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R Al-Safy
Al-Mustansiriya University

R Al-Mahaidi
Swinburne Institute of Technology

G P. Simon
Monash University

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NIR FOR STRUCTURAL CHARACTERIZATION OF NANOCLAY-MODIFIED ADHESIVE USED IN CFRP APPLICATIONS

R. Al-Safy*
Materials Engineering Department, Al-Mustansiriya University, Baghdad, Iraq,
rawaa.alsafy@gmail.com (Correspond Author)

R. Al-Mahaidi
Faculty of Science, Engineering and Technology, Swinburne Institute of Technology,
Hawthorn, Victoria, 3122, Australia. ralmahaidi@swin.edu.au

G.P. Simon
Department of Materials Engineering, Monash University, Melbourne, Australia.
George.Simon@monash.edu

ABSTRACT

The chemical and mechanical properties of cured adhesives are sensitive to variations in the starting material. Many parameters are responsible for the properties of the final epoxy network. The chemical structure of the epoxy network is one of these parameters affected by reactions during the curing process. In this work, a commercially-available bonding adhesive, MBrace® Saturant, is used for modification with different concentrations, (0,1,2.5 5 and 7.5 wt%),of Nanomer® I.30E using direct mixing method. The bonding adhesive is commonly used thermosetting polymer for bonding CFRP to concrete members. Characterization of the structure of the adhesive with and without modification was investigated by Near-Infrared spectroscopy (NIR). The results provide qualitative information about the structure of the epoxy network, with and without modification with nanoclay, and enable understanding of the nature and extent of the chemical reactions during the curing process in the presence of nanoclay. No influence was found of nanoclay on the cure reactions and spectrometric changes of cure reactions could be better observed by NIR.

KEYWORDS

NIR, adhesive, nanoclay, epoxy resin, CFRP.

INTRODUCTION

Nanomaterials have been widely used to enhance the properties of polymeric matrices due to their properties such their high surface-to-volume ratio (Frisch and Mark 1996, Zeng *et al* 2005, Becker *et al.* 2007). In recent years, more attention have been given to modify thermosetting polymers with various types of nanomaterials to use in Carbon Fibre Reinforced Polymer (CFRP) applications; namely in strengthening concrete members (Al-Safy *et al.* 2011, Al-Safy *et al.* 2012). The performance of CFRP/concrete system was evaluated at various service conditions using nanomaterials modified adhesives. However, it is important to characterize the structure of the modified adhesive to understand the influence of nanomodifiers on the final properties of the adhesive and hence on the performance of the CFRP/concrete system.

The chemical and mechanical properties of cured adhesives are sensitive to variations in the starting material (Chike *et al.* 1993), and many parameters are responsible for the properties of the final epoxy network. The chemical structure of the epoxy network is one of these parameters affected by reactions during the curing process. Various analytical techniques are available to provide qualitative information about the structure of the epoxy network and enable understanding of the nature and extent of the chemical reactions during the curing process. In addition, such analytical techniques were used to characterize the degree of nanomaterial dispersion within the epoxy adhesive. Near-Infrared Spectroscopy (NIR) is an analytical technique which developed in the 1960s (Dannenberg and Harp 1956). NIR is not affected by the transition state from liquid to solid, and enables the monitoring of cure reactions throughout the epoxides conversion from the liquid epoxide mixture to the glassy epoxy resin (Billaud *et al.* 2002).

EXPERIMENTAL PROGRAM

Materials

A commercially-available bonding adhesive, MBrace® Saturant (BASF, Chemical Construction, Pty. Ltd., Australia) was used for modification with nanoclay in this investigation. The adhesive is a two-part system of ambient temperature curing. It is a commonly-used thermosetting polymer for bonding CFRP materials to concrete substrates. Its glass transition temperature is 70°C measured by Dynamic Mechanical Thermal Analysis (DMTA) (Al-Safy *et al* 2009). The nanoclay used in this investigation is a commercially available Nanomer I.30E modifier smectite (Nanocor, USA). It comprises layered silicate of clays with platelets of 1 nm, with aspect ratio's of 400–1000. The clay mineral is a natural montmorillonite modified with an octadeyl amine surface treatment of the interlayer gallery surfaces.

Fabrication of NC/epoxy Adhesive

The direct mixing method was used to disperse nanoclay into the epoxy resin. A pre-calculated amount of nanoclay was dispersed in Part A of MBrace® Saturant epoxy adhesive using a mechanical stirrer at 500 rpm. The stirring procedure was carried for 1hr then the nanoclay/Part A mixture was removed from the hot plate and allowed to cool to ambient temperature. The amine, Part B of MBrace® Saturant, was then added to and mixed manually to produce a homogeneous mixture.

Testing

Measurements of unreacted epoxy after curing

The amount of unreacted epoxy groups after curing for each adhesive mix was determined using the Pekin Elmer Spectrum GX FT-IR System. Small discs were cut from large adhesive discs with 100 mm diameter and 4 mm thickness. The small discs were 1 mm in thickness and 13 mm in diameter. These discs were placed in the sample holder in the NIR equipment and scanned in 16 successive scans in a wave range of 10000-3000 cm^{-1} with 4cm^{-1} resolution. The spectrum obtained for each adhesive disc was analysed to identify the remaining epoxy groups after full curing. The typical heights at 4530 cm^{-1} and 4065 cm^{-1} for the epoxy groups and phenyl groups respectively were identified with their heights. The degree of curing was then calculated from Equation 1 (Poisson *et al.* 1996) as shown below:

$$x = 1 - (\frac{h}{h_0}) \quad (1)$$

where:

x = degree of curing , h= height of 4530 epoxy peak, h_0 = height of 4065 phenyl peak

Monitoring the curing process of epoxy adhesive

NIR technique was used to monitor the curing process for unmodified adhesive and for adhesives modified with the addition of nanoclay. After mixing the monomer (Part A) with the hardener (Part B), the mixture was poured into a mould of Teflon sheet which was sandwiched on both sides with clear glass slides, since glass is transparent in the NIR spectral region. NIR measurement of the degree of curing followed the same procedure as mentioned previously for the solid small discs.

RESULTS AND DISCUSSION

The NIR technique was used in this study to monitor the extension of the curing reaction of unmodified MBrace® Saturant epoxy adhesive after different periods from mixing the monomer (Part A) and the hardener (Pat B). The NIR measurements were taken by scanning 16 successive scans in the range 10000-3000 cm^{-1} with 4cm^{-1} resolution. As shown in Figure 1, various peaks are observed from NIR Septra of liquid state to glass state (rigid) for different periods from mixing. The peaks of interest in the NIR measurements are the epoxy peak at 4530 cm^{-1} and the phenyl band as a reference internal band at 4065 cm^{-1}.

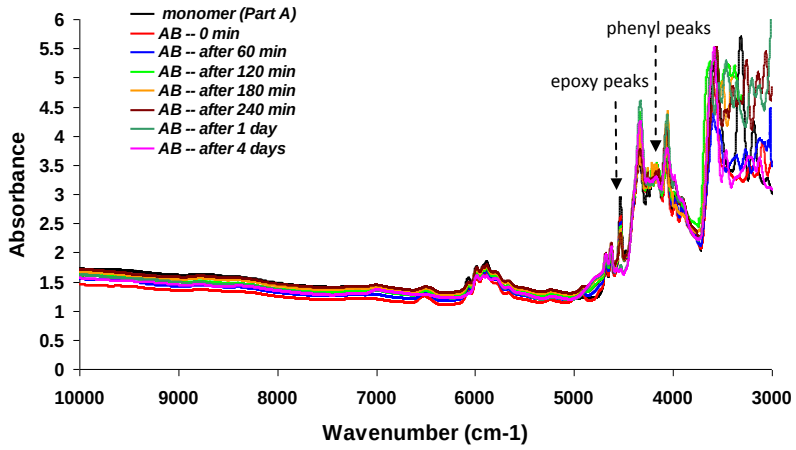

Figure 1. Typical NIR spectrum from monitoring the curing process of MBrace® Saturant epoxy adhesive after different periods from mixing the monomer with the hardener at ambient conditions

The changes in the height of the epoxy group are indicated in Figure 2, which shows the measurements from the typical NIR spectrum in Figure 1. The observed intensity of the epoxy band decreases with increasing cure time, which means a reduction in the epoxy groups. Peaks at 4532 – 4539 cm^{-1} are observed in the typical NIR spectrum to identify the epoxy group and these peaks are demonstrated and listed in Table 1. These peaks differ from the typical epoxy peak (4530), and this could be attributed to the molecular chains having little movement during the curing process. These observed peaks are a combination of the epoxide CH fundamental at 3050 cm^{-1} and the CH_2 fundamental at 1460 cm^{-1} (Poisson *et al.* 1996; Hussain *et al.* 2004). The phenyl peaks are within the range of 4060-4116 cm^{-1}. These peaks are different from the typical phenyl band at 4065 cm^{-1} which represent the aromatic combination band.

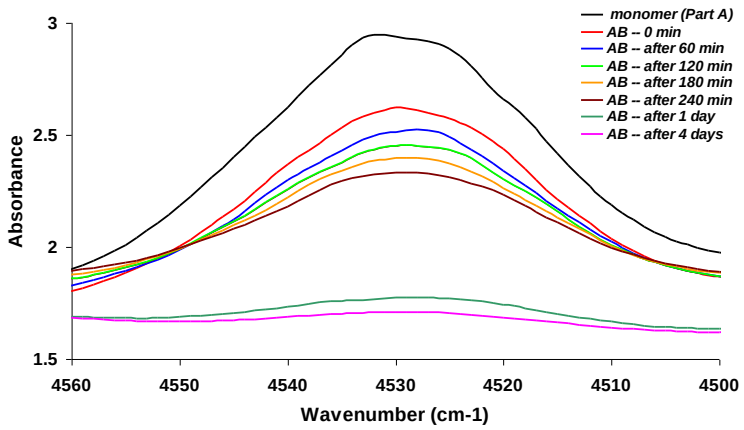

Figure 2. Typical epoxy peaks from NIR spectrum for MBrace® Saturant epoxy adhesive

The epoxy peaks after one year of curing at ambient conditions were measured and listed in Table 2. These peaks appear to have disappeared and are hard to recognize at 4526–4534 cm^{-1} for adhesives with and without nanoclay addition, as shown in Figure 3. This figure was obtained from NIR spectrum in Figure 4 from scanning small, fully cured solid discs of the unmodified and NC modified adhesive after approximately one year from mixing the monomer (Part A) with the hardener (Part B). No significant change in the pattern of NIR spectrum can be observed in Figures 3 and 4 with nanoclay addition, compared with unmodified epoxy adhesive.

The epoxy's degree of curing was calculated from the heights of the epoxy peak and phenyl peak for each mix and for different curing periods of time at ambient conditions. The calculated values are listed in Table 1. In terms of unmodified adhesive in liquid state, the degree of curing increases with increased the curing time as the epoxy group reduces during the reaction. In addition, the degree of curing of samples with nanoclay addition was determined and the results are presented in Table 2. Even after one year of curing, unreacted epoxy remains within the final epoxy adhesive network.

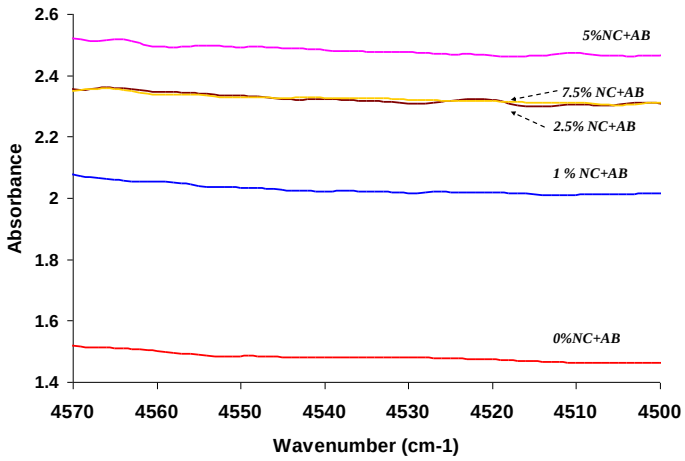

Figure 3. Typical epoxy peaks from NIR spectrum for MBrace® Saturant epoxy adhesive modified with NC after one year from mixing the monomer with the hardener at ambient conditions

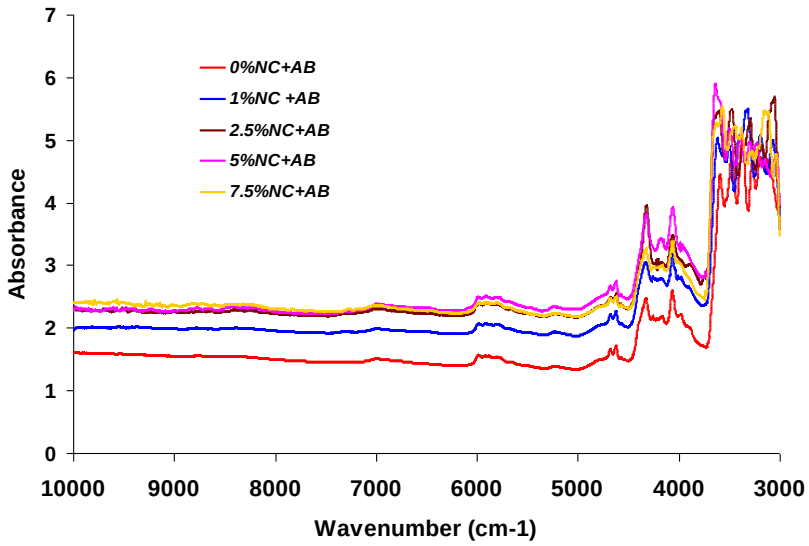

Figure 4. Typical NIR spectrum from monitoring the curing process of NC modified MBrace® Saturant epoxy adhesive after one year from mixing the monomer with the hardener at ambient conditions

Table 1. Results from NIR spectra for unmodified MBrace® Saturant epoxy adhesive after different curing times at ambient conditions

Sample code	Wavenumber for epoxy group (cm^{-1})	height of epoxy peak	Wavenumber for phenyl group (cm^{-1})	height of phenyl peak	Degree of curing (%)
Part A	4532	1.1.851	4065	0.06488	-
AB -- 0 time*	4530	0.84069	4065	0.97205	13.51
AB --1 hr	4530	0.59418	4060	0.93381	36.37
AB -- 3 hr	4530	0.42268	4069	1.05814	60.05
AB -- 1 day	4537	0.09	4039	0.43542	79.3
AB -- 4 days	4539	0.07694	4116	0.47523	83.81

*MBace® Saturant epoxy adhesive

Table 2. Results from NIR spectra for MBrace® Saturant epoxy adhesive with NC modification after one year of curing at ambient conditions

Sample code	Wavenumber for epoxy group (cm^{-1})	height of epoxy peak	Wavenumber for phenyl group (cm^{-1})	height of phenyl peak	Degree of curing (%)
0% NC+AB***	4530	0.00264	4060	0.46046	99.43
1% NC+AB	4526	0.00306	0.04439	0.04439	93.11
2.5%NC+AB	4533	0.00311	0.43364	0.43364	99.28
5%NC+AB	4530	0.00315	0.5953	0.5953	99.47
7.5%NC+AB	4534	0.00232	0.12754	0.12754	98.18

*Nanoclay
**MBace® Saturant epoxy adhesive

CONCLUSIONS

Near-Infrared Spectroscopy (NIR) was employed in this work for structural characterization of nanoclay modified adhesive that used for bonding CFRP to concrete members. Epoxy peaks in NIR of epoxy resins were found to occurr in the wavenumber range of 4532 – 4539 cm^{-1} and allowed monitoring of the curing process of unmodified epoxy adhesives for different periods of ambient temperature curing (up to 4 days). These values were slightly shifted from the typical epoxy peak 4530 cm^{-1} seen in the monomer. After one year of curing at ambient temperature, the epoxy peaks were observed with difficulty at 4526–4534 cm^{-1} for nanoclay-modified epoxy adhesive and unmodified adhesive. The calculated degree of curing for these samples indicated the availability of a very small amount of unreacted epoxy in the final adhesive network.

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