Surface Modified and Medicated Polyurethane for Application in Athletic Footwear

G. Saraswathy[1], Y Lakshminarayana[1], SN Jaisankar[1], Ganga Radhakrishnan[1], Gautham Gopalakrishna[2], BN Das[2] and AB Mandal

[1] **Polymer Laboratory,** [2] **Shoe Design and Development Centre**
Central Leather Research Institute,
Chennai – 600020.

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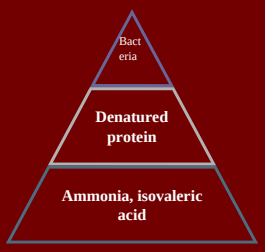
BACKGROUND OF THE PROBLEM

- There are approximately 250,000 sweat glands in a pair of feet and they excrete as much as half a pint of moisture each day.
- The inherent properties of the footwear material such as leather, fabrics, etc., and design of footwear provide room for growth of microorganism
- The structure of human skin also support growth of microbes.
- Environmental factors such temperature and humidity
- Metabolism of micro-organism



Role of Insole in footwear

- Inner layer of sole of the footwear or shoe which is subjected to force from body weight on standing, walking and running
- Insoles offer uniform distribution of pressure and increased contact area under the foot and thus prevent the occurrence of plantar pressure spots.
- It is common to use insole as removable inserts in conventional shoes for foot comfort.

NEED OF BIOSHEILD INSOLE WITH MOISTURE ABSORBING PROPERTY

- To avoid cross infection by pathogenic micro organism
- To control keratolysis by microbes
- To arrest metabolism in microbes in order to reduce the formation of odor producing compounds
- To safeguard shoes from staining, discoloration and quality deterioration

Diseases due to the influence of microbes

Infections occur when dermatophytes grow and multiply in the skin.

Erythema and scaling due to Trichophytum rubrum infection extending from the side of the foot to the sole

Pitted keratolysis due to a combination of hyperhidrosis and C . minutissimum infection.

Umbilicated papules on the sole due to Molluscum contagiosum.

Athlete's foot or tinea pedis

Pale, flaky and spilt skin in toe web space

Aim of the project:

To reduce sweat accumulation and control sweat related diseases (foot infection) in Athletes / hyperhidrosis people

Objective of the project :

To develop new insole materials based on polyurethane having hydrophilic and antimicrobial coating

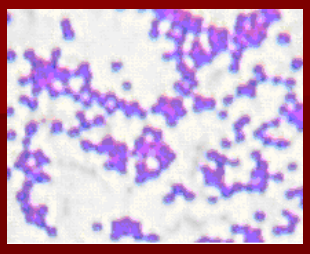
Identification of microbes in sweat

Staphylococci colonies

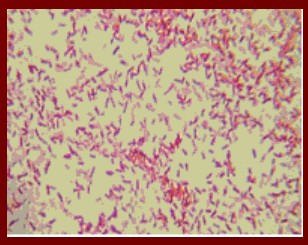
C. Diphtheroids – colonies

Pseudomonas colonies

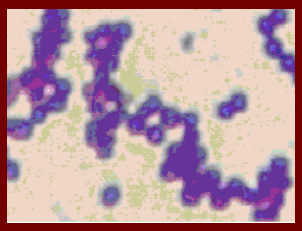
Micrococci colonies



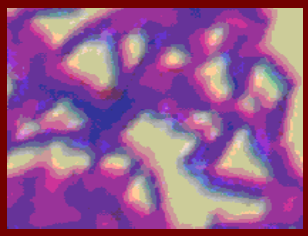
Staphylococci



Pseudomonas



Micrococci



Corybacterium Diphtheroids

MATERIALS AND METHODS

- Porous viscoelastic polyurethane sheets developed by phase inversion method using different concentration of PU solution such as 15, 20, 25, 30, 35 and 40 % W/V
- These PU materials were already reported as effective insole material
- In this project, hydrophilic and antimicrobial properties are introduced into these materials for application in Athletic footwear to absorb perspiration and control foot infection

Cushion Properties of developed PU insoles

Sample code	Cushion Energy (N.mm)		Cushion Factor	
	CE_W	CE_R	CF_W	CF_R
DRS	26.8	38.9	9.2	12.0
HPS	48.9	74.7	14.9	18.7
20-cpu	71.4	161.6	5.8	4.9

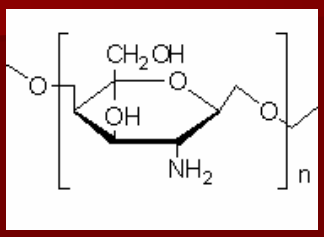
Physical Properties of developed PU insoles

Sample code	Hardness, Shore A	Density (g/cm^3)	Compression set (%)	Water absorption (%)
DRS	5-7	0.2527	6.1	39.0
HPS	4-6	0.1618	6.3	29.5
20-cpu	17-22	0.2924	1.6	25.9

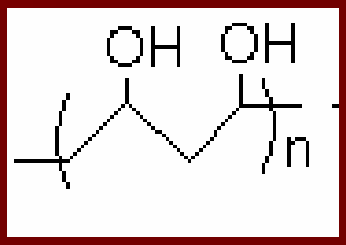
Porous viscoelastic PU sheets and insoles made out of them

- Development of Polyurethane based Sheets by Phase Inversion Method for Therapeutic Footwear Applications: I. Synthesis, Fabrication and Morphological Characterization.
  G Saraswathy, et al. J. of Appl. Poly. Sci., 111 (5), 2387- 2399 (2008).
- Development of Polyurethane based Sheets by Coagulation Method and Study of Mechanical and Cushion Properties for Therapeutic Footwear Applications. G Saraswathy, et al. *Poly. Plast. Tech. Engg.,* 48 (30) 1 -12 (2009)

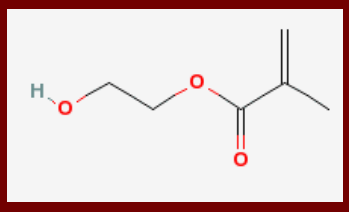
Chitosan



PVA



p-HEMA



PEG

HO—CH2—(—CH_2—O—CH_2—) n—CH_2—OH

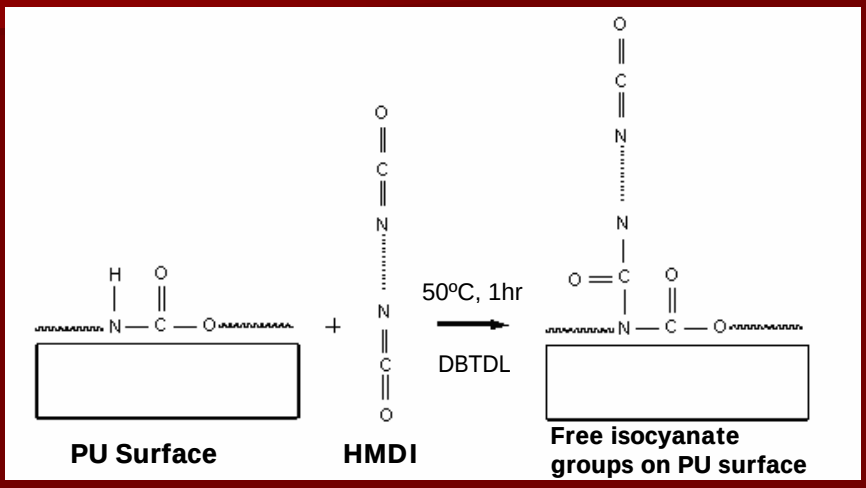
Polyvinyl alcohol

- High hydrophilicity
- Excellent film forming property
- Good water absorption and evaporation property
- Gel - sufficient mechanical property by cross linking
- Widely accepted in medical field as contact lens , hydrogel, wound dressing, etc...

Chitosan

- Water binding capacity
- Bioactivity
- Biodegradability
- Nontoxicity
- Biocompatibility
- Antifungal activity
- Biomaterial and for drug delivery

Surface modification of polyurethane via Diisocyanate bridges



Surface modification of HMDI modified PU sheets by grafting with hydrophilic polymers

Two methods of grafting:

- Grafting through chemical reaction between isocyanate and hydroxyl group
- Grafting through physical coating

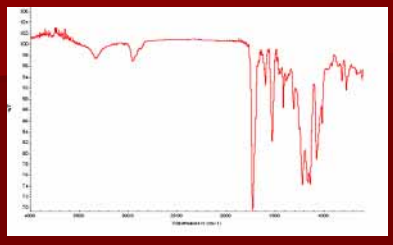
Grafting Polymer

1. Poly 2-hydroxyethyl methacrylate
2. Polyethylene glycol (1000)
3. Polyethylene glycol (2000)
4. Polyvinyl alcohol
5. Chitosan/ Polyvinyl alcohol
6. Chitosan

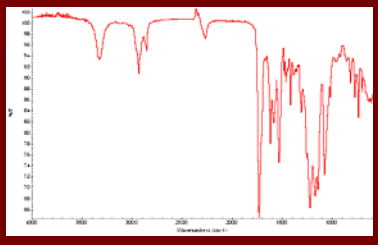
Physicochemical Characterization

- ATR- FTIR Spectroscopy
- Thermo gravimetric analysis
- Molecular weight of PU sheet was determined by GPC
- Water absorption characteristics
  - Water immersion method
  - Contact angle measurements.

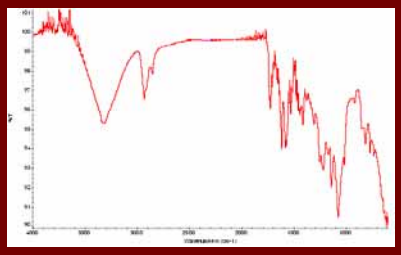
ATR- FTIR Spectra



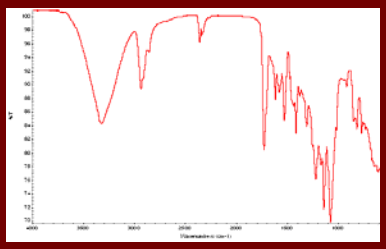
Unmodified PU



PU modified with HMDI



PU grafted with PEG-2000



PU coated with PVA

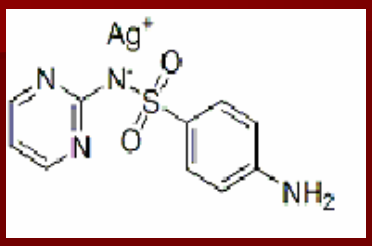
Water absorbance PU sheets grafted with PEG/p-HEMA

S. No	Grafted Polymer	Water absorbance (Swelling) in (%)					
		PU 15%	PU 20%	PU 25%	PU 30%	PU 35%	PU 40%
1.	PEG1000	28.87	2.277	3.199	4.925	2.773	6.815
2.	PEG2000	7.145	2.664	8.55	11.184	9.164	4.316
3.	P-HEMA	5.163	3.048	3.99	6.388	3.79	1.482
4.	PU (unmodified)	39.98	15.428	3.616	6.75	10.48	3.676

Water absorbance PU sheets (25%) grafted with PVA/Chitosan

S.No	Grafted or coated polymer	Swelling in (%)	Contact Angle (Degree)
1.	PVA grafted	7.0616	26
2.	Chitosan grafted	4.413	46
3.	Chitosan/PVA grafted	5.648	19
4.	Chitosan/PVA coated	7.642	31
5.	Chitosan coated	14.728	45
6.	PVA coated	18.321	18
7.	PVA cross-linked	13.758	43
8.	PU unmodified	3.616	66

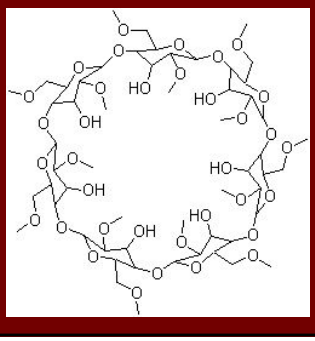
SILVER SULPHADIAZINE (AgSD)



CYCLODEXTRIN

Protection of the active ingredients against:

- Oxidation
- Light induced reactions and
- Decomposition



Determination of Minimum Inhibitory Concentration

- The biological activity of the selected polymers PVA and Chitosan with or without Silver Sulfadiazine (SS) were tested against the isolated microorganisms (Corynebacteria, Micrococci, Coagulase negative Staphylococci and Pseudomonas aeruginosa)
- The monitoring of antibacterial activity was performed by determination of the MIC, the smallest amount of the agent that inhibits the multiplication of the pathogen.

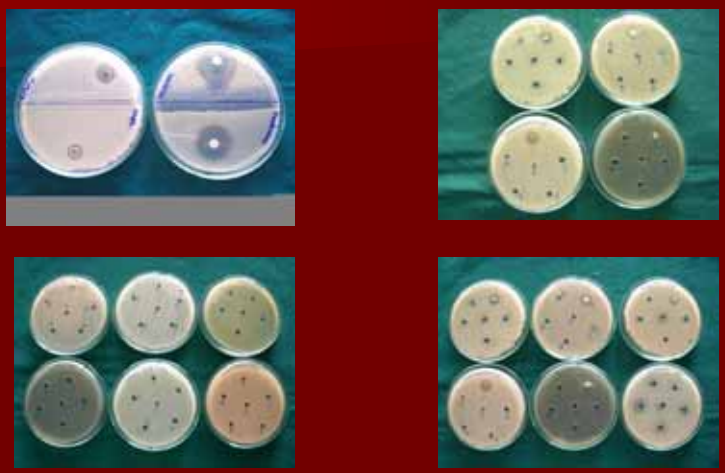
M.I.C studies of silver sulfadiazine (SS) with PVA and chitosan

- The varying concentrations of SS such as 1250 µg, 250µg, 62.5 µg, 31.5µg, 15µg was impregnated in PVA or CH and were tested against our bacterial isolates by agar well diffusion method.
- The actual antimicrobial concentration was represented by the diameter of the zone of inhibition formed around the discs impregnated with the polymer in different composition ratio of SS.

Incorporation of SS on surface modified PU

- Widely used Antibacterial and Antifungal agent
- Size plays vital role , reduced size having high efficacy than the normal size
- Allowable dose 1000 mg. 20mg in the size range from 10 nm to 50 nm has eight fold advantage, because it imbibe with hydrogel
- SS was dispersed in minimum quantity of sterilized water and coated uniformly on the surface modified PU sheet on one side and dried at 40 °C for 3 h.

In vitro antimicrobial test



The maximum inhibition was found for Pseudomonas (20 mm) followed by Micrococci (17mm), Diphtheroids (16 mm) and Coagulase Negative Staphylococci (12 mm)

Summary & Conclusion

- Porous viscoelastic PU sheets were successfully grafted with hydrophilic polymers through HMDI modification
- Water absorption properties of surface modified PU sheets help to give antimicrobial coating on PU sheet
- During perspiration of foot these grafted polymers will swell and release SS
- The unmodified PU sheets were already reported for application in therapeutic footwear as cushion insole
- So these surface modified sheets can be used as insoles in athletic shoes to control infection and odor

Thank you…

Optical micrographs of SS coated PU sheet

Unmodified PU surface

Grafted with CH: PVA (SS)

Grafted with CH: PVA (SS: CD)

Grafted with CH (SS: CD)