

## CONTENTS

| No.              | Title   | Page No.    |
|------------------|---|-------------|
| I                | Abstract  | i           |
| II               | List of Abbreviations   | ii          |
| III              | List of Tables  | iv          |
| IV               | List of Schemes   | v           |
| V                | List of Figures   | vi          |
| <b>Chapter 1</b> | <b>Introduction</b>   | <b>1-4</b>  |
| <b>Chapter 2</b> | <b>Review of Literature</b>   | <b>5-34</b> |
| <b>2.1</b>       | <b>What are Polyurethanes?</b>                                      | <b>5</b>    |
| <b>2.2</b>       | <b>History of Polyurethanes</b>                                     | <b>5</b>    |
| <b>2.3</b>       | <b>Polyurethane Types</b>   | <b>6</b>    |
| 2.3.1            | <i>Fibers</i>   | <b>6</b>    |
| 2.3.2            | <i>Films</i>  | <b>6</b>    |
| 2.3.3            | <i>Castables</i>  | <b>7</b>    |
| 2.3.4            | <i>Thermoplastics</i>   | <b>7</b>    |
| 2.3.5            | <i>Foams</i>  | <b>7</b>    |
| 2.3.6            | <i>Millables</i>  | <b>8</b>    |
| <b>2.4</b>       | <b>Polyurethane Elastomers</b>                                      | <b>8</b>    |
| <b>2.5</b>       | <b>Chemistry of Polyurethane Elastomers</b>                         | <b>9</b>    |
| 2.5.1            | <i>Chemical reactions and polyurethanes synthesis</i>               | <b>10</b>   |
| 2.5.1.1          | Primary Reactions   | <b>10</b>   |
| 2.5.1.2          | Secondary Reactions   | <b>11</b>   |
| <b>2.6</b>       | <b>Basic Chemical Components for Polyurethane Reaction</b>          | <b>13</b>   |
| 2.6.1            | <i>Isocyanates</i>  | <b>13</b>   |
| 2.6.2            | <i>Polyols</i>  | <b>14</b>   |
| 2.6.3            | <i>Chain extenders</i>  | <b>16</b>   |
| 2.6.4            | <i>Catalysts</i>  | <b>16</b>   |
| <b>2.7</b>       | <b>Synthesis of Polyurethanes</b>                                   | <b>17</b>   |
| 2.7.1            | <i>One shot process</i>   | <b>18</b>   |
| 2.7.2            | <i>Two step process</i>   | <b>19</b>   |
| <b>2.8</b>       | <b>Structure- Property Relationships of Polyurethane Elastomers</b> | <b>19</b>   |
| 2.8.1            | <i>Surface Morphology</i>   | <b>20</b>   |
| 2.8.2            | <i>Hydrogen Bonding(Physical crosslinking)</i>                      | <b>22</b>   |
| <b>2.9</b>       | <b>Thermal Degradation of Polyurethanes</b>                         | <b>24</b>   |
| <b>2.10</b>      | <b>Polyurethanes Based on Aliphatic Diols</b>                       | <b>26</b>   |
| <b>2.11</b>      | <b>Polyurethane Based on Aromatic, Cycloaliphatic and</b>           | <b>28</b>   |

|                  |  |              |
|------------------|--|--------------|
|                  | <b>Aliphatic Diisocyanates</b>   |              |
| <b>2.12</b>      | <b>Coloured Polyurethanes</b>  | <b>30</b>    |
| <b>Chapter 3</b> | <b>Materials and Methods</b>   | <b>35-51</b> |
| <b>3.1</b>       | <b>Chemicals and instruments Used in the Study</b>   | <b>35</b>    |
| 3.1.1            | <i>Chemicals</i>   | <b>35</b>    |
| 3.1.2            | <i>Techniques used for the determination of polymer constitution</i>   | <b>36</b>    |
| <b>3.2</b>       | <b><i>Synthesis of Polymers</i></b>  | <b>36</b>    |
| 3.2.1            | <i>Analysis of the reactants</i>   | <b>36</b>    |
| 3.2.2            | <i>Synthesis of polyurethane (PU)</i>  | <b>36</b>    |
| <b>3.3</b>       | <b>Characterization</b>  | <b>39</b>    |
| 3.3.1            | <i>Spectral Analysis</i>   | <b>39</b>    |
| 3.3.1.1          | Fourier transform infrared (FTIR) spectroscopy   | <b>39</b>    |
| 3.3.1.2          | Nuclear magnetic resonance (NMR) spectroscopy  | <b>39</b>    |
| 3.3.1.3          | Ultraviolet and visible (UV/ vis) spectroscopy   | <b>41</b>    |
| 3.3.1.4          | X-ray diffraction (XRD)  | <b>41</b>    |
| 3.3.2            | <i>Thermal Analysis</i>  | <b>42</b>    |
| 3.3.2.1          | Differential scanning calorimetry (DSC)  | <b>42</b>    |
| 3.3.2.2          | Thermogravimetric and differential thermal analysis (TG/DTA)   | <b>43</b>    |
| 3.3.3            | <i>Mechanical Analysis</i>   | <b>44</b>    |
| 3.3.3.1          | Tensile testing  | <b>44</b>    |
| 3.3.3.2          | Hardness   | <b>45</b>    |
| 3.3.4            | <i>Surface morphology</i>  | <b>45</b>    |
| 3.3.4.1          | Contact angle measurement (Goniometry)   | <b>45</b>    |
| 3.3.4.2          | Scanning electron microscopy (SEM)   | <b>45</b>    |
| 3.3.4.3          | Assessment of water absorption (%)   | <b>46</b>    |
| 3.3.4.4          | Density of the polyurethane samples  | <b>47</b>    |
| <b>3.4</b>       | <b>Synthesis of Polyurethanes</b>  | <b>47</b>    |
| 3.4.1            | <i>Part I: Synthesis, structural, thermomechanical and surface characterization of polyurethane elastomers extended with a series of aliphatic alkane diols (based on 2-6 methylene units)</i> | <b>47</b>    |
| 3.4.1.1          | Chemicals  | <b>47</b>    |
| 3.4.1.2          | Synthesis of Polyurethane Elastomers (PUEs)  | <b>48</b>    |
| 3.4.1.3          | Measurements   | <b>49</b>    |
| 3.4.2            | <i>Part II: Synthesis and structural, thermomechanical &amp; surface characterization of polyurethane elastomers based on aromatic, cycloaliphatic and aliphatic diisocyanates</i>             | <b>49</b>    |
| 3.4.2.1          | Materials and synthesis of polyurethane elastomers (PUEs)  | <b>49</b>    |
| 3.4.2.2          | Measurements   | <b>49</b>    |
| 3.4.3            | <i>Part III: Synthesis and characterization of Disperse Red 5/1,4-butane diol (BDO) based dyed PUEs</i>  | <b>50</b>    |

|                  |   |               |
|------------------|---|---------------|
| 3.4.3.1          | Chemicals   | <b>50</b>     |
| 3.4.3.2          | Synthesis of PU based on BDO (E6)   | <b>50</b>     |
| 3.4.3.3          | Synthesis of PU based on mixture of Disperse red 5 dye/<br>BDO (E13-E16)  | <b>50</b>     |
| 3.4.3.4          | Measurements  | <b>51</b>     |
| 3.4.3.5          | Leachability of the colorant from dyed polyurethane<br>elastomers   | <b>51</b>     |
| <b>Chapter 4</b> | <b>Results and Discussion</b>   | <b>52-131</b> |
| <b>4.1</b>       | <b>Part I: Synthesis, Structural, Thermal, Mechanical &amp;<br/>Surface Characterization of Polyurethane Elastomers<br/>Extended with Series of Aliphatic Alkane Diols</b>                      | <b>52</b>     |
| <i>4.1.1</i>     | <i>Fourier Transformed Infrared (FTIR) Studies</i>  | <b>57</b>     |
| 4.1.1.1          | FTIR spectral studies of HTPB based PUEs (E1, E5-E8)  | <b>57</b>     |
| 4.1.1.2          | FTIR spectral studies of Polycaprolactone based PUEs (E9)   | <b>62</b>     |
| 4.1.1.3          | NMR Studies   | <b>62</b>     |
| <i>4.1.2</i>     | <i>X-ray Diffraction Studies</i>  | <b>64</b>     |
| <i>4.1.3</i>     | <i>Thermal Analysis</i>   | <b>69</b>     |
| 4.1.3.1          | Differential scanning calorimetry (DSC) studies   | <b>69</b>     |
| 4.1.3.2          | Differential scanning calorimetry (DSC) studies   | <b>70</b>     |
| <i>4.1.4</i>     | <i>Mechanical properties</i>  | <b>75</b>     |
| <i>4.1.5</i>     | <i>Surface Morphological Studies</i>  | <b>78</b>     |
| 4.1.5.1          | Contact angle measurement   | <b>78</b>     |
| 4.1.5.2          | Assessment of water absorption (%)  | <b>80</b>     |
| 4.1.5.3          | Scanning electron microscopy  | <b>81</b>     |
| <b>4.2</b>       | <b>Part-II: Synthesis, Structural, Thermal, Mechanical &amp;<br/>Surface Characterization of Polyurethane Elastomers<br/>Based on Aromatic, Cycloaliphatic and Aliphatic<br/>Diisocyanates.</b> | <b>83</b>     |
| <i>4.2.1</i>     | <i>Characterization</i>   | <b>87</b>     |
| 4.2.1.1          | FTIR study of tolylene diisocyanate (TDI) based PUE (E1)  | <b>87</b>     |
| 4.2.1.2          | FTIR study of isophorone diisocyanate (IPDI) based PUE<br>(E2)  | <b>91</b>     |
| 4.2.1.3          | FTIR study of hexamethylene diisocyanate (HDI) based PUE<br>(E3)  | <b>94</b>     |
| 4.2.1.4          | FTIR study of trimethyl-1,6-diisocyanato hexane (TMDI)<br>based PUE (E4)  | <b>97</b>     |
| <i>4.2.2</i>     | <i>X-ray Diffraction Studies</i>  | <b>98</b>     |
| <i>4.2.3</i>     | <i>Thermal Analysis</i>   | <b>101</b>    |
| 4.2.3.1          | Thermogravimetric and differential thermal analysis<br>(TG/DTA) studies   | <b>101</b>    |
| 4.2.3.2          | Differential scanning calorimetry (DSC) studies   | <b>103</b>    |
| <i>4.2.4</i>     | <i>Mechanical Properties</i>  | <b>106</b>    |
| <i>4.2.5</i>     | <i>Surface Morphological Studies</i>  | <b>107</b>    |
| 4.2.5.1          | Contact angle measurement   | <b>107</b>    |
| 4.2.5.2          | Assessment of water absorption (%)  | <b>108</b>    |

|                  |  |                |
|------------------|--|----------------|
| 4.2.5.3          | Scanning electron microscopy   | <b>109</b>     |
| <b>4.3</b>       | <b>Part III: Synthesis and characterization of disperse red 5/1,4-butane diol (BDO) based dyed PUEs</b>                                    | <b>111</b>     |
| 4.3.1            | <i>Characterization</i>  | <b>115</b>     |
| 4.3.1.1          | Ultraviolet and visible & Fourier transformed infrared (UV/Vis. & FTIR) study of disperse red 5  | <b>115</b>     |
| 4.3.1.2          | 4.3.1.2 Fourier transformed infrared (FTIR) studies of coloured polyurethane elastomers (E13-E16) based on disperse red 5/ 1,4-butane diol | <b>115</b>     |
| 4.3.2            | <i>X-ray Diffraction Studies</i>   | <b>116</b>     |
| 4.3.3            | <i>Thermal Analysis</i>  | <b>120</b>     |
| 4.3.3.1          | Thermogravimetric and differential thermal analysis (TG/DTA) studies   | <b>120</b>     |
| 4.3.3.2          | Differential scanning calorimetry (DSC) studies  | <b>124</b>     |
| 4.3.4            | <i>Mechanical Properties</i>   | <b>125</b>     |
| 4.3.5            | <i>Surface Morphological Studies</i>   | <b>127</b>     |
| 4.3.5.1          | Contact angle measurement  | <b>127</b>     |
| 4.3.5.2          | Assessment of water absorption (%)   | <b>127</b>     |
| 4.3.5.3          | Scanning electron microscope   | <b>129</b>     |
| 4.3.6            | <i>Leachability of the colorant from dyed polyurethane elastomers</i>  | <b>131</b>     |
| <b>Chapter 5</b> | <b>Summary</b>   | <b>132-134</b> |
| <b>6</b>         | <b>Literature Cited</b>  | <b>135-147</b> |
|                  |  |                |
|                  |  |                |
|                  |  |                |
|                  |  |                |