Injection Moulded Biodegradable Polyurethane Shoe Soles: Development, Characterization and Process Optimization

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**Background**

- Currently different types of soling material like leather, rubber, polyurethane, PVC, EVA, TPR and TPU have been used in footwear.

- PU soles have been replacing PVC soles in the past decade, and the majority of the formal and higher priced leather shoes use PU for soles.

**Advantage**
- Versatile physical properties
- Light weight
- High Production Rate

**Disadvantage**
- Expensive comparing to other non-leather footwear
Polyurethane Foam

Biodegradable/Renewable Precursors (expensive)
Objective

- Preparation of environmental friendly PU from cost-effective biodegradable polymer
- Physico-chemical characterization of fabricated PUs
- Characterization for Sole applications
Selection of raw Material

- Cost-effective
- Without modifying the existing production facilities
- Compatibility
- Environmental friendly
Challenges involved in selection of reactants

- Inherent properties of reactants
- Desirable physico-chemical properties of foams for footwear application
- Cost effective, compatibility with existing raw materials, biodegradability, biocompatibility
Why Polycaprolactonediol?

♦ Cost effectiveness
♦ Biodegradability
♦ Polyester based PU > Polyether based PU
♦ Environmental friendly
♦ Availability
Foowear Sole Preparation - Reaction Injection Molding
Development of Biodegradable PU- nano-clay based Shoe soles
Development of Injection molded Biodegradable PU-nano-clay based Shoe soles

- RIM unit in Coim India Pvt Ltd, Bahadurgaur, Haryana, India
- The polyurethane soles are manufactured with different nanoclay percentages like (0.5%, 1%, 1.5%, 2% and 3%) and with different isocyanate index like (78, 85, 95, 100, 105 and 110) and cup test is performed in order to check the sole properties using indentometer.

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Brand Name</th>
<th>amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol</td>
<td>CAPA7201A</td>
<td>100 %</td>
</tr>
<tr>
<td>Isocyanate</td>
<td>T400</td>
<td>85 (ICN index)</td>
</tr>
<tr>
<td>Catalyst</td>
<td>C2LPE20</td>
<td>12.2%</td>
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</tbody>
</table>
## Optimization of Process

<table>
<thead>
<tr>
<th>Description</th>
<th>Setting</th>
<th>Description</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>PCL+ Catalyst+ Water+ ISO+ NP (1%)</td>
<td>Poly delivery</td>
<td>28.08 g/sec</td>
</tr>
<tr>
<td>Mixing Ratio</td>
<td>100:95</td>
<td>Poly speed pump</td>
<td>1798 rpm</td>
</tr>
<tr>
<td>Poly tank Temp</td>
<td>48°C</td>
<td>ISO delivery</td>
<td>21.92 g/ sec</td>
</tr>
<tr>
<td>Poly pipe Temp</td>
<td>45</td>
<td>ISO speed pump</td>
<td>911 rpm</td>
</tr>
<tr>
<td>Poly Temp</td>
<td>48</td>
<td>Cream time</td>
<td>5 sec</td>
</tr>
<tr>
<td>ISO tank Temp</td>
<td>42</td>
<td>Tact Free time</td>
<td>22 sec</td>
</tr>
<tr>
<td>ISO pipe Temp</td>
<td>39</td>
<td>Pinch time</td>
<td>39 sec</td>
</tr>
<tr>
<td>ISO Temp</td>
<td>42</td>
<td>Free Rise Density</td>
<td>0.174 g/cc</td>
</tr>
<tr>
<td>Mould Temp</td>
<td>62</td>
<td>Demolding time</td>
<td>6 minutes</td>
</tr>
</tbody>
</table>
Developed PU Soles
Physical Properties

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% nanoclay</th>
<th>Shore A Hardness</th>
<th>Density (g/cc)</th>
<th>Abrasion (mm³)</th>
<th>Tensile Strength (Mpa)</th>
<th>Elongation at Break (%)</th>
<th>Flexing resistance (cycles)</th>
<th>ICN Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUBC0</td>
<td>0</td>
<td>60</td>
<td>0.43</td>
<td>50.0</td>
<td>7.8</td>
<td>261</td>
<td>10000</td>
<td>85</td>
</tr>
<tr>
<td>PUBC1</td>
<td>0.5</td>
<td>45</td>
<td>0.44</td>
<td>137.7</td>
<td>2.7</td>
<td>175</td>
<td>30000</td>
<td>87</td>
</tr>
<tr>
<td>PUBC2</td>
<td>1</td>
<td>47</td>
<td>0.43</td>
<td>159.6</td>
<td>4.8</td>
<td>235</td>
<td>20000</td>
<td>47</td>
</tr>
<tr>
<td>PUBC3</td>
<td>2</td>
<td>52</td>
<td>0.45</td>
<td>142.3</td>
<td>4.2</td>
<td>167</td>
<td>5000</td>
<td>52</td>
</tr>
</tbody>
</table>
Viscosity Study
There is no significant change in TGA and DSC of PU with Nanoclay as the nanoclay content is less.
SEM pictures of cross section at 300 X magnification of Samples
A) PUBS, B) PUBS-0.5 NP, C) PUBS-1% NP, D) PUBS-3% NP
Bulk Production - Physical Properties

120 pairs of footwear were developed at Manjeet Plastics Industries, Bahadurgaur, Haryana, India for distribution to different professionals and for testing the used footwear after 3, 6 and 9 months of regular usage.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Commercial PU</th>
<th>Biodegradable PU (0 % Nanoclay)</th>
<th>Biodegradable PU (0.5 % Nanoclay) (-5 g weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness, Shore A</td>
<td>53-57</td>
<td>52- 56</td>
<td>55- 59</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>0.4</td>
<td>0.39</td>
<td>0.35</td>
</tr>
<tr>
<td>Abrasion (mm³)</td>
<td>120</td>
<td>90</td>
<td>110</td>
</tr>
</tbody>
</table>
Field Trial

- The injection molded PU footwear based on biodegradable polyol using the existing RIM facilities in PU footwear industry are distributed to CLRI staff, research scholars and contract workers and also to school students. After 50 days of regular usage, feedback is good and the footwear and sole are intact.
Conclusions

• From the above results, it can be concluded that biodegradable polyol based PU shoe soles have been developed which is suitable for PU footwear application.

• The optimized process can be used for making direct injection molded PU footwear using biodegradable polyol without changing the existing facilities of PU footwear industries.

• To reduce the cost of polyol, nanoclay based blowing agent is added and the properties of PU clay composite based soling materials are developed and characterized.
Conclusions

- As volume is increasing and free rise density is decreasing with the addition of nanoparticles, it can implicit that the interlayer water molecule is reacting with isocyanate and generates foaming.
- So the appropriate adjustment of isocyanate index was also performed in our present invention to reduce the quantity of polyol used.
- Thus the developed technology is cost effective and can be implemented without affecting the existing industrial production facilities.
Acknowledgment

- Department of Science and Technology, Govt. of India
- Euro Shoe Components Ltd, Ranipet- Industry partner of this project
- Coim India Pvt Ltd.
- Manjeet Plastics Industries
- My Student Ms. Moumita Mukherjee
- Co- PI of this project- Dr. Sujata Mandal, Senior Scientist, & Dr. BN Das, Chief Scientist, CSIR-CLRI
Thanks for your kind Attention!!!
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