Soybean Oil-based Non-Isocyanate Polyurethanes for Commercial Applications

Report - 1

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By

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Graphical Summary

The graphical summary of the work performed using soybean oil for adhesive and coating application is provided in Figure 1.

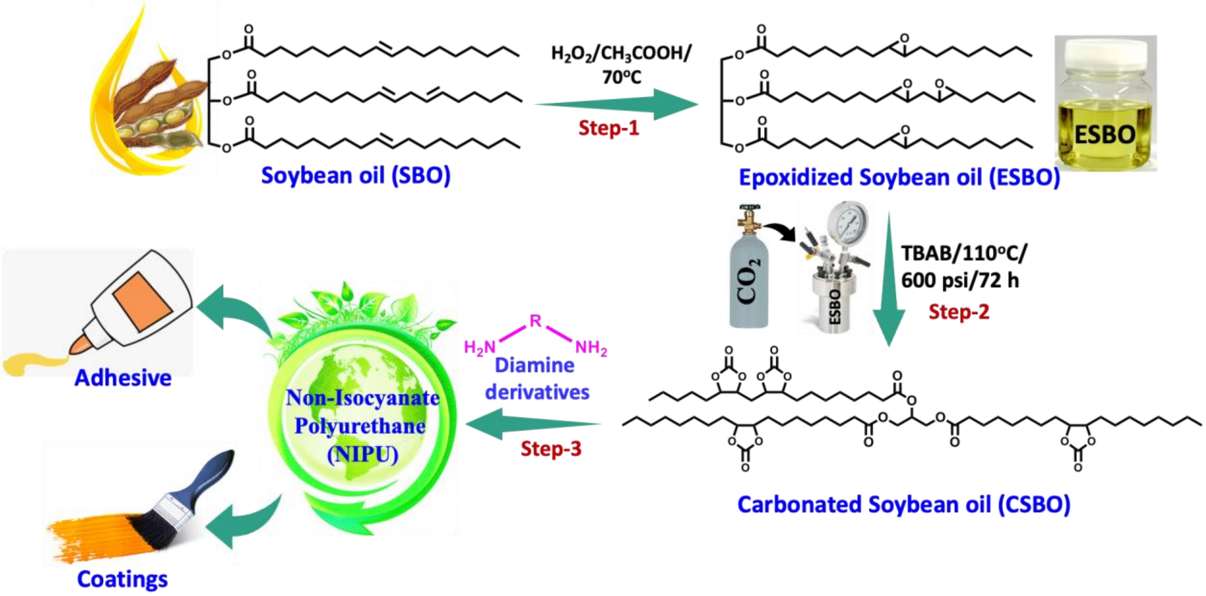

Figure 1. A schematic diagram for the synthesis of non-isocyanate polyurethane (NIPU) for adhesive and coating applications.

Detailed Report of the Work Performed

We have already synthesized the carbonated soybean oil (CSBO) from the corresponding Soybean oil (SBO) over a two-step (step-1 & step-2) process followed by characterization using FT-IR analysis, viscosity measurements at 25°C as elaborately discussed in the last update. As per our last discussion, however, we have confirmed the successful formation of CSBO from ESBO by FT-IR analysis and viscosity measurement studies, the ^{1}H NMR spectra further confirm the formation of CSBO as shown in Figure 3. The disappearance of the proton signal at δ: 2.80-3.10 ppm corresponding to oxirane ring C-H proton in ESBO (Figure 2) and the appearance of a set of new characteristics carbonate C-H proton signals in CSBO (Figure 3) at δ: 4.22-4.32 and 4.46-4.50 are well agreement with epoxy conversion under the given reaction condition.

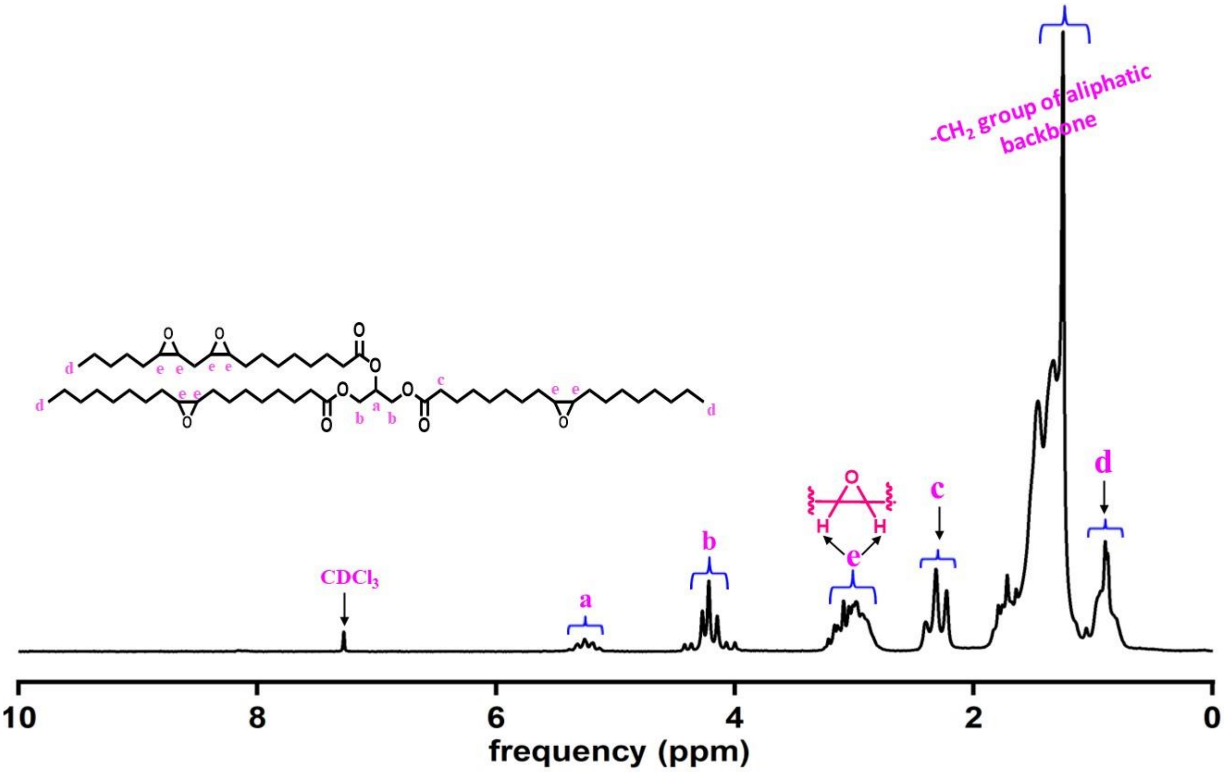

Figure 2. ^{1}H NMR spectrum of ESBO in CDCl$_3$.

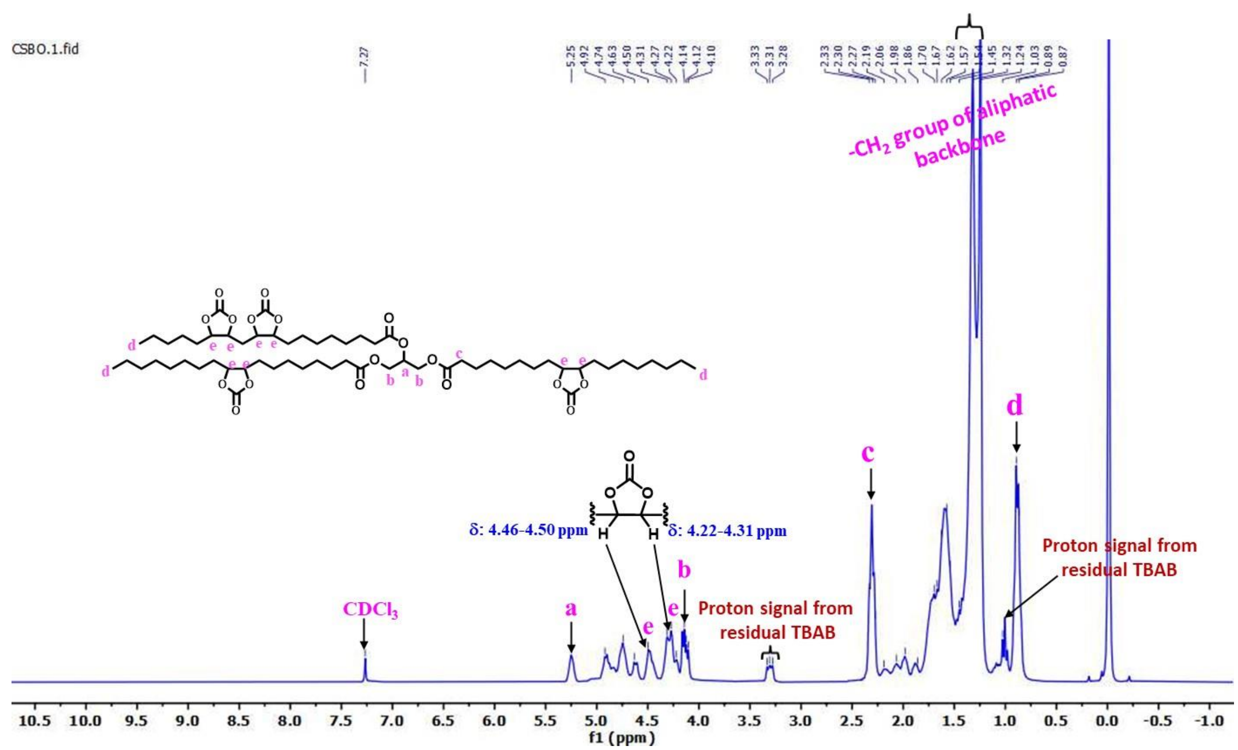

Figure 3. ^{1}H NMR spectrum of CSBO in CDCl$_3$.

Preparation of NIPU Adhesive from CSBO and Isophorone Diamine (IPDA)

After the successful synthesis of carbonated soybean oil (CSBO), we have combined different diamines *e.g*. isophorone diamine (IPDA) and *meta*-Xylylenediamine (*m*-XDA) or a triamine *e.g*. tris(2-aminoethyl)amine (TAA) with CSBO to investigate their effect on the adhesive property of non-isocyanate polyurethane (NIPU) by screening different parameters like reaction time, temperature and the stoichiometric equivalent of different amine cross-linker. In the last update, initially, we performed a reaction between CSBO (1.0 equiv.) with 3.5 equiv. of isophorone diamine (IPDA) in different curing temperatures (RT, 30ºC, 50ºC, 70ºC, and 80ºC) for 24 h, and the reaction was monitored by FT-IR analysis which demonstrates the progress of the reaction by reduction of carbonate carbonyl peak intensity with a gradual increase in temperature as shown in Figure 4a. Furthermore, a typical tensile stress-strain curve elucidates the strength of the particular NIPU adhesive (CSBO/IPDA$_{1:3.5}$) in wood coupon under given conditions (Figure 4b). From the aforesaid optimization, it was seen that the 70ºC cured sample exhibited more tensile strength (1.26 MPa) compared to the 50ºC cured specimen (1.06 MPa) although a traces unreacted carbonate carbonyl peak at 1795 cm^{-1} was still present in both the specimen according to FT-IR analysis.

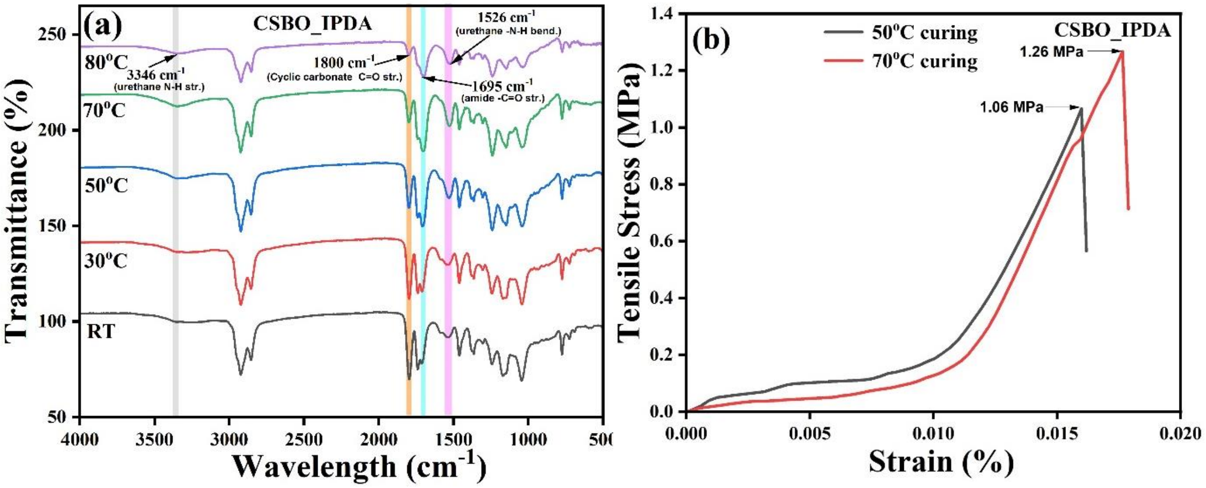

Figure 4. (a) Monitoring FT-IR spectra and (b) tensile stress-strain curve of CSBO_IPDA (3.5 eq.) adhesive specimen.

After that, we altered the IPDA stoichiometric equivalent in CSBO/IPDA ratio of 1:4 and 1:2.5 under different curing temperatures (50ºC, 70ºC, and 90ºC) for 24 h to get the optimized condition for improved NIPU adhesive. In this context, using a 1:4 mol ratio of CSBO/IPDA it was observed that, at 70ºC the carbonate carbonyl peak fully disappeared whereas at 90ºC the peak intensity again regenerates (Figure 5a) along with the concomitant decline of tensile strength from 1.11 MPa to 0.61 MPa (Figure 5b).

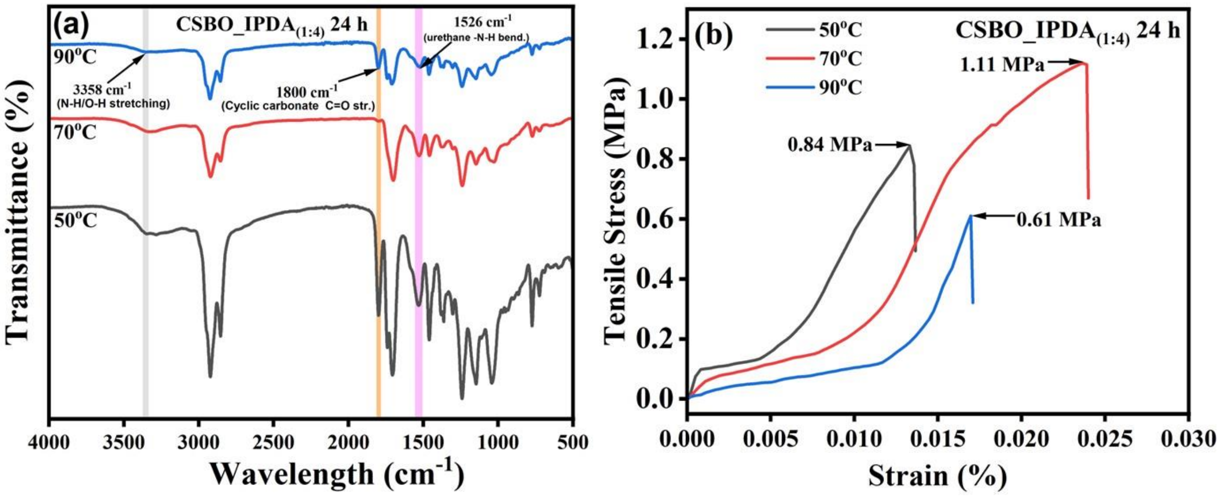

Figure 5. (a) Monitoring FT-IR spectra and (b) tensile stress-strain curve of CSBO_IPDA (4.0 eq.) adhesive specimen.

After that to elucidate the thermal transition of the NIPU specimen (CSBO/IPDA$_{1:4}$) we performed the differential scanning calorimetry (DSC) which displays a sharp glass transition temperature (T_g) at 30.96ºC along with other transitions with a shoulder peak at >100ºC (Figure 6a). Furthermore, thermogravimetric analysis (TGA) was performed to understand the thermo-oxidative behavior of the NIPU specimen (CSBO/IPDA$_{1:4}$) under an inert atmosphere as shown in Figure 6b. Next, we also performed a reaction of CSBO (1.0 equiv.) with lower stoichiometric equivalent of IPDA (2.5 equiv.) under different curing temperature (50ºC, 70ºC and 90ºC) for 24 h (FT-IR monitoring, Figure 7b) to check the impact of lowering of amine equivalent on the tensile strength of the NIPU adhesive (CSBO/IPDA1:2.5) in wood coupon under given condition (Figure 7b).

From the above-described studies of NIPU adhesive preparation from CSBO and stoichiometric equivalent IPDA, it was revealed that the better adhesive on wood coupon can be formulated using 3.5-4.0 equiv. IPDA with 1.0 equiv. of CSBO at 70ºC curing temperature for 24 h (curing time was also optimized based on the result obtained from *m*-XDA derived NIPU adhesive, discussed later).

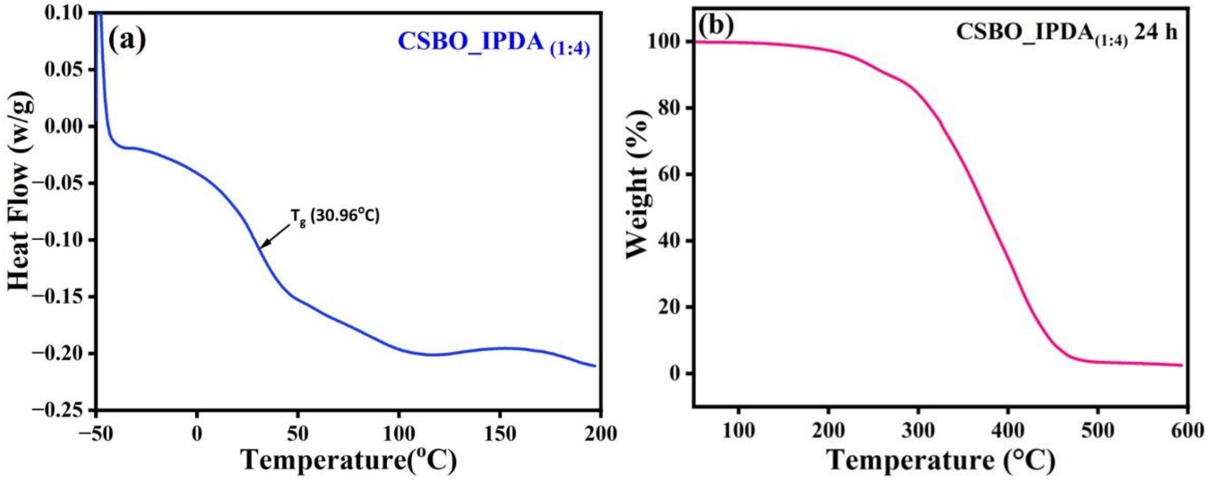

Figure 6. (a) DCS traces and (b) TGA curve of CSBO_IPDA 4.0 eq. adhesive specimen.

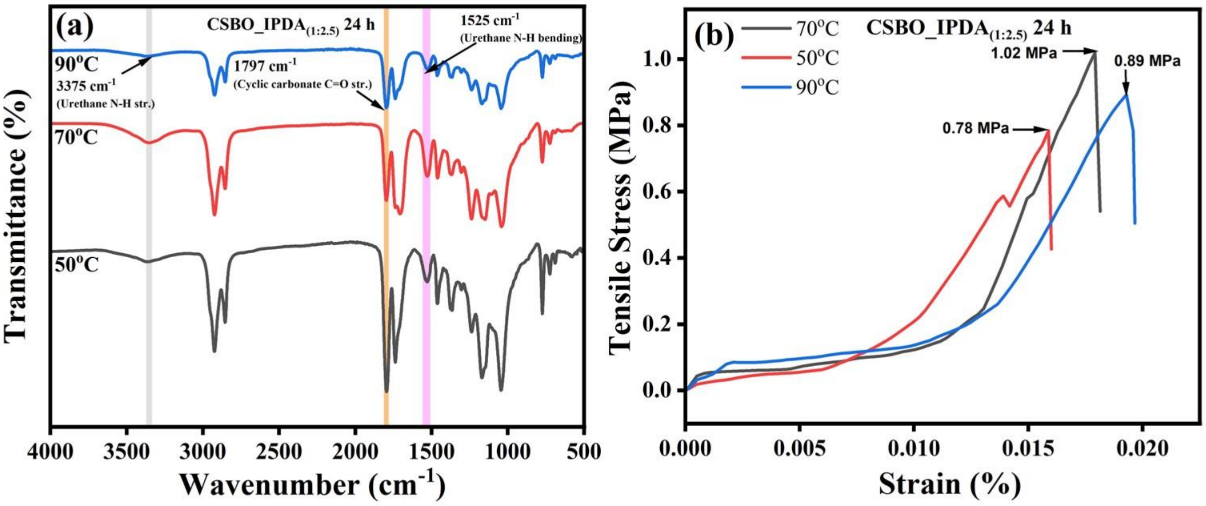

Figure 7. (a) Monitoring FT-IR spectra and (b) tensile stress-strain curve of CSBO_IPDA (2.5 eq.) adhesive specimen.

Preparation of NIPU Adhesive from CSBO and *meta*-Xylylenediamine (*m*-XDA)

Initially, here we performed a reaction of CSBO (1.0 equiv.) with 2.5 equiv., 3.0 equiv. of *m*-XDA and curing kinetics were monitored by FT-IR studies under different curing times (1, 2, 3, 4, 5, 6, 7, 12, 16, and 24 h) and temperature (50ºC, 70ºC, and 90ºC) to get the optimized formulation for NIPU adhesive sample. These optimization studies revealed that at 70ºC, both the NIPU adhesive specimen CSBO/*m*-XDA$_{1:2.5}$ and CSBO/*m*-XDA$_{1:3.0}$ mostly cured (minimization of carbonate carbonyl peak intensity) at 20 h and 16 h respectively (marked by green dotted box) as demonstrated in the monitoring FT-IR optimization studies (Figure 8 and Figure 9).

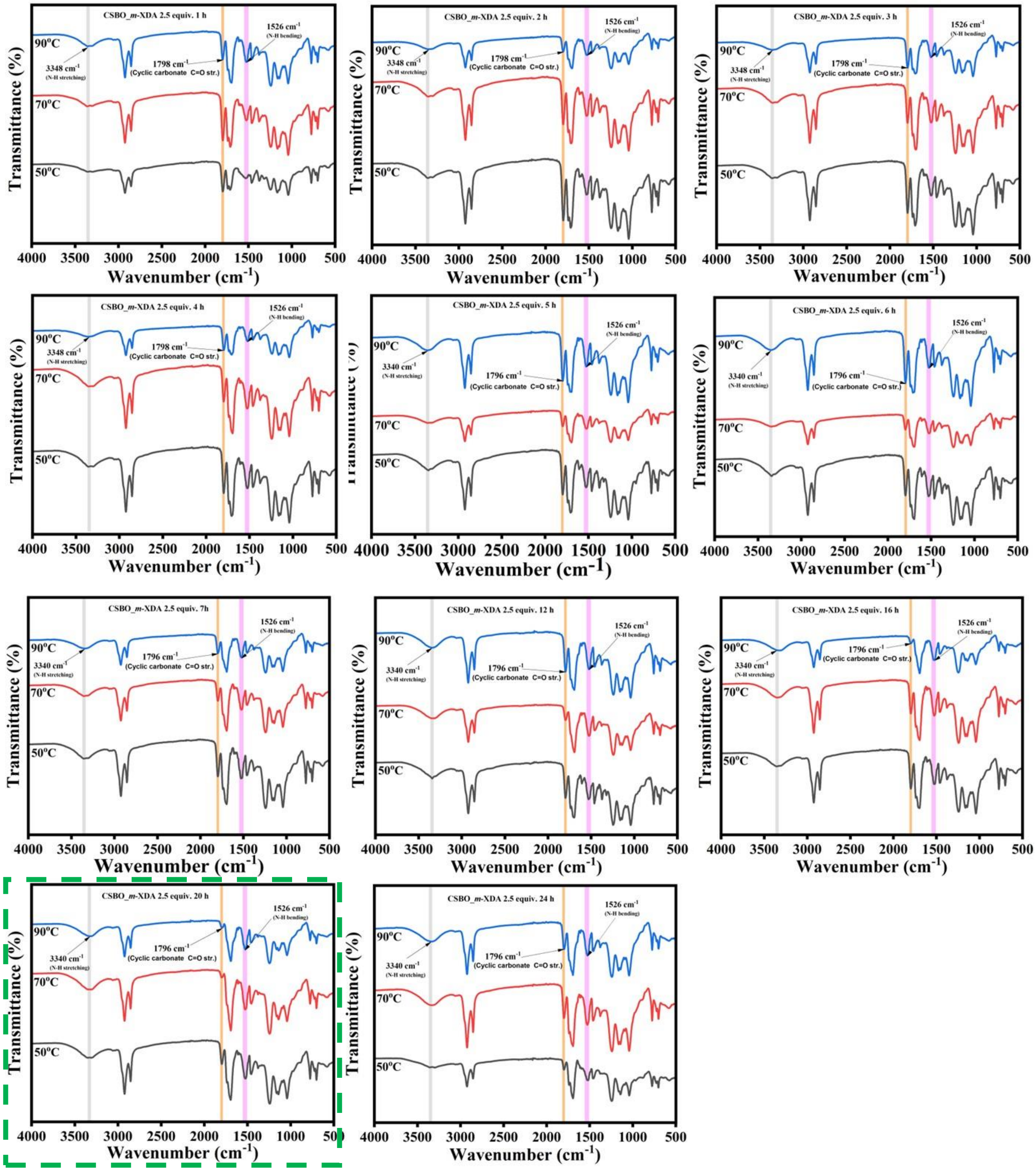

Figure 8. Monitoring FT-IR optimization studies of CSBO_*m*-XDA (2.5 eq.) adhesive specimen.

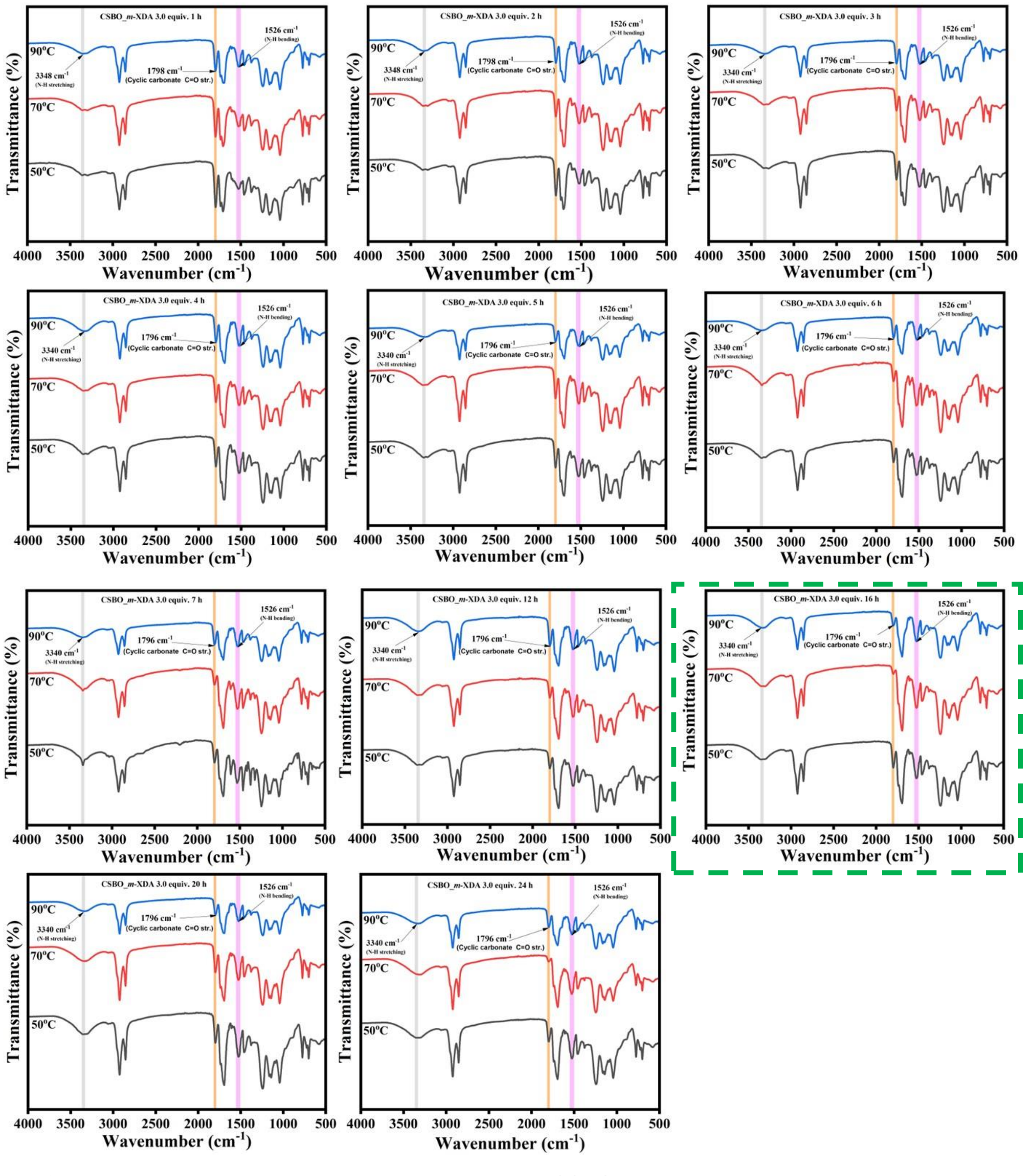

Figure 9. Monitoring FT-IR optimization studies of CSBO_*m*-XDA (3.0 eq.) adhesive specimen.

After that, we again increase the stoichiometric equivalent of *m*-XDA from 3.0 to 3.5 equiv. and cured the NIPU specimen sample (CSBO/*m*-XDA$_{\mathbf{1:3.5}}$) at 70ºC for the different periods (12 h, 16 h, and 24 h) and it was observed that both at 16 h and 24 h curing time the carbonate carbonyl peak intensity almost diminishes according to the FT-IR spectra (Figure 10a) along with the arrival of maximum tensile strength of 4.97 MPa (70ºC cured) compared to 50ºC and 90ºC cured specimen (3.47 MPa and 4.58 MPa) at 16 h were documented for the NIPU adhesive on wood coupon as depicted in the typical stress-strain curve (Figure 10b).

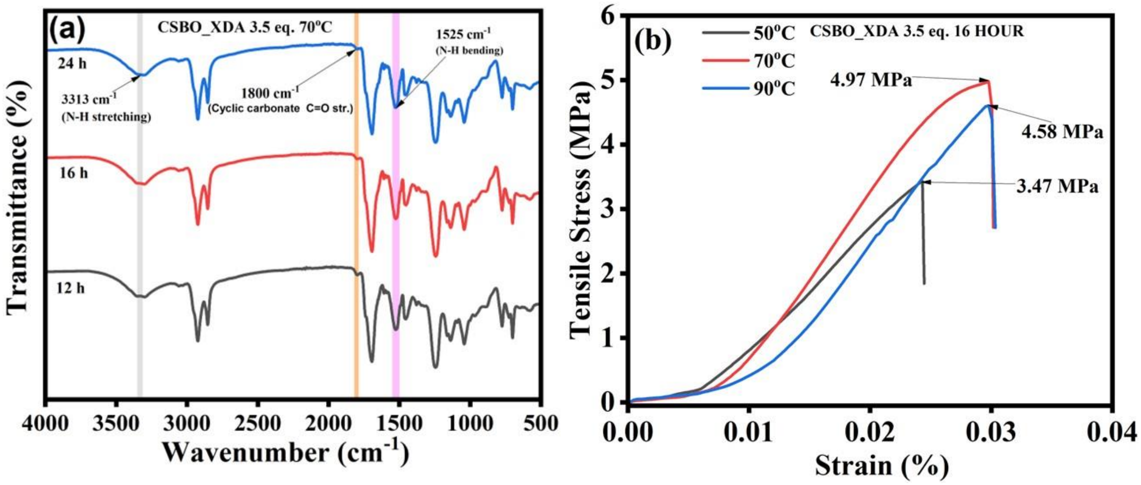

Figure 10. (a) Monitoring FT-IR spectra and (b) tensile stress-strain curve of CSBO_*m*-XDA (3.5 eq.) adhesive specimen.

After that, the thermal transition and also thermal behavior of the NIPU specimen (CSBO/*m*-XDA$_{1:3.5}$) cured at 70ºC for 24 h have been demonstrated using differential scanning calorimetry (DSC) which exhibits a glass transition temperature (T$_g$) at 18.82ºC (Figure 11a) and thermogravimetric analysis (TGA) under an inert atmosphere as shown in Figure 11b.

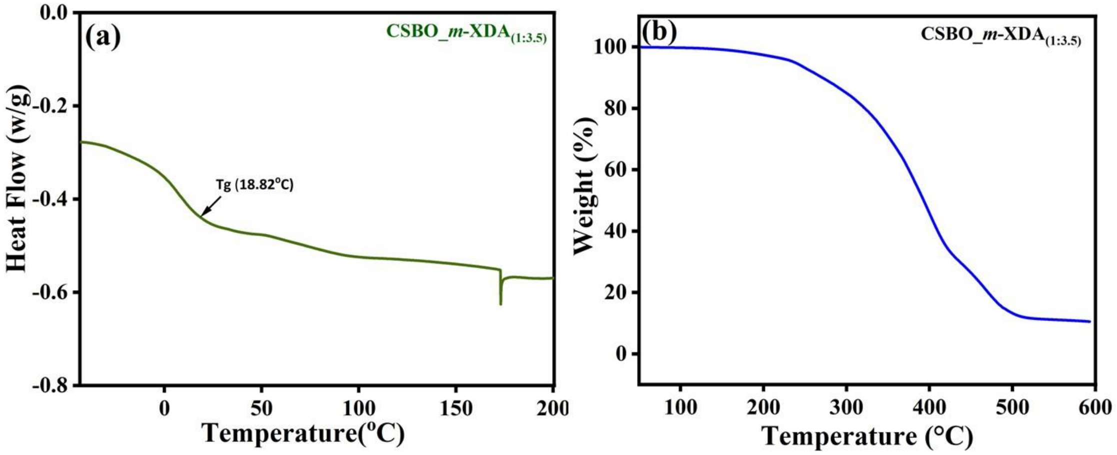

Figure 11. (a) DCS traces and (b) TGA curve of CSBO_*m*-XDA 3.5 eq. adhesive specimen.

We have also observed that when the loadings of *m*-XDA further increase from 3.5 to 4.0 equiv. and cured the NIPU specimen (CSBO/*m*-XDA$_{1:4.0}$) at 70ºC for 24 h, the carbonate carbonyl peak intensity further increased slightly (FT-IR, Figure 12a) along with sharp drop-down of tensile strength for both CSBO/*m*-XDA$_{1:3.5}$ and CSBO/*m*-XDA$_{1:4.0}$ in comparison to NIPU specimen CSBO/*m*-XDA$_{1:3.5}$ cured for 16 at 70ºC as shown in Figure 12b.

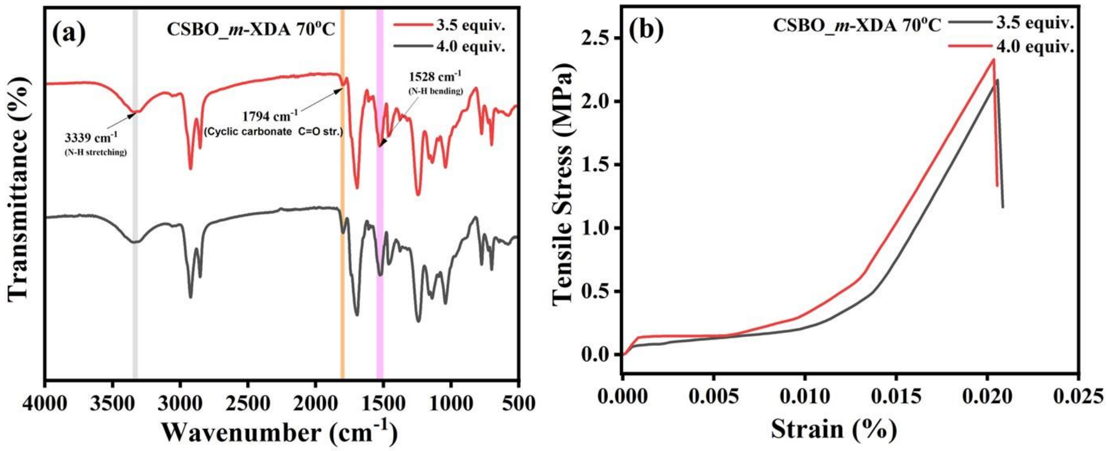

Figure 12. (a) Monitoring FT-IR spectra and (b) tensile stress-strain curve of CSBO_*m*-XDA (3.5 vs 4.0 eq.) adhesive specimen.

In summary, from the aforementioned studies of NIPU adhesive preparation from CSBO and the stoichiometric equivalent of *m*-XDA, it was revealed that the better adhesive application on the wood coupon can be done using 3.5 equivalent of *m*-XDA with 1.0 equivalent of CSBO at 70ºC curing temperature for 16 h.

Preparation of NIPU Adhesive from CSBO and Tris(2-aminoethyl)amine (TAA)

Here, in the same way, we have performed reaction between CSBO (1.0 equiv.) and Tris(2-aminoethyl)amine (TAA) using different equivalent ratio of TAA (2.0, 2.5, 3.0 equiv.) under different curing time (1, 2, 3, 4 and 5 h) and temperature (50ºC, 70ºC and 90ºC) to get the optimized time, temperature and also the stoichiometric equivalent of TAA for NIPU adhesive. All these optimization studies were monitored by FT-IR analyses which were summarized below in Figures 13, 14, and 15.

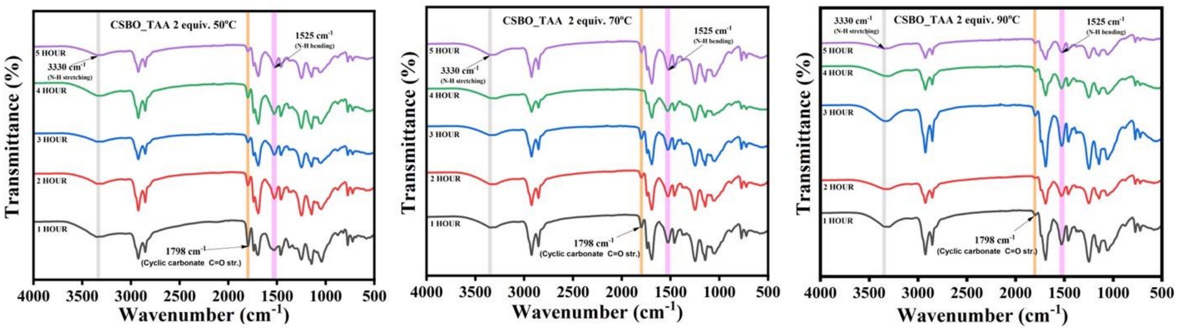

Figure 13. Monitoring FT-IR studies of CSBO_TAA (2 equiv.) with varying reaction temperature and time.

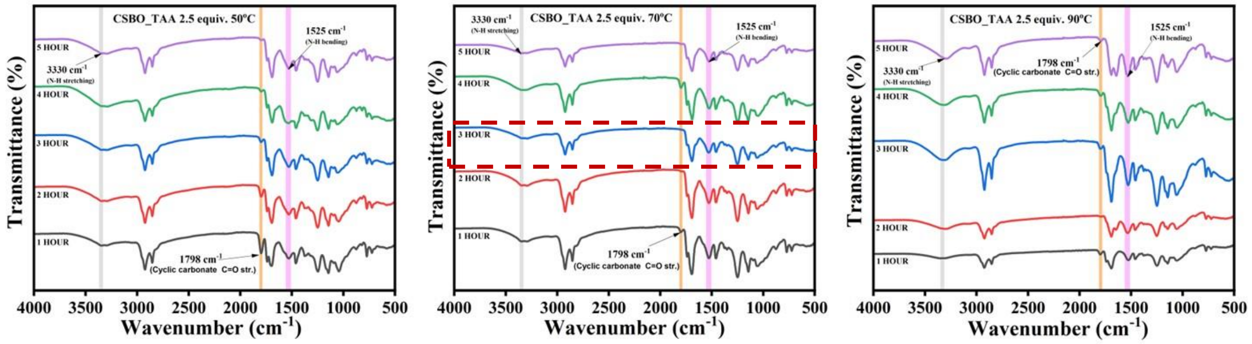

Figure 14. Monitoring FT-IR studies of CSBO_TAA (2.5 equiv.) with varying reaction temperature and time.

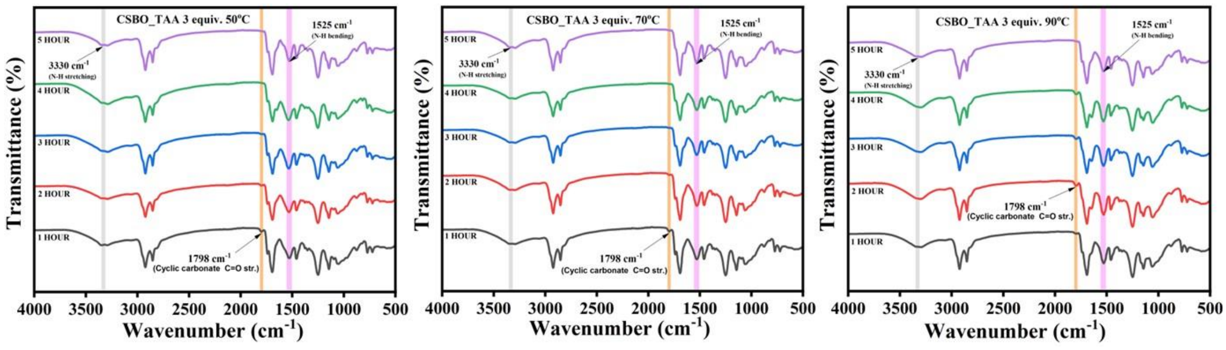

Figure 15. Monitoring FT-IR studies of CSBO_TAA (3.0 equiv.) with varying reaction temperature and time.

From the above FT-IR monitoring studies, it was revealed that 2.5 equiv. TAA is effective loading for reaction with 1.0 equiv. CSBO at 70ºC for 3 h with almost complete disappearance of carbonate carbonyl peak (Figure 14, marked by dark red dotted box) in the fabrication of NIPU specimen (CSBO/TAA$_{1:2.5}$) for adhesive application. The initial trial for the tensile test of CSBO/TAA$_{1:2.5}$ NIPU adhesive specimen on wood coupon under optimized conditions was unsuccessful due to adhesive failure as shown in Figure 16.

Figure 16. Adhesive failure of CSBO_TAA (2.5 equiv.) under optimized conditions.