

PHYSICAL AND PHOTO PROPERTIES OF
4,4'- METHYLENEBIS(PHENYLISOCYANATE) AND
POLYTETRAHYDROFURAN BASED POLYURETHANES

By

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award of the Degree of Doctor of Philosophy in Chemistry on
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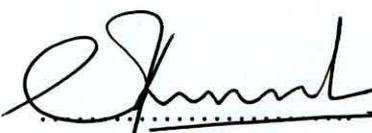
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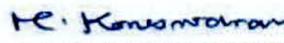
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DECLARATION

The work described in this thesis was carried out by me under the supervision of Prof. Laleen Karunanayake, Dr. Shantha Amarasinghe, Prof. Veranja Karunaratne and Dr. Masilamani Koneshwaran and a report on this has not been submitted in whole or in part to any University or any other institution for another Degree /Diploma.

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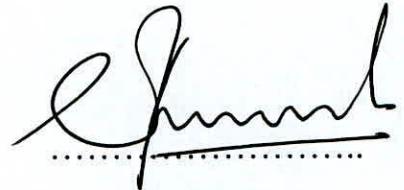
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ABSTRACT

Polyurethane is a versatile industrial polymer which can be modified in various methods to achieve different properties depending on their particular application. In the field of polymer based research, polyurethanes have achieved a higher rank in the priority list due to their utility in diverse applications. In the work described, attention was paid to the fluorescence properties of 4,4'- methylenebis(phenylisocyanate) (MDI) based polyurethanes to open up a new path to develop different applications. As volatile organic compounds is a huge problem in the polymer industry, through the introduction of hydrophilic group to the polyurethane backbone, the highly hydrophobic polyurethanes were made hydrophilic in such a way that they can be dissolved in water based medium. Dispersion and film properties of those hydrophilic polyurethanes were optimized.

The polyurethanes which are synthesized using MDI and long chain hydrophobic PTHF are highly hydrophobic. In order to achieve the hydrophilic nature to the polyurethane chains, a monomer having a hydrophilic pendant carboxylic group; dimethylolpropionic acid (DMPA) was introduced. That additional monomer was acted as a chain extender and distributed over the polymer chain uniformly. By varying the DMPA/PTHF molar

ratio, five different polyurethane dispersions were prepared in a 30% DMF-WATER mixture. Dispersion properties of those polyurethane dispersions were analyzed. Particle size and Zeta potential data suggested that all the five dispersions which were prepared are stable. Absence of phase separations or sedimentations over long period of time proves the stability of the dispersions. With higher DMPA/PTHF molar ratios, it was able to achieve a higher stability as proven by zeta potential data in such a way that zeta potential was increased gradually from -44.9 mV to 54.9 mV with the increase of molar ratio from 1:1.5 to 1:0.38. The increased stability was attributed to the increased hydrophilicity in the higher DMPA/PTHF systems.

In addition to the films obtained from above dispersions, polyurethane prepolymer films also used to investigate the fluorescence properties of MDI based polyurethanes. Polyurethane prepolymers were prepared by reacting long chain polytetrahydrofuran (PTHF) which has 2000 molar mass and MDI.

As there were two peaks around 356 nm and 423 nm in the emission spectra of polyurethane films, it was able to identify that, there is an internal fluorophore in the MDI based polyurethanes. The detailed analysis confirmed that the peak around 356 nm was due to isolated hard segments and peak around 423 nm was due to crystalline hard segment bundles. Understanding of the microstructural arrangements of polyurethanes was necessary to explain the fluorescence behavior. XRD, DSC and FT-IR results were used to understand the microstructure of polyurethanes.

As explained by XRD, DSC and FT-IR results, polyurethane prepolymers have a crystalline soft segment matrix where hard segments are available only as isolated hard segments while films from polyurethane dispersions have crystalline hard segment bundles.

By comparing the XRD, DSC and FT-IR results of films of five dispersions, it was able to show that the hard segment crystallinity was increased with increasing DMPA/PTHF molar ratios which results in higher hard segment contents.

The extended analysis showed that in addition to the excitation of fluorophores, the localized melting was taken place in polyurethane films with the exposure to 293 nm wavelength. This melting allowed the available isolated hard segments to come close to each other to form crystalline hard segment bundles via hydrogen bonds. Subsequently, the 423 nm peak intensity was increased while reducing the 356 nm peak with the exposure time to the 293 nm peak. Even though during the UV exposure hard segments come closure, when UV exposure was ceased, some of the hard segments separate apart due to the tensile forces. As a result of this re-increase in 356 nm peak intensity and re-decrease in 423 nm peak intensity was observed after the UV cease. These tensile forces are retarded by residual solvent molecules when solvent molecules are small enough to embed in to the matrix retarding reversibility.

Correlation of microstructure, microstructural rearrangements during the UV exposure and UV cease with the observed fluorescence behavior has explained the complete picture of the fluorescence behavior.