THERMAL AND PHOTOCHEMICAL DEGRADATION OF POLYURETHANES BASED ON RENEWABLE MATERIALS

ANIKA ZAFIAH BINTI MOHD RUS

THE UNIVERSITY OF WARWICK

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THERMAL AND PHOTOCHEMICAL DEGRADATION OF
POLYURETHANES BASED ON RENEWABLE MATERIALS

ANIKA ZAFIAH MOHD RUS

A thesis submitted in partial fulfilment of the requirements for the degree
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<td>CI</td>
<td>Carbonyl Index</td>
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<tr>
<td>DMTA</td>
<td>Dynamic Mechanical Thermal Analysis</td>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>ESO</td>
<td>Epoxidized Soybean Oil</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray Ionisation</td>
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<tr>
<td>FAB</td>
<td>Fast Atom Bombardment</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
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<tr>
<td>HALS</td>
<td>Hindered Amine Light Stabilizers</td>
</tr>
<tr>
<td>MDI</td>
<td>Methylene di-p-phenyl diisocyanate</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight Average Molecular Weight</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
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<td>NMR</td>
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<td>PVC</td>
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<tr>
<td>QUV</td>
<td>Accelerated Weatherometer</td>
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<td>Hydroxylated Rapeseed Oil</td>
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<td>Rapeseed Polyurethane</td>
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<td>SF-PU</td>
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<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
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</tr>
<tr>
<td>TiO₂</td>
<td>Titanium Dioxide</td>
</tr>
<tr>
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<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal Gravimetric Analysis</td>
</tr>
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<td>Ultra Violet</td>
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<tr>
<td>UVAs</td>
<td>Ultraviolet Light Absorbers</td>
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DECLARATION

The work described in this thesis is entirely original and my own, except where otherwise indicated. It has not been submitted for a higher degree elsewhere.

Parts of this work were presented at international conferences, namely:

Polymer Degradation Meeting, University of Sussex, September 1-3, 2005, Awarded First Prize (see Appendix)

Royal Society of Chemistry Group, April 4, 2006, Runcorn, Cheshire, UK

Signed

Date

19/2/2007

Signed

Date
ABSTRACT

In recent years, the use of polymers made from renewable materials has been developed in diverse areas especially in furniture, mattresses, automotive or building components. Polyurethanes (PU's) made from renewable materials are one of the most important groups of polymers because of their versatility and they can be manufactured in a wide range of grades, densities and stiffness. In this project, polymers based on renewable materials such as rapeseed (RS) and sunflower oil (SF) were synthesized and cross-linked with methylene di-p-phenyl diisocyanate (MDI) to form polyurethanes.

Treatment with titanium dioxide (TiO₂) was found to affect the physical properties of the polyurethane in a systematic way. As the loadings of TiO₂ were increased (up to 10% of monomer weight), large strain responses were obtained; thus the stress vs. strain curves plotted by the Instron tensile test showed an increase from 5% to 31%. This study also revealed a remarkable characteristic in the pigmented polymer exhibiting soft – but – tough behaviour at high TiO₂ loading.

The DMTA test also showed that the properties of the sample loaded with 10 % TiO₂ increased its tan delta peak (damping factor) from 0.43 to 0.7. The tan delta peak showed that the damping properties of the material were improved markedly upon loading with TiO₂. This is useful since noise is radiated by vibration, and the application of damping materials to the vibrating surface converts the energy into heat, which is dissipated within the damping materials rather than being radiated as airborne noise. Increase in TiO₂ loading also gave a progressive increase of hardness (Shore D) for both RS and SF oil – based polyurethanes.

The effect of prolonged exposure to UV₂ light, in general promotes photodegradation for both RS and SF-based polyurethanes, both neat and also material loaded with TiO₂. The photodegradation of the PU’s depends on the grade of titanium dioxide. The addition of 10 % Degussa P25 pigment, gives the greater degradation while PUs loaded with 5 % Kronos 2220 show the slowest rates of degradation due to the effect of the coating of this pigment.

The photostabiliser Tinuvin 770 also offers high protection from UV₂, while the combination of Tinuvin 770 and Degussa P25 gave the highest protection from UV₂. Addition of Tinuvin 770 at the stage of preparation of the PUs also greatly reduced the undesirable yellow colouration prevalent during PU syntheses.
CHAPTER 1
INTRODUCTION

1.1 Polymers based on renewable materials

1.1.1 Survey of approaches to renewable polymers

Polymers play a major role in industrial and domestic life, a role which is always increasing. The raw materials for the production of polymers are traditionally derived from petroleum products (oil) and natural gas. The use of petroleum-based monomers in the manufacture of consumer products is expected to decline in coming years because of the continuous rise in the price of oil and the high rate of depletion of known oil reserves [1,2]. Recently, the use of renewable resources has attracted the attention of many researchers [3-10] because of their potential to substitute petrochemical derivatives. Moreover, with the need to conserve these non-renewable resources, interest has begun to develop in the topic of preparing feed-stocks for the polymer industry that come from renewable resources, particularly from vegetable crops.

By renewable resource is meant agricultural products, where the materials are synthesized by sunlight. These natural products are already processed by the chemical industry and used in many fields of application and include in particular sugar, starch, cellulose, proteins and natural fats and oils [11]. Starch, for example, is a complex homo-polymer composed of α-D-glucose units linked together in two different forms: the linear form amylose and the highly branched amylopectin [12]. The composition and structure of starch granules varies considerably between different plants, affecting