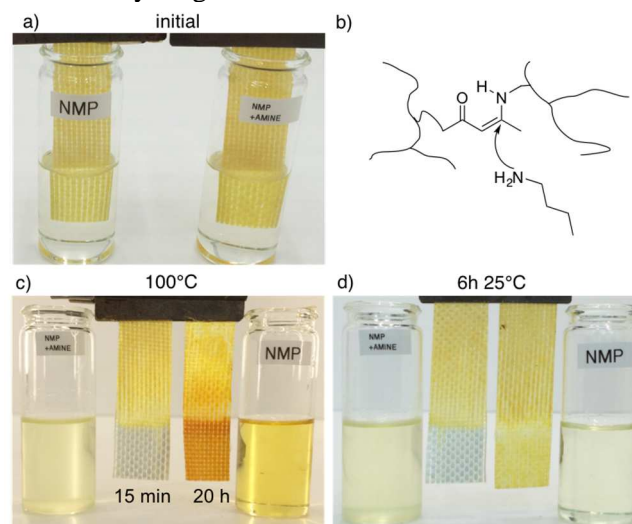


Figure 8: Illustration of the recycling potential of the glass fibre reinforced vitrimer

4 Conclusions

A new type of polymers, namely vitrimers, have been assessed for its applicability as matrix materials for fibre reinforced polymers. For the current research, a covalent associative network was chosen, based on vinylogous urea. These polymers showed most promising results with respect to intrinsic exchange kinetics in combination with promising mechanical properties on the polymer level.

In a next step, glass fibre fabrics were impregnated with the uncured polymer to obtain prepregs by means of a hand lay-up process, with good results. The obtained prepregs were then considered for both hot pressing and autoclave technique to manufacture composite plates. After some optimization, transparent composites with limited to no voids were achieved.

Next, a mechanical characterization was done on both a $[0^\circ/90^\circ]_{2s}$ and $[\pm 45^\circ]_{2s}$ stacking sequence to obtain values for stiffness, Poisson's ratio and failure load. Again, the vitrimer showed promising results, although the composites still have the tendency to delaminate fairly early, hinting a low interlaminar strength. Further research and optimizations are therefore necessary to improve the interlaminar properties of fibre reinforced vurea.

The thermoforming capabilities of a two-layer composite plate were also assessed and a preliminary trial was successful. Finally, it was proven that the polymer can be easily removed from the fabric by using solution of primary amines., yielding again the neat fabric without apparent damage to the fibres.

As such, it can be concluded that the vurea based vitrimer shows very promising results to be considered for fibre reinforced polymers, although further research and optimization will still be necessary.

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