Synthesis and Processing of Polyurethane as Porous Viscoelastic Sheets for Application in Therapeutic Footwear

G Saraswathy, Gautham Gopalakrishna, BN Das, Y Lakshminarayana, Ganga Radhakrishnan and AB Mandal*

Central Leather Research Institute, Chennai-600020. INDIA

Abstract: Polymeric foams and elastomers are used in shoes to enhance the shock-absorbing and pressure distributing functions of natural fat pad beneath the foot. In the present work, effort was made to develop viscoelastic porous polyurethane sheet of 3 - 6 mm thickness having the properties of both PU elastomer and foam. Polyether based PU was prepared by chain extending the isocyanate terminated prepolymer with compounds aromatic semicarbazides or in combination with diol. The fibrous elastic polymers obtained were blended with commercial polyester based polyurethane in 1:1 ratio in dimethyl formamide (DMF) and developed into sheets by phase inversion method using water as coagulant. Sheets of various density, hardness and thickness were developed by varying the composition and concentration of polymer solution. The resultant viscoelastic sheets were tested for cushioning and mechanical properties. The surface and inner morphology of sheets were studied by scanning electron microscopy (SEM). The sheets developed with only CPU had shown better mechanical properties and those developed with combination of CPU and PUSC had shown better cushion properties than that of commercial materials. Especially the % compression set (CS) had obtained less than 5 %. The micro and macro pores on the surface and fibrous structures inside the sheet help in cushion and water absorption properties of the materials. Therefore these sheets can be used as insole material in therapeutic footwear for uniform distribution of pressure under the foot and to prevent ulcer formation.

Keywords: Insole, therapeutic footwear, viscoelastic, polyurethane, phase inversion method.

1. Introduction:

Polymeric foams and elastomers are used in shoes to replace the shock-absorbing and pressure distributing functions of natural fat pad beneath the foot that was lost due to some conditions such as diabetes, arthritis, age or overuse [1]. Common materials include foam rubbers, such as latex, and cellular polymers such as polyethylene (PE), ethylene vinyl acetate (EVA), polyurethane (PU), and polyvinyl chloride (PVC). Essentially solid materials such as viscoelastic polymers and natural cork are also used effectively. EVA offers good cushioning and shock absorption, but tends to suffer high compression set, meaning these properties deteriorate quite rapidly in wear. PE and PVC can provide reasonable cushioning and shock absorption but PE, like EVA, suffers high permanent compression set. Latex rubber foams tend to be too soft and 'bottom out' under low loads. They offer little cushioning or shock absorption and they primarily serve to cosset the foot. PU foam and viscoelastic PUs are offering good cushioning and shock absorption properties without suffering compression set [2].

The unique elastic nature of segmented polyetherurethane (SPEU) materials and versatile fabrication techniques allow researchers to design and fabricate SPEU with biomechanical properties that are required. The two-phase micro-domain structure exhibited by SPEU is responsible for their superior physical and mechanical properties [3]. SPEU materials combine flexibility with high strength, wear resistance and a degree of hardness.

The aim of this research work was to prepare SPEU and fabricate into porous viscoelastic sheets of 3-6 mm thickness for application in

therapeutic footwear and accessories such as heel pad, metatarsal pad, etc.

*Corresponding Author: Phone: +91-44-24422059; Email: clrieco@vsnl.com

2 Experimental

In this paper we have reported the synthesis of various SPEUs by chain extending the isocyanate terminated prepolymer with terephthalic dihydrazide (TDH), 5-hydroxy isothalic dihydrazide (OH-IDH) and 1, 4 butane dial (BD). Polymers were developed into sheets by phase inversion method using dimethyl formamide (DMF) as solvent and water as nonsolvent. To improve the mechanical properties of PU sheets the polymer solution was blended with high molecular weight commercial polyester based polyurethane (CPU) in 1:1 ratio.

2.1 Materials

Poly (teramethyleneoxyglycol) (PTMG) with a molecular weight of 1000 was purchased from Aldrich chemical company, USA. The polyol was dried and degassed at 90-100°C *in vacuo* for 6-7 h before use. Methylene bis (phenylisocyanate) (MDI) from Sigma- Aldrich was purified by removing the white residue (dimmer) obtained by melting the compound at 45 – 50°C and filtering off. Terephthalic acid (Sisco Research Laboratories, Mumbai, India), 5-Hydroxy isothalic dimethyl ester (Lancaster, UK) and hydrazine hydrate (99%: s. d. fine chemicals, ltd., Boisar, India) and dibutyltin dilaurate (Sigma-Aldrich, Germany) were used as received. Polyester based polyurethane Desmopan 8078 (CPU) with Shore A hardness 70 was obtained from Bayer Science Materials (Mumbai, India).

2.2 Synthesis of Polyetherurethane

Segmented polyether polyurethanes were synthesized by chain extending the isocyanate terminated prepolymer with terephthalic dihydrazide (PUSC 1) and in combination with 1, 4 butane dial (PUSC 2), with 5-hydroxy isothalic dihydrazide (PUSC 3) , and in combination with terephthalic dihydrazide (PUSC- 5). Prepolymer was synthesized by reaction of polyteramethyleneoxyglycol (PTMG 1000) with methylene bis (phenyl isocyanate) (MDI) developed into sheets by blending with commercially available thermoplastic polyester urethane (Desmophan 8078), obtained from Bayer Materials, Mumbai, India. Sheets of different density, hardness, porosity and thickness were developed by varying the composition and concentration of polymer and volume of solvent in polymer solution.

2.3 Preparation of PU Sheets

The processing method used to develop porous viscoelastic sheets is phase inversion or coagulation method. Dimethyl formamide was used to prepare PU solution and distilled water was used as nonsolvent or coagulant. According to reported procedures in literature [4], the glass plate or tunnel containing layer of PU solution was immersed in coagulation medium and left for few hours to develop microporous PU membranes for biomedical applications. In the present work, PU solution in room temperature was taken in polypropylene tray to a thickness of 3 – 10 mm and left for 15-20 minuets to evaporate the solvent to form a microskin layer over the surface. Then the coagulant, distilled water was sprayed uniformly over the surface to a thickness of 2 mm and left for 15 minuets. Then the tray was filled with distilled water and left for over night. The coagulated PU sheet was removed from the tray and

washed well with water to remove all the solvent. Then the sheets were dried at 35 to 50 ° C for 1 to 2 days.

PU sheets were prepared with blends of commercial polyester PU and synthesized polyether PU in 1: 1 ratio. Further PU sheets were prepared with commercial polyesterurethane alone in various concentrations. 15%, 20%, 25%, 30%, 45% and 50% W/V of PU solutions were prepared with DMF and made into sheets by the same method. Properties of markedly available insole materials, Dr. Scholl's insole (DRS), Dr. Scholl's heel pad (HPS), micro cellular polymer (MCP), PU foam (PUF) were also studied.

3 Characterization

3.1 Hardness Testing

Hardness of the sheets was tested with Durometer hardness tester (SATRA TM 205). Hardness is a major characteristic of any outsole, midsole or foam foot bed as it relates to the ease flexing and cushioning effect.

3.2 Density of insole materials

Density of the insole materials were measured by following the test method: SATRA TM 12. The dimensions of a test specimen are measured and its volume calculated. The mass of the test specimen is then measured and the average density determined.

3.3 Compression set (%)

Compression set (CS) was determined by constant stress method SATRA TM 64. This is a measure of retention of shape and elastic properties. The percentage change in thickness of a test specimen is calculated after it has been compressed by a predefined pressure for a set time and allowed to recover for a further set time. The % Compression set was calculated as,
% CS = Initial thickness – Final thickness/ Initial thickness X 100

3.4 Cushioning properties of insole materials

Cushioning properties of insole materials were studied by using the test method: SATRA 159. In this test, a sample is compressed under a pressure equivalent to those in walking and running. The method assesses two different cushioning properties:
1. Cushioning Energy – The energy required to gradually compress a specimen of the material upto a standard pressure is measured with a tensile testing machine. This is termed the cushion energy [CE]
2. Cushion Factor – This is a bulk material property and is assessed using a test specimen greater than sixteen millimeters thick.
The cushion factor for the materials was calculated using the formula:
[CFw] = [T] x 113 / [CEw]
[CFr] = [T] x 216 / [CEr]

4 Results and Discussion

4.1 SEM

SEM micrographs have shown the presence of macro pores on surface of the materials and fibrous porous structure in cross sections of CPU: PUSC blends which can contribute for viscoelastic property of the materials. Figure 1 shows the outer surface morphology of CPU: PUSC blends. Once the PU solution comes in contact with the coagulant (water), the exchange of the non-solvent water molecule

and the DMF molecule occurs immediately and results in coagulation of PU during which pores form inside and also on upper surface[6]. The SEM photographs of cross section of lower side of CPU: PUSC blends showed different cellular structure from that of upper side. As the rate of solvent exchange becomes slow in the direction perpendicular to the polymer solution, the dominant phase separation mechanism is nucleation and growth that results in the cellular structure. Figure 2 shows the cross sections of CPU sheets of various concentrations. There is no significant difference between the upper and lower side of the sheet. A higher polymer concentration is seemed to surpass the formation of macrovoids.

4.2 Hardness

Hardness of the developed PU sheets and commercial insoles had shown in Table 1. Based on the hardness values, 21 types of sheets developed were grouped into 4. Sheets with hardness in the range of 4 – 12 shore A (Sample No. 1, 2, 6, 11, and 13) were grouped as the softest sheets (Group I). Sheets with hardness in the range of 15 – 19 shore A (Sample No. 3, 10, 12, and 15) were grouped as softer materials (Group II). The increase in hardness than Group I sheets is due to increase in polymer concentration and high molecular weight of polyurethanes. Sheets with hardness in the range of 20 – 22 shore A (Sample No. 4, 7, 14, 15, 17, and 18) were grouped as soft materials (Group III). The ideal range of hardness of insole materials is 18 to 22 Shore A because the materials will deform on walking and regain its original thickness before the second step. Therefore Group II and Group III sheets can be used as insole materials where uniform pressure distribution under the foot is essential. Sheets with hardness in the range of 25 – 33 shore A (Sample 19, 20 and 21) were grouped as hard materials (Group IV). The polymer used in these sheets is polyester urethanes of high molecular weight. In case of commercial insoles DRS, HPS and PUF (Sample No. 22, 23, 25) had low range of hardness of 4-10 shore A and MCP (Sample No. 24) of 12 – 14 shore A.

4. 3 Density

Density of the developed PU sheets ranges from 0.14 to 0.4875 g/cm^3 (Table 1). The concentration and volume of polymer solution had same effect on density of the developed PU materials as hardness. As the density increases hardness also increases. Therefore the samples which had lower range of hardness will be improved by increasing the density of the materials by increasing the polymer concentration.

4. 4 Compression set, %

All the samples had shown % CS less than 4.2 % (Table 1). The pores (air) inside the sheets make the sheets to deform under load. Since the pores did not collapse on removal of load, the sheets could regain its thickness. In case of commercial materials DRS and HPS had shown 6.1 and 6.3 % of CS respectively and MCP had shown 65.0 % of CS.

4.5 Cushion Properties

The higher the cushion energy, the greater the cushioning effect of the insole is likely to be in wear. Rigid materials and very weak soft foams both give low results since the former are incompressible and the later 'bottom out'. Typical values for a wide range of commercial insoles are from 30 to 130 N.mm and results depend on material thickness. Insoles giving values greater than 70 N.mm would be expected to reduce underfoot peak pressures in walking considerably. Also a low cushion factor indicates an effective material with typical values ranging from 8 to 4 [5]. Samples 1, 2, and 11 showed higher cushion factor which reflects the softness of the material due to the structural properties of the polymers.

For the rest of the materials CFw was obtained in the range of 4 to 8 (Table 1). Sample No. 14, 18 and 19 had given CEw above 70 N.mm for comparable thickness. They also have a better cushion factor.

5 Conclusions

SPEUs which were synthesized had shown required morphological and cushioning properties that are essential for insole materials. Phase inversion method had proved as simple and best method to develop porous sheets without any chemical additives. Combination of CPU with SPEU worked well and proved from test results. The newly developed PU sheets can be used as insole, heel pad, cushion pad, metatarsal pad in therapeutic footwear for uniform distribution of plantar pressure and prevent foot ulcer and pain.

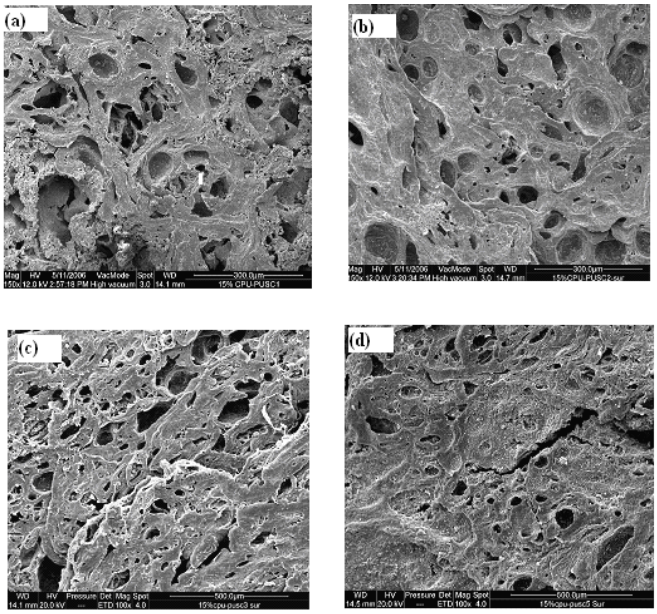

Fig. 1 Scanning Electron Micrograph of Upper surface of CPU: SPEU sheets

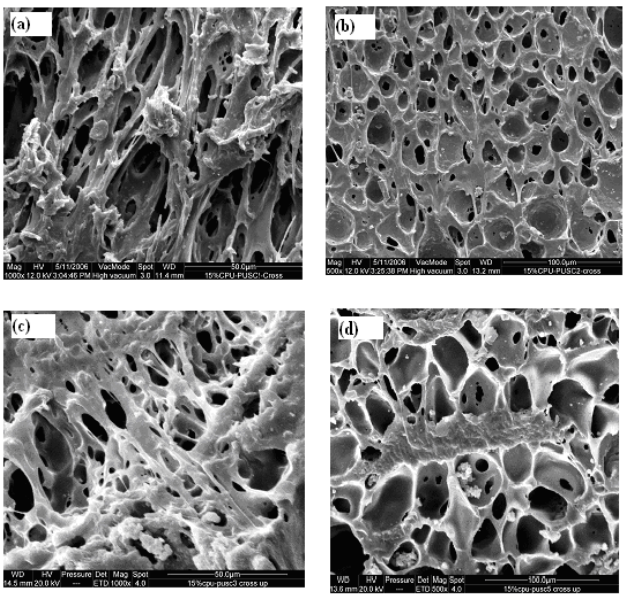

Fig. 2 Scanning Electron Micrograph of Upper surface of CPU sheets of various concentration

Tab. 1 Properties of PU Cushion sheets

Sample No.	Sample code	Hardness, Shore A	Density (g/cm^3)	Compression set (%)	CEw	CFw
1	15-pusc-2	4-7	0.1651	1.7	25.3	12.1
2	15-cpu-pusc-1	8-12	0.1400	2.3	28.2	10.2
3	15-cpu-pusc-1h	15-19	0.1630	1.8	69.2	8.6
4	20-cpu-pusc-1	17-22	0.2896	1.8	67.1	6.0
5	25-cpu-pusc-1	24-29	0.3197	3.7	65.1	5.3
6	15-cpu-pusc-2	13-17	0.1887	2.1	33.3	7.8
7	20-cpu-pusc-2	17-22	0.3191	3.5	46.0	6.5
8	25-cpu-pusc-2	25-30	0.3221	1.6	65.87	5.5
10	20-cpu-pusc-3	15-19	0.2771	2.9	30.0	8.0
11	15-cpu-pusc-5	5-9	0.1916	3.2	33.5	12.3
12	15-cpu-1h	11-15	0.2432	0.0	31.9	7.7
13	15-cpu-1	6-9	0.2053	0.5	53.6	6.2
14	20-cpu-1h	17-22	0.2924	1.6	71.4	5.8
15	20-cpu-1	17-22	0.3124	1.9	48.7	6.5
16	25-cpu-1	15-19	0.2810	1.6	55.9	6.3
17	30-cpu-1	15-20	0.3397	0.2	65.8	5.4
18	35-cpu-1	18-22	0.3800	1.2	71.7	5.3
19	40-cpu-1	25-30	0.3818	3.4	80.5	5.3
20	45-cpu-1	28-32	0.4580	4.2	59.0	6.9
21	50-cpu-1	29-33	0.4875	3.5	61.6	7.0
22	DRS	5-7	0.2527	6.1	26.8	9.2
23	HPS	4-6	0.1618	6.3	48.9	14.9
24	MCP	12-14	0.0822	65.0	153.6	4.7
25	PUF	9-10	0.2580	1.7	102.0	7.3

References

[1] Jahhs, M.H., Kummer, F., and Michelson, J.D. Investigations into the fat pads of the sole of the foot: heel pressure studies. *Foot Ankle* 1992; 13:227-232.

[2] Pratt, D.J.: Polyurethanes in orthotics and orthopaedics. *Plastics Rubber Intl.* 1989a; 14: 21-24.

[3] Aruna P, Venkateshwaralu U, Ganga R. *J Appl Polym Sci* 2002; 83: 86–93.

[4] Khorasoni MT, Shorgashti S. *J Biomed Mater Res part B: Appl Biomater* 2006; 76B: 41-48.

[5] SATRA Bulletin, October 1991: 262-263.