

KUE 309

Final Report Guidelines

1. Final reports should be written according to the format of Journal of Physical Science.
2. Reports can be written either in English or Bahasa Malaysia and should be typed on one side of A4 paper, doubled-spaced throughout, including the reference section, with a 4-cm margin on all-sides. All manuscript pages should be numbered in the following order: title, abstract, text, references, figures and tables.
3. The title and abstract should be combined on one page.
4. All reports should be summarized in an abstract of not more than 100 words in both English and Bahasa Malaysia. Avoid abbreviations, diagrams, and reference to the text. Provide a maximum of six keywords and these should be placed after the abstract.
5. References should be cited in the text by an Arabic numeral in superscript. References should be listed in numerical order.
6. References to periodicals should include initial(s) and name(s) of author(s), title of the periodical, volume number, page number, and year of publication.
7. References to books should include initial(s) and names(s) of author(s), title of the book, name of publisher, place of publication, and year of publication.
8. References to websites, although not encouraged, should include name(s) of author(s), year published, title of article, name of website, date accessed.

For items 6 to 8, please refer to examples given below:

- i. Bucknal, C.B. (1977). *Toughened plastics*. London: Applied Science Publishers.
- ii. Barry, G.B. and Chorley, R.J. (1998). *Atmosphere, weather and climate*. 7th edition, London: Ruthledge.
- iii. Campbell, D.S. (1978). Graft copolymers from natural rubber. In: Roberts, A.E. (ed.). *Natural rubber science and technology*. New York: Oxford University Press, 679-689.

- iv. Ha, C.S. and Kim, S.C. (1989). Tensile properties and morphology of the dynamically cured EPDM and PP/HDPE ternary blends. *Journal of Applied Polymer Science*, 37, 389-405.
 - v. <http://www.hawking.org.uk/home/hindex.html>: accessed 3 July 2008.
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- 9. Tables and figures should not be inserted in the text but should be included as separate sheet of files with clearly labeled captions, legends, keys and footnotes, if any. Each table should be typed on a separate sheet of paper. Tables should be numbered consecutively in Arabic numerals.
 - 10. Figures should be numbered consecutively in Arabic numerals. Please submit one figure per page.
 - 11. The maximum number of pages of the text is 20.

(contoh)

**DETERMINATION OF SUDAN DYES IN SPICES
USING REVERSED PHASE HPLC**

by

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Final report submitted in partial fulfillment of the requirements for KUE 309

– Final Year Project

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March 2009

(contoh)

**PENENTUAN PEWARNA TIRUAN DI DALAM MINUMAN MENGGUNAKAN
KAEDAH KROMATOGRAFI CECAIR PRESTASI TINGGI**

oleh

KOO JIN SHENG

**Laporan akhir yang diserahkan untuk memenuhi sebahagian keperluan
bagi KUE 309 – Projek Tahun Akhir**

Penyelia: Dr.

**Pusat Pengajian Sains Kimia
Universiti Sains Malaysia**

Mach 2009

(contoh)

FTIR CHARACTERIZATION OF MOISTURE CURED POLYURETHANE

Abstract

The urethane prepolymer product and its microstructure produced throughout the curing process were investigated by Fourier Transform Infrared (FTIR) spectroscopy. The coating process was adapted from one-component polyurethane coating system, where prepolymer was applied as the undercoat layer. The obtained infrared spectrum confirmed that both urethane and urea carbonyl groups existed with small portion of isocyanate remained unreacted in the system. The depreciation trend of isocyanate peak and shifting pattern of other absorption bands such as NH and carbonyl group were observed and explained in this paper. Peak area measurement confirmed that isocyanate content decreased with the progress of curing reaction. The FTIR results showed that the urethane C=O band shifted to lower frequency while the urea C=O shifted slightly to the higher frequency. The study also found that the polymer microstructure became more disordered at the end of curing reaction, which was indicated by the decrease of the ordered C=O peak intensity as the disordered peak increased.

Keywords: Isocyanate, prepolymer, curing, peak shifting

Abstrak

Hasilan prapolimer uretana dan mikrostruktur yang terbentuk ketika berlangsungnya proses pematangan diselidiki dengan menggunakan spektroskopi inframerah transformasi Fourier (FTIR). Proses pelitupan diadaptasi daripada sistem perlitupan satu-komponen, dengan prapolimer digunakan sebagai lapisan salutan bawah. Spektrum inframerah yang diperolehi mengesahkan kehadiran kedua-dua kumpulan uretana dan urea di samping sedikit baki isosianat yang tidak bertindak balas. Corak penurunan puncak isosianat dan pergerakan jalur serapan NH dan C=O diperhatikan dan diperjelaskan dalam kertas kerja ini. Ukuran keluasan puncak mengesahkan bahawa kandungan isosianat menurun ketika proses pematangan berlangsung. Keputusan FTIR menunjukkan kumpulan uretana karbonil teranjak ke frekuensi yang lebih rendah manakala kumpulan urea karbonil teranjak ke frekuensi yang lebih tinggi. Kajian ini juga mendapati bahawa mikrostruktur polimer menjadi lebih tidak bertertib pada akhir tindak balas pematangan, seperti yang ditunjukkan melalui penurunan puncak keamatan C=O yang teratur apabila puncak keserapan urea karbonil yang tidak teratur meningkat.

Katakunci: Isosianat, prapolimer, pematangan, anjakan puncak

1. INTRODUCTION

Polyurethane is a widely used polymer in modern industry due to its durability, reliability and high performance. The use of this polymer in industries is very extensive which includes automotive, furniture, thermal insulation, construction, footwear and coating industries¹. Generally in the coating industry, there are two modes of surface coating which are undercoat (also known as basecoat) and topcoat. Polyurethane undercoat is normally use for automotive underseals, boats hull coating, tent roofing, flooring and many more². Apart from these common applications, polyurethane coatings can be utilized in metallization process. Some studies used polyurethane as substrates for metallization³⁻⁴ and other use it as undercoat before metallization regardless of the type of substrates⁵.

In this study, polyurethane that is formed from prepolymer liquid is characterized through Fourier Transform Infrared (FTIR) spectroscopy. FTIR can monitor progress of reaction by monitoring the depreciation trend of isocyanate peak, which is possible through real-time or near-real-time application⁶. However, if catalyst is used to accelerate the reaction, monitoring using real-time by means of modern spectroscopic tool is definitely necessary, especially if the scanning time interval is set very narrow, i.e. 60 seconds etc. This will not be practical for moisture-curing system as presented in this study since the reaction normally takes longer time, with a minimum of 24 hr¹. Therefore for monitoring the

progress of reaction of moisture-cured system and estimating the stabilization time of isocyanate reaction for metallization studies, development of 3D spectra through manual FTIR scanning is believe to be endurable.

The prepolymer is a mixture of MDI and polyol. The prepolymer is cured for 8 days by allowing it to cure at room temperature for 24 hours, which is subsequently followed by post-curing in an oven at 70 °C for several days. This technique is adapted from one-component polyurethane coating system¹⁻² and classified as polyurethane coating Type II in the ASTM D16 standard⁷. An aromatic isocyanate was chosen in this work because it can produce harder coating, good chemical resistance and low cost¹⁻². The primary curing reaction is between isocyanate and atmospheric moisture, to yield substituted urea at the end of the curing process^{1,7}. The use of heat at 70 °C is to accelerate the curing due to moisture presence, which requires relatively longer working time. Moreover the substrates that are currently employed in the related works are engineering grade acrylonitrile butadiene styrene (ABS) plastics, which are heat sensitive materials, and the deform temperature is not far off from 70 °C⁸⁻⁹. In addition, curing at 70 °C can yield allophanate and biuret linkages that promote additional branching and cross linking to the polyurethane system¹⁰. Generally, curing at higher temperature provides improve chemical resistance and adhesion^{1,10-11}.

Blister, bubbles and pinholes are common coating defects that normally occur at higher humidity level and temperature due to the release of carbon dioxide, especially if thicker coating is applied. This problem can be overcome through the use of viscosity reducer such as solvent, glycol ethers, propylene carbonate or others. In this work, polyether base polyol was used because it is known to provide low viscosity coating system for easy flowing and aid processing¹.

The main objective of this study is to confirm that the prepolymer product obtained according to this undercoating and curing technique described above is a urethane polymer. In addition, near-real time FTIR spectra are also recorded to observe the trend of isocyanate reaction and its duration required for stabilization. The spectra are also used to elucidate microphase change the curing reaction progresses. The phases that are of particular interest are classified as ordered and disordered phases. The spectra show the absorption peaks in the range of 1660 – 1670 and 1630 – 1645 cm^{-1} respectively¹². The absorption regions that were attributed to the ordered and disordered phase were closely monitored.

2. EXPERIMENTAL

2.1 Materials and preparation of prepolymer solution

Poly(ethylene) glycol divinyl ether 200 (polyol) and diphenylmethane-4,4'-diisocyanate (MDI) were obtained from Merck-Schuchardt, Germany and were

used without further purification. Prepolymer solution was prepared by mixing the polyol and MDI in 1:1 ratio in an amber bottle at room temperature. The bottle then was properly sealed to avoid contact with air moisture. It was allowed to settle at room temperature for at least 12 hours before used.

2.2 FTIR analysis

A thin layer of prepolymer solution was applied on a zinc selenide crystal. The sample was immediately scanned in the range of 4000 to 650 cm^{-1} using a Perkin Elmer Spectrometer System 2000 as a near zero-time spectrum. The spectral resolution was set at 4 cm^{-1} . The subsequent mid-IR spectra were recorded according to the following time sequences: 10, 20, 30, 40, 50, 60, 70, 80, 90, 120, 150, 180, 240, 300, 360, 420, 480 minutes; followed by 24, 26, 28, 30, 32 hours and then 2, 3, 4, 5, 6, 7 and 8 days. From 0 to 24 hours, the sample was cured at room temperature. While from the period of 24 hours to 8 days, the sample was post-cured in an oven at 70 °C.

3. RESULTS AND DISCUSSION

The mid-IR spectrum for the prepolymer product after subjecting to the curing design is shown in Figure 1. The spectrum confirmed that the product materialized from the prepolymer liquid is polyurethane due to clear existence of the main absorption peaks such as peaks of NH, CH (methylene), urethane carbonyl, urea carbonyl and CN^{13, 14 – 15}. The corresponding functional groups are in accordance with the absorption wave numbers extracted from literatures as summarized in Table 1. The peak at 2277 cm⁻¹ indicates that there is still some fraction of isocyanate remains unreacted in the system. Both urethane and urea carbonyls are present in the system. The polyurea yield is expected since the curing process is based on moisture curing reaction. Meanwhile urethane carbonyl is believed to be derived either from the sub-reaction of isocyanate with the polyol or the breakdown of allophanate or biuret into isocyanate, urethane and urea at elevated temperature^{1, 10}. This phenomenon (of having both urethane and urea in a polymer system) is not unusual since polyurea linkages would exist in many polyurethane products⁷.

In order to probe the progress of the reaction, the prepolymer and prepolymer product spectra were overlaid in a similar manner as near-real time FTIR according to the pre-scheduled time interval as presented in Figure 2, 3, 4 and 5. The changes in the intensity of the isocyanate peak at around 2277 cm⁻¹ are

clear evident that the curing reaction is progressing (Figure 2). It implies that as the curing time increases, the intensity of isocyanate peak decreases.

In this study, the depreciation trend is quantified using peak area measurement as presented by Mary A. Thomson *et al.*⁶. Peak area is calculated using Perkin Elmer V3.02 software, where the highest position or tip of each peak is manually set in the peak-fitting menu in the program. The resulting plot as shown in Figure 6 obviously indicates that the isocyanate peak area decreases with the progress of the curing reaction. The reduction of the peak area is due to gradual consumption of the isocyanate groups of the prepolymer, which react with air moisture to form polyurea linkages which eventually leads to the curing of the prepolymer^{1, 10 - 11}. The relative humidity level in the laboratory where the work is conducted is measured between 65 and 85 %, suggesting that the moisture needed for the reaction is sufficient. It had been reported that for a successful coating application, the minimum relative humidity should be above 30 %¹. It can be seen that from the peak area measurement, the isocyanate reaction is decreasing over time. The reaction started to stabilize approximately on the fifth day of curing. It is believed that the intensity of isocyanate peak will continue to decrease if post-curing period is further extended however the depreciation rate is expected to be insignificant. This is because the plot of isocyanate peak area from the fifth onwards had acquired a flat line.

The isocyanate group is said to be reactive since it has four resonance structures¹. These electronic structures expose their C to be easily attacked by electron donor, while their N is prone to electron acceptor attack. This behaviour renders the isocyanate to react with atmospheric moisture to produce an intermediate carbamic acid product that later break down into carbon dioxide and primary amine. The amine later reacts with other isocyanate to form symmetrical urea^{1, 2, 10-11}. This reaction yields NH and C=O groups, while C-O-C is expected to form from the resins of polyether base polyol.

It is clear from the spectral topography that the isocyanate reaction with air moisture started upon the exposure of prepolymer to the air (Figure 2). Although the isocyanate was consumed at the beginning of exposure process, the development of NH, urethane C=O and urea C=O only became pronounce after approximately 4 hours as shown in Figure 3 and Figure 4 respectively. It is observed that an absorption band at approximately 1725 cm^{-1} appeared within 0 to 60 minutes (Figure 3). This band according to Blanchard *et al.*¹⁶ is one of the C=O stretching bands of carbamic acid (C=O bands are assigned at 1725, 1717 and $\sim 1700\text{ cm}^{-1}$). This finding suggested that the system did not immediately form urethane upon exposure to air moisture but formed the intermediate carbamic acid, which was in agreement with a typical polyurethane reaction^{1, 2, 10-11}.

In the case of NH, the increase in NH peak intensity is also accompanied by significant rise of other NH absorption peaks at 1510 cm^{-1} that represents NH bending while the peak at 1542 cm^{-1} represents CN stretching with NH bending (Figure 5). Since prepolymer product consists of active hydrogen-containing group (NH) that acts as proton donor and C=O group as proton acceptor, the formation of intermolecular forces is very much expected. In this study, the effect of intermolecular forces is indicated by the shifting of NH peak from 3393 cm^{-1} (prepolymer) to 3333 cm^{-1} at the end of curing process (Figure 3). The formation of hydrogen bond between NH and C=O (either from urethane or urea group) will minimize the freedom of H from NH group to vibrate, therefore lowering its IR absorption frequency. The same explanation also goes to carbonyl group that represents urethane C=O. The hydrogen bond between NH and urethane C=O rendered this carbonyl group to undergo shifting from 1727 cm^{-1} (prepolymer) to 1708 cm^{-1} (Figure 4).

Meanwhile the absorption peak that corresponds to hydrogen bonded urea carbonyl is perceived at 1659 cm^{-1} at the end of recording spectrum as clearly shown in Figure 4. It is interesting to note that this peak only became pronounced after 24 hours of curing. It is also interesting to observe that another urea carbonyl peaks at approximately 1637 cm^{-1} which was intense at the beginning but gradually decreased in the spectral topography. Based on the recording spectra, the peak become insignificant (appeared as shoulder) after 2 days of curing (Figure 4). These two peaks according to E. Yilgör *et al.*¹³, which are

summarized in Table 2, can be attributed to the ordered and disordered H-bond urea carbonyl stretching respectively. The ordered phase represents molecular arrangement of urea carbonyl groups that are hydrogen-bonded to urea N-H groups in a 'three-dimensional' hydrogen bond. Meanwhile disordered phase is a state where carbonyl group is hydrogen-bonded to only one urea or urethane N-H, in a disordered fashion^{12, 17}. It is observed in this study, as the curing time increases, the polymer system becomes more disordered. This finding probably can be correlated to phase separation studies performed by Garret *et al.*¹⁷. They suggested that the decrease of the ordered peak to that of disordered is due to a decrease in hard segment – soft segment separation. In general, the hard segments are often composed of aromatic diisocyanate products, while the soft segments are made of the polyether or polyester polyol. If there is a strong electronic interaction existed between hard and soft segments, this will usually lead to a phase mixing.

Hydrogen bonding will usually decrease the absorption wave number of hydrogen-bonded groups. However, it is surprising to observe that this phenomenon did not happen to urea carbonyl group (both ordered and disordered). In fact there was a slight increase in the absorption frequency (Table 2). The most possible explanation for this phenomenon is probably best described by Yilgör *et al.*^{12, 13}. They reported that there is strong competition between C-O-C and C=O in forming hydrogen bonding with NH group, which is reflected by a shift in C=O peak to higher frequency. The development of H-bond

between ether oxygen and NH group leads to the depreciation of the intermolecular H-bonding of urea C=O and NH group. As a consequence, H from NH group attains more freedom to vibrate, therefore increases its IR absorption frequency. Meanwhile no significant shift of ether peak is observed. It remained consistent at 1110 – 1108 cm^{-1} throughout the curing reaction.

4. CONCLUSIONS

The results of this study show that moisture curing of polyol and MDI mixture yields both urethane and urea groups with trace of isocyanate still remained unreacted in the system. FTIR analysis demonstrates that isocyanate reaction began upon exposure to atmospheric moisture and stabilized only on the fifth day of curing. The intermolecular forces due to H-bonding causes the urethane C=O band to shift to lower frequency but slightly to higher frequency for urea carbonyl. The polymer system becomes more disordered at the end of curing reaction. This is indicated by the decrease of the intensity of the ordered urea C=O peak and the increase of the disordered urea C=O peak.

5. ACKNOWLEDGEMENTS

The authors would like to express their appreciation to Universiti Sains Malaysia for the financial support given through the USM Short Term Grant Scheme (304/PKIMIA/635055)

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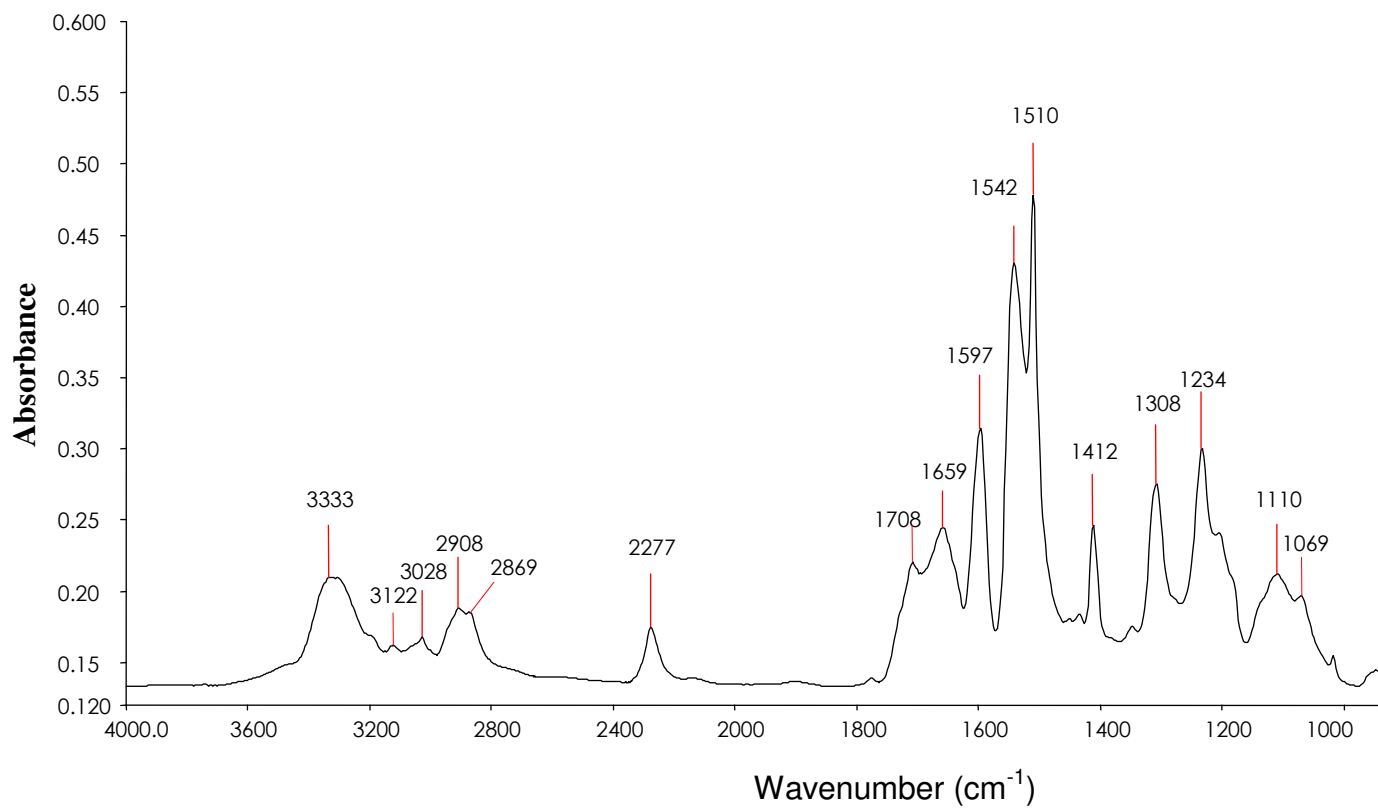


Figure 1. IR spectrum of moisture cured polyurethane derivative after 8 days of curing

Table 1

Attribution of IR absorption frequencies for the polyurethane derivative

Wave number (cm ⁻¹)	Functional groups	Reference
3333	N-H (H-bonded)	14 – 15
3122, 3028	C-H (aromatic)	
2908	C-H (methylene), ν_{as}	
2869	C-H (methylene), ν_s	
2277	N=C=O	16, 18
1708	C=O (urethane) (H-bonded)	12, 13, 14
1659	C=O (urea) (H-bonded)	
1597	C=C (phenyl)	14 – 15
1542	C-N stretch with N-H	
1510	N-H bending	
1412	C-C (aromatic ring)	
1308	C-N & N-H	
1234	C-N	
1110	C-O-C	
1069	C-O-C of C-O-C=C urethane	

Table 2

The peak shifts of NH and carbonyl groups of the polyurethane derivative

Band	Wave number (cm ⁻¹)		Δ (cm ⁻¹)	Assignment
	Initial	Final		
NH	3393.1	3333.1	60	NH (H-bonded)
C=O	1727.9	1708.3	19.6	Urethane C=O (H-bonded)
C=O	1635.8	1638.0 (sh.) ^a	-2.2	Urea C=O (ordered)
C=O	1657.1 ^b	1659.6	-2.5	Urea C=O (disordered)

^aReading at 32 hours (after that peak appeared as shoulder onwards)

^bReading at 24 hours where disordered peak started to emerge