EFFECT OF ENVIRONMENTAL CONDITIONS ON CURING OF POLYURETHANE ADHESIVE INVESTIGATED WITH FTIR ANALYSIS

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Resume
The use and significance of adhesives in various industries are explored, highlighting the growth of the adhesive market and the crucial role of time in adhesive bonding. The composition of adhesives, particularly polyurethane adhesives (PUR), is detailed, emphasizing their sensitivity to environmental factors, like moisture and UV radiation. Various factors influencing adhesive properties, such as reactivity and curing-induced shrinkage, are discussed, along with the importance of catalysts in adjusting reaction rates. One-component moisture-curable PUR adhesives are presented as versatile and continually improving alternatives in structural adhesive applications. The research's focus was to investigate the curing speed of Sikaflex-252 1-component PUR structural adhesive under different conditions, including room temperature, room temperature with ~30% humidity, and room temperature with ~100% humidity.

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1 Introduction

The majority of PUR adhesives are quite insensitive to moisture penetration [1]. For adhesives that cure with moisture, saturation with moisture does not lead to a reduction in values. The PUR adhesives consist of hard and soft segments. The soft segments are usually derived from hydroxyl-terminated polyester, polyether, polybutadiene or polyisobutylene polyols, while the hard segments (HS) contain isocyanates and diamine chain-extending moieties [2]. Increasing the HS content generally increases the elastic modulus and reduces elongation. Therefore, by varying these two types, the properties of PUR adhesives can be varied [3]. Polyurethanes are mainly made up of difunctional and trifunctional OH-terminated molecules that react with di- or triisocyanates [4]. The length and stiffness of the chain determine the mechanical properties of the final polymer. The chain can be made up of polyethers, which makes them flexible and hydrophilic, polyesters, which provide greater stiffness, polycarbonates or other OH- or NH-terminated molecules [5].

The concentration of the trifunctional molecules, which can be either the OH or isocyanate component, determines the cross-linking density, a factor influencing the stiffness pattern [6-7]. A structural adhesive must have trifunctional groups to guarantee a covalent three-dimensional network, otherwise it would have thermoplastic properties. In some places, curing-induced volume shrinkage plays a prominent role. If a thick layer of adhesive is not allowed or able to move during the curing due to spacers or other design constraints, shrinkage will cause significant stress, reducing the load-bearing capacity of the bond. The PURs based on prepolymers show less shrinkage and thermal expansion during curing. The building blocks of adhesives also have different reactivity, and catalysts are needed to adjust these reaction rates. However, too fast reactions can cause problems in wetting, as the liquid adhesive must first fully wet the surface to achieve adhesion before it solidifies, and if solidification is faster than wetting, adhesion can be significantly reduced [8-9].

Moisture curing adhesives cure by the diffusion of moisture into the adhesive, a process controlled only by the rate of water diffusion, which also depends on temperature and humidity, and hydrophilic/hydrophobic properties. Water must be added to accelerate the cross-linking reaction of the moisture-curing adhesive. This is not easy, because even very small amounts of water are difficult to mix into a water-repellent, highly viscous material, but it can be done by adding a specially formulated water paste (booster) [10]. Curing takes place slowly through the humidity, even without a booster. Booster systems are used when thick bond lines are required for materials with no or slow diffusion of water vapour. A problem in such applications may be a tendency to bubble formation caused by rapid curing with large amounts of water [11]. Adhesives are strongly influenced by the properties of the environment in which they are used [12-13]. One example is the PUR type adhesive we use as our primary adhesive, which crosslinks more quickly as the humidity in the environment increases. In addition to ambient humidity, another influencing factor is temperature, although this is more important for two-component adhesives. In addition to the two factors mentioned above, boosters are the third accelerating factor, but these are optional. Without a booster, the process is slower and may not be complete, but the reaction does not take place below water (humidity) or below a minimum temperature. During our experiments we did not use the help of boosters.

The aim of our research was to investigate the speed of different cross-linking processes; to compare the reaction rates of Sikaflex-252 1-component PUR structural adhesive crosslinked at room temperature, crosslinked at room temperature and ~30% humidity, crosslinked at room temperature and ~100% humidity.

2 Description of adhesives tested and test methods

2.1 SIKAFLEX-252

Sikaflex-252 is a structural adhesive. The adhesive is a one-component polyurethane (PUR) that crosslinks when exposed to moisture. It is suitable for bonding under dynamic loads. It can be applied on many faces to substrates of different materials, such as wood, plastics, ceramics, aluminium, steel and other metals. It also has good vibration damping, is electrically non-conductive and has a high elongation at break. The bonding of sikaflex-252 adhesive is not among the fastest bonding adhesives, nor even among the fast ones, as it bonds to moisture [9].

3 Description of the test procedure

3.1 Fourier transform infrared spectroscopy

The measurement instrument is a JASCO 4600 FT-IR spectrometer, characterized by a measurement range spanning from 7800 to 350 cm^{-1}. With a resolution capability of up to 0.7 cm^{-1}, this instrument is versatile, accommodating both transmission and reflection measurements. Additionally, it features a rapid scan function, allowing for the swift data acquisition at a rate of up to 7-8 measurements per second.

3.2 Description of the test procedure

In our experimental investigations, our primary objective was to assess the cross-linking kinetics and reaction rates of adhesives. This encompassed examining the variation in cure rates among different formulation types and assessing the cross-linking rate of specific single-component adhesives (PUR) undergoing curing in the presence of moisture across diverse humidity conditions. To ensure precise measurements, each sample was positioned on polyethylene foil with spectroscopy serving as a recorded background. Furthermore, each sample was affixed to a wooden sample holder, which remained undisturbed until the completion of the tests. Samples subjected to 100% humidity for cross-linking were placed in a desiccator containing water, as opposed to silica gel typically used for drying and dehumidification. This modification aimed to establish the appropriate humidified environment within the enclosed system. Our measurements demonstrated a remarkable consistency across all adhesive materials. The process involved meticulous sample placement, selection of the background assigned to each sample, and execution of the measurement program in the FTIR, generating results from 64 measurements recorded in transmittance. The post-measurement steps included identifying the reaction group, applying baseline fitting if necessary, and converting results to absorbance. The recorded data were documented within absorbance-converted measurements. Subsequent to this, results were calculated using the method described below and graphically plotted, providing a visual representation of the obtained data.

4 Results and evaluation

In the presentation of our findings, a comprehensive analysis of the binding speed for each sample is provided, along with an examination of the variation in binding

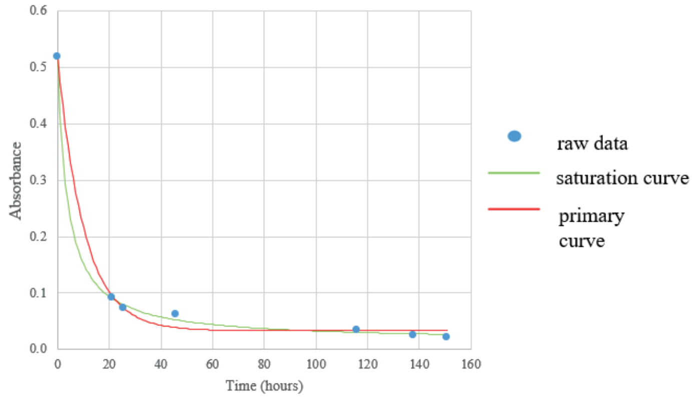

Figure 1 *Cross-linking of sample A*

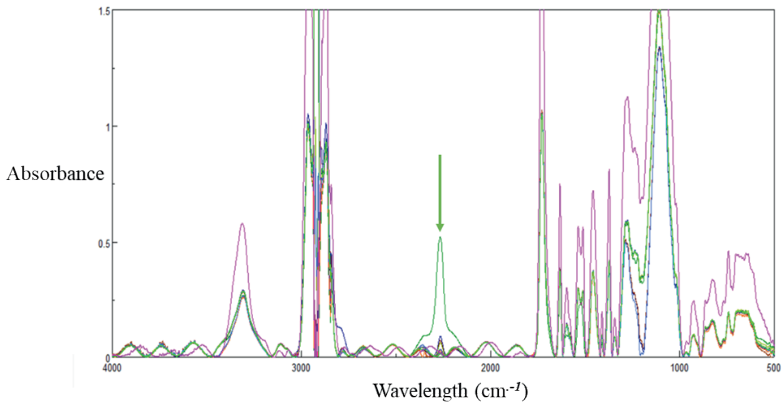

Figure 2 *Results of measurement "A" in FTIR Spectra Analysis*

speed among sample pairs. It is important to note that the sample pairs exclusively pertain to the single-component polyurethane structural adhesive and the single-component silicone sealant adhesives. All the measurements and cross-linking were performed at the accredited laboratory permissible temperature. The results never reach 0 or a certain number, so they were considered cross-linked only when the values of the reaction groups had not been greatly reduced. The values do not remain constant even for "fully" cross-linked adhesives, either because of minimal inaccuracy of the measuring equipment or because of the continuous decomposition and re-bonding of the reaction groups. To minimise the influence on the results of the measurement, the samples were placed in a separate holder for each of them. Thus, each adhesive was named with an assigned letter.

4.1 Sikaflex-252

4.1.1 "A" Sample - Investigation of curing chemical composition in normal 50% humidity condition

The aim of sample A was to find the reaction group and to know the total cross-linking time. Here a problem arose, as shown in Figure 1, that during the first 20 hours, shown in Figure 2, the absorbance of the material decreased sharply, making the calculation of the reaction rate inaccurate.

For this reason, the half hourly time interval measurements were required for the first 4 hours of the glue. More frequent measurements would have affected adhesives that crosslinked at 100% humidity.

In Sikaflex-252, a polyurethane, one-component adhesive, the reaction group is located around ~2265. In Figure 3, the green arrow indicates the location of the reaction group. In Figure 4, the reaction direction is visible.

Given groups are located at a given wavenumber, these general locations are shown in Figure 5, they can only be shifted slightly. Based on Figure 6, the reaction group is isocyanide. Isocyanide (also known as isonitrile or carbylamine) is an organic compound with the functional group N≡C. It forms bonds through nitrogen.

4.1.2 "B" Sample - Curing mechanism in outdoor, unconditioned environment of PUR adhesive

The "B" pattern is a nearly 100% cross-linked adhesive. The sample was measured in FTIR in an outdoor environment with 30-40% humidity.

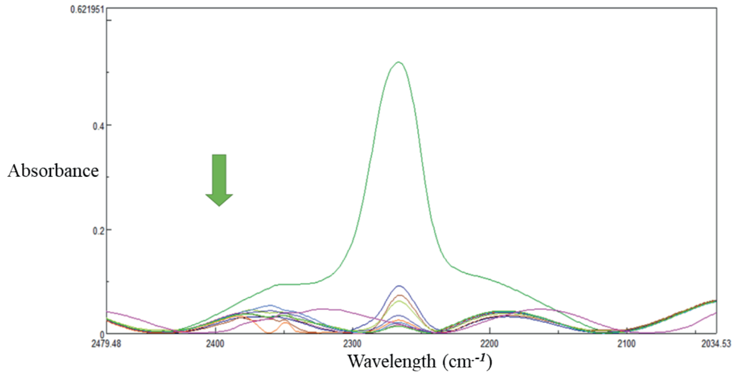

Figure 3 *Results for reaction groups in sample A with direction of change in absorbance*

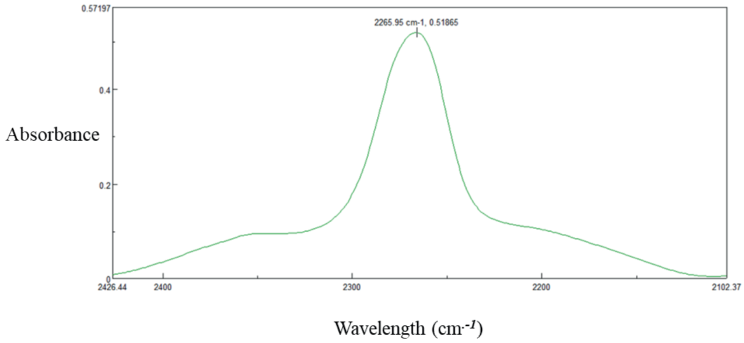

Figure 4 *Reaction group with peak at wavelength 2265*

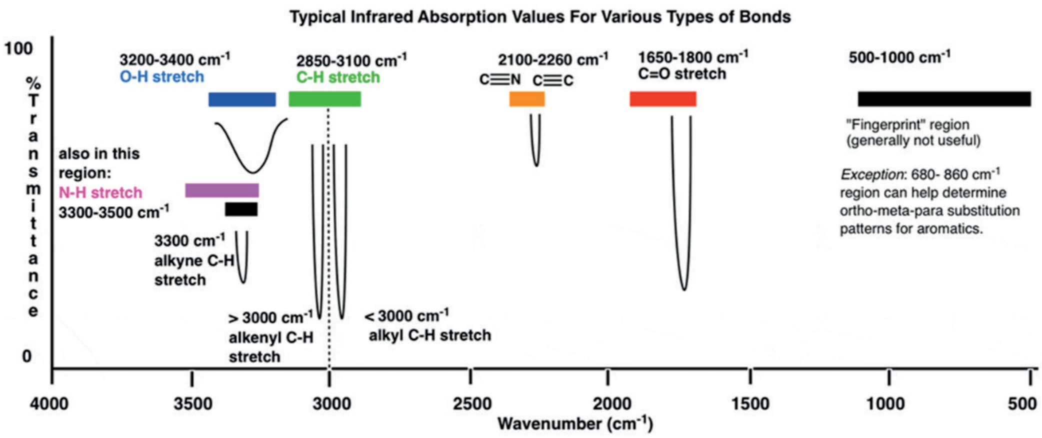

Figure 5 *General locations of different joints*

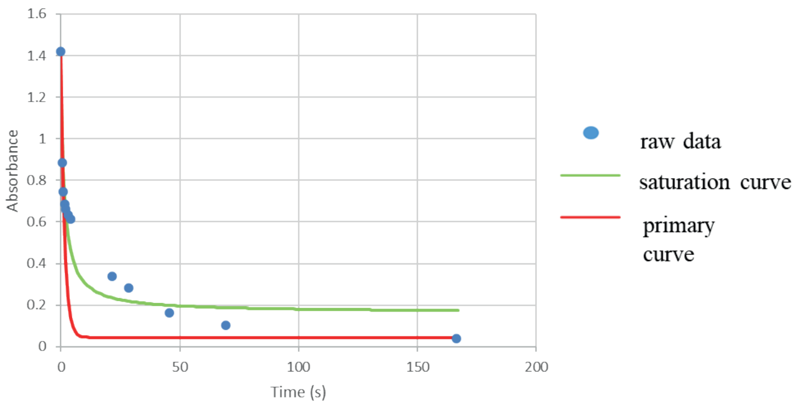

Figure 6 *Cross-linking of sample B*

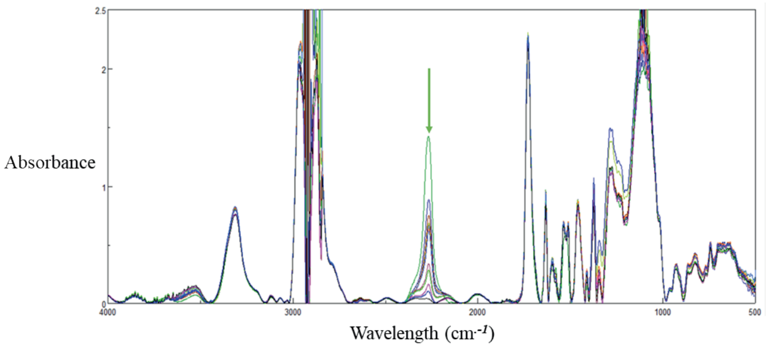

Figure 7 *Results of measurement "B" in FTIR Spectra Analysis*

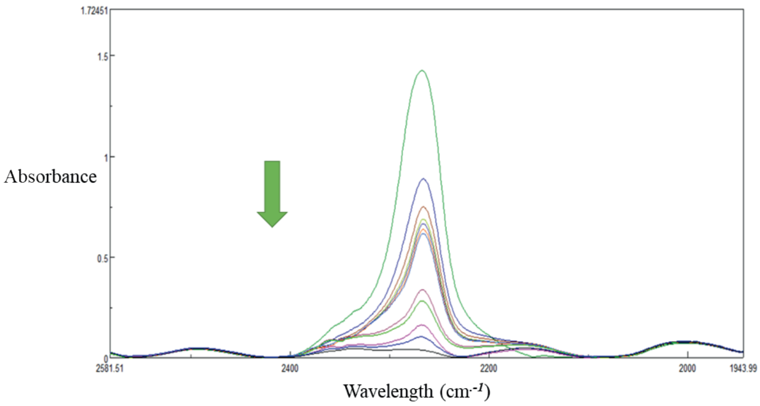

Figure 8 *Results for reaction groups in sample B with direction of change in absorbance*

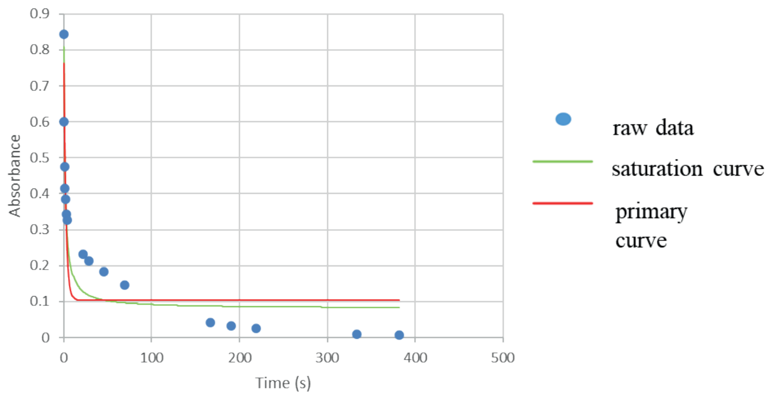

Figure 9 *Cross-linking of sample "C"*

As can be seen, the absorbance varied steeply during the first 4 hours (Figure 7). The reaction rate was the highest here and as time went on, the cross-linking process slowed down as the number of reactive groups decreased (Figure 8).

4.1.3 „C" sample - Curing mechanism in 30% humidity in laboratory, controlled environment of PUR adhesive

In Figure 9 sample C was solidified in a laboratory environment of ~30% humidity and 24 ± 5 °C. As seen in sample B, the reaction is the fastest in the first 4 hours and gradually slows down (Figure 10). The decreasing of the absorbance in the FTIR results can be seen in higher resolution in Figure 11.

4.1.4 Comparison of samples B and C to determine the humidity difference

In Figure 12 the results show that the glue in the humid environment reached the cross-linked state one day earlier, but it is difficult to distinguish the onset of the cross-linked state, as the initial state is considered to be similar for both samples.

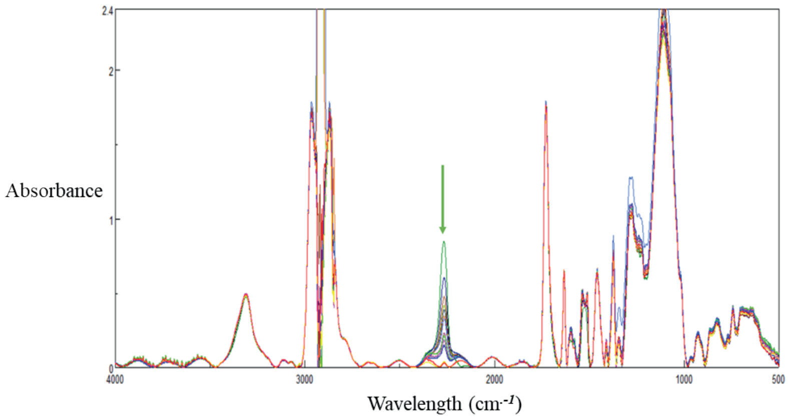

Figure 10 *"C" measurement results in the FTIR Spectra Analysis program*

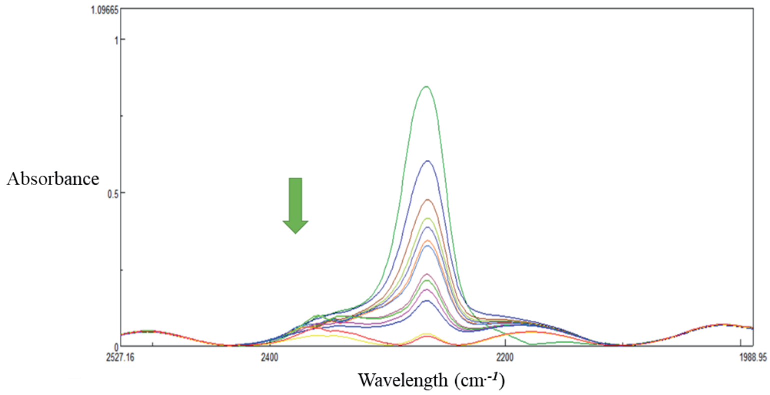

Figure 11 *Results for reaction groups in sample C with direction of change in absorbance*

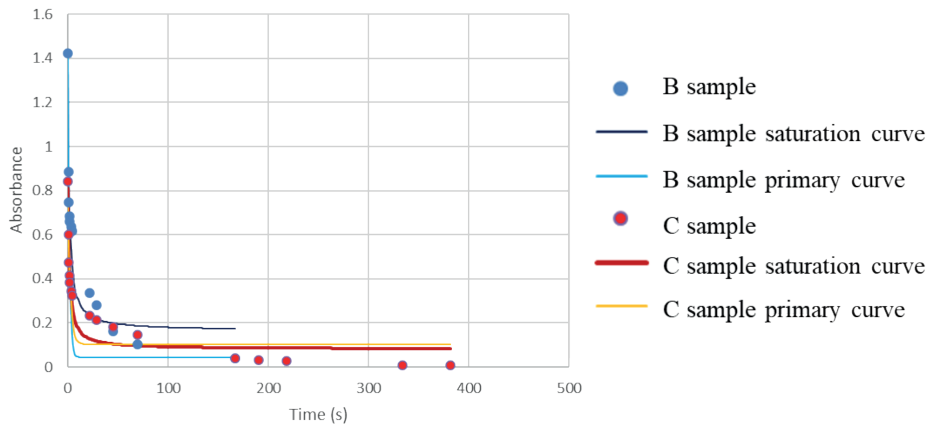

Figure 12 *Crosslinking speed of sample pair B and C relative to each other*

4.1.5 „D" sample - Curing mechanism in 80% humidity in laboratory, controlled environment of PUR adhesive

The results of the higher 80% humidity samples can be seen in Figures 13 and 14. The results show that higher humidity increases the starting procedure of curing or PUR. In Figure 15 a decreasing tendency of absorbance can be seen in the chemical groups during the FTIR.

4.1.6 „E" sample - Curing mechanism in 60% humidity in laboratory, controlled environment of PUR adhesive

The curing of sample E, at 60% humidity, took 14 days (Figure 16). Thus, confirming the claim that in a humid environment, the reaction rate is faster. In Figures 17 and 18 the decreasing tendency of the absorbance of reaction groups can be seen in details.

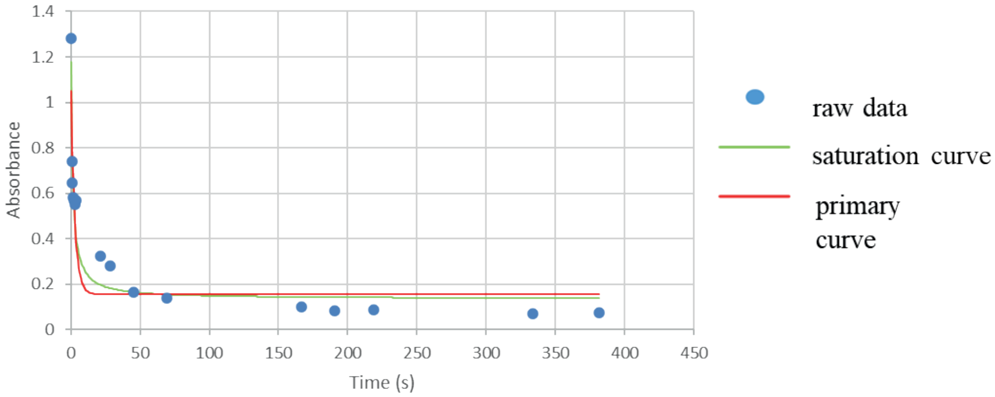

Figure 13 *Cross-linking of sample D*

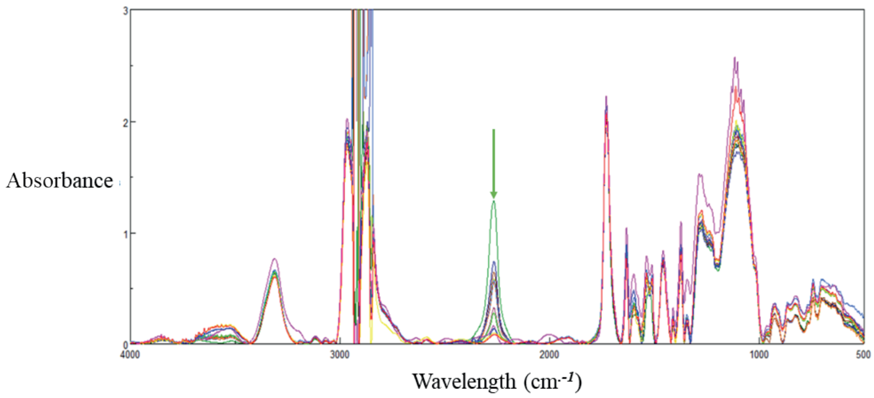

Figure 14 *"D" measurement results in FTIR Spectra Analysis*

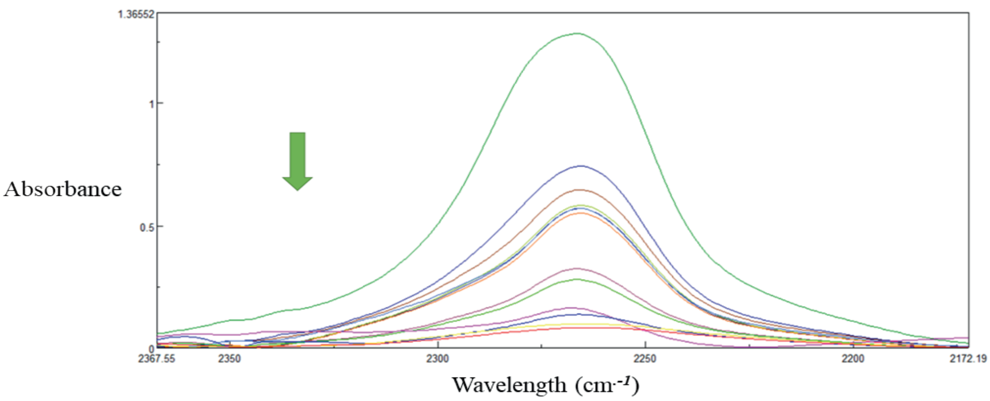

Figure 15 *Results for reaction groups in sample D with direction of change in absorbance*

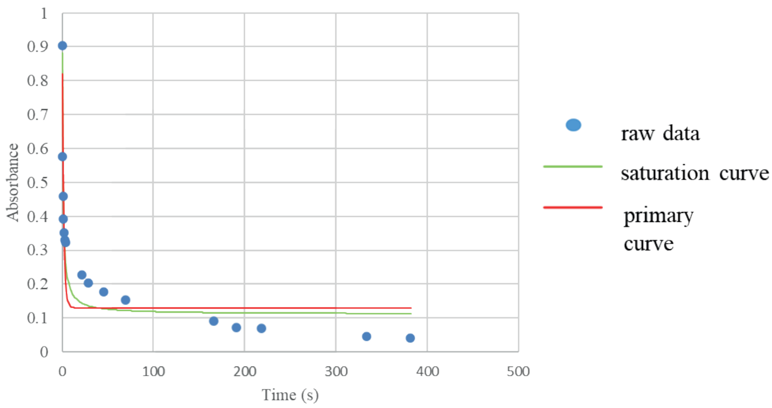

Figure 16 *"E" sample cross-linking*

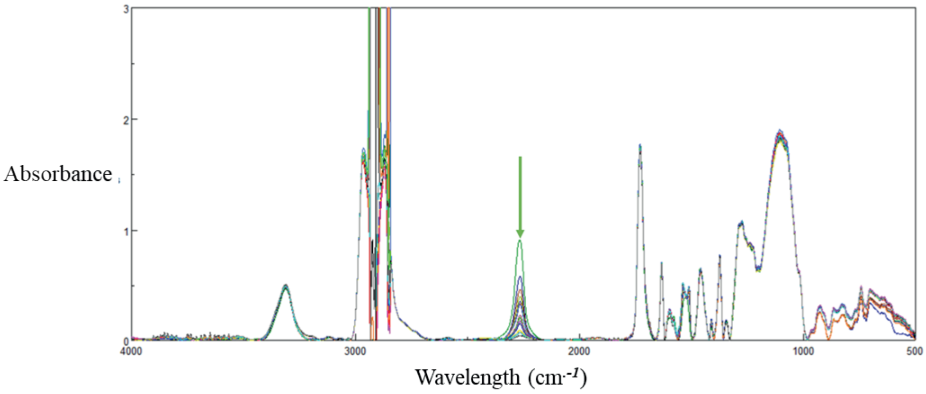

Figure 17 *"E" measurement results in FTIR Spectra Analysis*

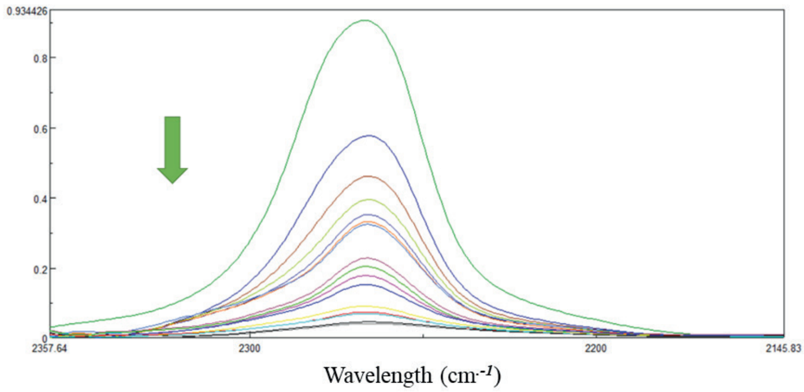

Figure 18 *Results for reaction groups in sample E with direction of change in absorbance*

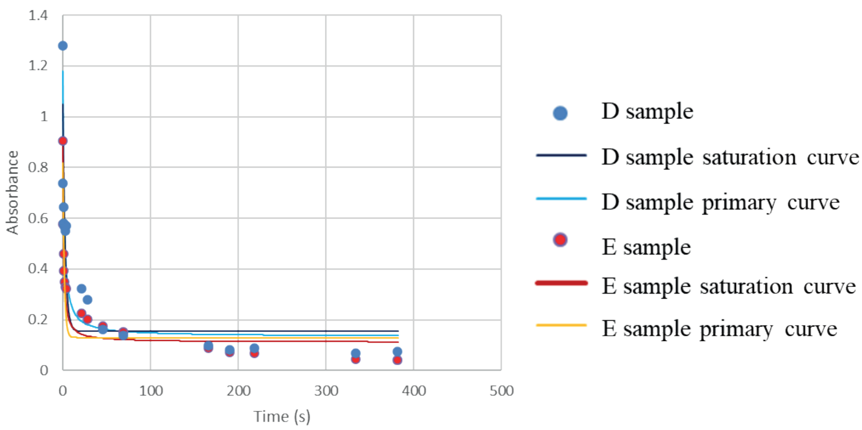

Figure 19 *Cross-linking speed of sample pair "D" and "E" relative to each other*

4.1.7 Comparison of "D" and "E" sample to investigate the effect of humidity

In Figure 19. The results show that adhesive in the higher humidity environment cured much faster. Here, as in the two measurements above, the first 4-8 hours have the highest reaction rate. The results obtained show that the humidity plays an increasingly important role towards the end of the crosslinking process, with almost no difference between the two environments at the beginning and a steadily increasing role as the crosslinking process progresses.

5 Summary

The first objective of this research was to study the Sikaflex-252 structural adhesive; reaction group that induces cross-linking and the speed and difference of this cross-linking with respect to a counterpart in another environment. This study was concerned with the reaction rate constants of the reaction groups of the material. The results suggest that the cross-linking rate of the adhesive varies significantly with the environment. Humidity plays an increasingly important role in bond formation over time. The second objective was to investigate the cross-linking rates of other types of adhesives and to gain a broader understanding of them. Upon scrutinizing the results, we have arrived at the conclusion that the environmental factors are not to be neglected in the context of bonding. Consequently, the surrounding environment holds significant importance in the application of adhesives. In our forthcoming research, authors aim to further enhance their understanding of adhesives and explore materials that were not included in the current experiments. Additionally, authors plan to conduct the further research employing alternative methodologies.

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Conflicts of interest

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

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