Solutions to Blistering: Modification of a Poly(urea-*co*-urethane) Coating Applied to Concrete Surfaces

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Thesis submitted to the faculty of Science and Engineering
of Flinders University
in fulfilment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY
in
CHEMISTRY

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December 2008
Adelaide, South Australia

Dedicated to
my mum, dad, sisters,
papou and yiayia

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Summary

Blistering, during cure, resulting in subsequent coating delamination has been found to occur in a poly (urea-*co*-urethane) cement composite coating used for the protection of new and existing industrial concrete surfaces. Refurbishment of the blistered material, leads to time delays and increased costs.

The reaction kinetics within this product is complex due to one of the reactants being water dispersed. The presence of water causes carbon dioxide evolution during cure through the decomposition of carbamic acid formed from the reaction between water and isocyanate functional groups of the resin. Water also reacts with cement and lime in the reactive aggregate, thus a multitude of reactions occurs, during cure of these complex materials. Due to the complexity of the composite coating, the cure chemistry for the polyurea and polyurethane reactions were investigated individually, with reference to the reactant ratios used by the industry. Although the competing reactions between isocyanate and hydroxyl groups and isocyanate and water molecules has been studied extensively for monomeric systems, carbon dioxide reduction in these systems has resided in the use of catalysts to increase the rate of the preferred reaction. This solution was not economically viable nor was it practical for the industry partners. Solutions were therefore aimed at the reduction or elimination of carbon dioxide in the coating formulation through the addition of a slower reacting polyol. Glycerol was chosen as the slower reacting polyol, because of its ability to reduce the viscosity of the polyol emulsion as well as increase gel times, improving the coating's pot-life and application ability.

The relative rates of cure of the polyurethane/polyurea reactions have not previously been attempted for oligomeric isocyanates with tri-functional polyols, such as castor oil and glycerol dispersed in water. There was a lack of literature describing cure of oligomeric isocyanates and polyol emulsions and the rate of carbon dioxide evolution from these systems. A novel Pressure Differential Scanning Calorimetry (PDSC) technique was used to understand the cure of the polyurea reaction as well as the carbon dioxide evolved from this system and was compared to volumetric tests for this system. The effect of changing the ratios of isocyanate and the reactive components of the polyol emulsion on carbon dioxide evolution was therefore investigated. Understanding how these changes affect the application of the coating system was also taken into consideration through rheological assessment of the polyol formulation. Hydrated lime or quicklime, added to polyurethane coatings was found to aid in the absorption of carbon dioxide, therefore improvements to the cement aggregate by the addition of hydrated lime or quicklime was also considered. The curing mechanism for the composite coating containing the cement and inert fillers was out of the scope of this thesis.

'I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.’

……………………………..

Eleni Papadopoulos

Acknowledgements

I would like to thank Flinders University, the Australian Research Council (ARC) Linkage grant scheme, Prestige Concreting Additives and Baker Technical Services for funding and sponsoring the industry research project.

Thank you to my supervisors; Stephen Clarke and Milena Ginic-Markovic for their support and encouragement throughout the last few years.

There have also been a multitude of people in these last few years who have brightened my days at Flinders University and who I consider to be good friends. Thank you to people past and present: Durkhanai, Elda, Tony, Tricia, Rachel, Dave C., Paul, Ian, Pamela, Simon, Taryn, Dave V., Andrew, Kim, Dee and Kristina.

I would like to give a special mention to all my friends who have endured having me as their “I can’t...I need to study” friend, over these few years. I have been extremely lucky to have such a great support group, who have given me so much.

I wish to express my most heart-felt gratitude to my family, especially my beautiful mum, Toula Papadopoulos, who has given me all the love and support I have needed to go on this journey. Thank you to my beautiful sisters, Athanasia, Penny and Christina, and to my dad, who although is not here at present, has given me the strength, character and support throughout my life and will be remembered in all my achievements. I would also like to thank the newest additions to my family, Martin, my brother-in-law and finally, Theodore!! My gorgeous little nephew, who has brought me the greatest joy in this past year and has made my journey so much easier.

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Glossary

Abbreviations

A(0)	Area underneath peak in FTIR spectra at zero time
A(t)	Area underneath peak in FTIR spectra at time *t*
A_p	Partial area underneath exothermic peak from DSC curves
A_t	Total area underneath exothermic peak from DSC curves
ATR	Attenuated Total Reflectance
CO*n*	Castor Oil fraction in emulsion series with total number of emulsions equal to *n*
COD	Coefficient of Distinction
DEG	Diethylene Glycol
DMA	Dynamic Mechanical Analysis
DOF	Degrees of Freedom
DOP	Dioctyl Phthalate
DSC	Differential Scanning Calorimetry
DTGS	Deuterated Triglycine Sulfate
DVLR10	Commercial name for oligomeric diphenylmethane diisocyanate obtained from Bayer Chemicals
E_a	Apparent activation energy
F*n*	Fillers formulation with total number of formulations equal to *n*
FTIR	Fourier Transform Infrared
G'	Storage modulus/elastic modulus
G''	Loss modulus/viscous modulus
H_{iso}	Isothermal heat of reaction from DSC exotherms
HLB	Hydrophilic-Lipophilic Balance
H_{res}	Residual heat of reaction from DSC exotherms
H_{rxn}	Heat of reaction
H_T	Total heat of reaction from DSC exotherms
k	reaction rate constant
KBr	potassium bromide
NCO	Isocyanate functional groups

NIR	Near Infrared
NMR	Nuclear magnetic Resonance
OH	Hydroxyl functional groups
P	Pressure
P*n*	Polyol emulsion formulation with total number of formulations equal to *n*
PDSC	Pressure Differential Scanning Calorimetry
PMDI	oligomeric diphenylmethane diisocyanate
PO	Pine Oil
R	Universal gas constant
RH	Relative Humidity
S*n*	Surfactant fraction in emulsion series with total number of emulsions equal to *n*
SO	Silicone Oil
tan δ	tan of the Loss angle δ
TDI	toluene diisocyanate
TGA	Thermogravimetric Analysis
t_g	gel time
T_g	Glass transition temperature
T_p	Peak temperature obtained in DSC exotherms
VOC	Volatile Organic Compound
W*n*	Water fraction in emulsion series with total number of emulsions equal to *n*

Greek alphabet

α	conversion
β	heating rate in non-isothermal DSC
γ^*	complex shear rate
Δ	represents change in a value
δ	loss angle in rheological analysis
ε	extinction coefficient in Beer-lambert’s law
η	viscosity obtained by rheological analysis
σ^*	complex shear stress

Terminology

Carbon dioxide evolution. Evolution of carbon dioxide specifically from the reaction between isocyanate and water in the coating measured through volumetric tests.

Diffusion control. Also known as vitrification, used to describe kinetics of cure when the material is cured below the glass transition temperature and there is a change from a chemically controlled system.

Gel time. The gel time is the time at which the reaction has reached a constant conversion, when an infinite molecular crosslinked network has formed.

Pot-life. The pot-life is considered as the time at which the mixed coating formulation is workable before application and is dependent on the gel time of the reactions.

%Reduction in CO_2. This is a measure of the change in carbon dioxide levels between the control sample and that which is being compared. These values are specifically obtained from the volumetric tests performed.

Viscosity build-up. The build up in viscosity represents the molecular weight growth of the polymer during rheological analysis.

Volumetric analysis. This term is used for all tests which measures the amount of carbon dioxide evolved from the coating mixture using the apparatus described in Chapter 2.