

Development of Polyurethane-Based Sheets by Phase Inversion Method for Therapeutic Footwear Applications: Synthesis, Fabrication, and Characterization

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ABSTRACT: It has been proved that polyurethane (PU) foam and viscoelastic PUs are offering better cushioning and shock absorption properties than other materials such as foam rubbers, polyethylene, ethylene vinyl acetate, and polyvinyl chloride which are used currently as insole materials in therapeutic footwear for diabetic and orthopedic patients to “offload” or redistribute high pressure under the foot. The aim of this research work was to prepare viscoelastic materials based on PUs having the highest degree of phase separation that provides for the elastomeric nature of these polymers. Polymer structures with a high concentration of amide groups can be made with the addition of hydrazine or a diacid hydrazide to a diisocyanate. We had prepared various PUs by chain extending the isocyanate-terminated prepolymer with terephthalic dihydrazide, 5-hydroxy isothalic dihydrazide, and 1,4-butanediol. Polymers were developed into sheets by

phase inversion method using dimethyl formamide as solvent and water as nonsolvent. To improve the mechanical properties of PU sheets the polymer solution was blended with polyester-based PU Desmopan 8078 (CPU) in 1 : 1 ratio and the solution mixture was developed into sheet by the same method. Further PU sheets based on only CPU were also developed with various concentrations of PU. The synthesized PU and their blends with CPU were characterized by infrared spectroscopy, differential scanning calorimetry, thermo gravimetric analysis, gel permeation chromatography, and dynamic mechanical analysis. Morphological characteristics of PU sheets were studied by scanning electron microscopy. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2387–2399, 2009

Key words: block copolymers; polyurethanes; viscoelastic polymers; therapeutic footwear; phase inversion method

INTRODUCTION

Polyurethanes (PUs) are used in wide physical forms, such as resins, elastomers, gels, adhesives, laminates, reinforcements, and soft and rigid foams, because they can be synthesized into materials with a variety of functions from various combinations of diisocyanates and diol monomers depending on the application.^{1,2} A number of therapeutic approaches to “offload” or redistribute high plantar pressure in diabetic and orthopedic patients have been reported in the last 10 years.^{3–6} Usage of therapeutic footwear turns out to be an effective tool for managing normal gait and reduction of peak plantar pressures. Flexible, custom-made orthotic shoe insoles, which reduce elevated local pressures at the plantar foot-shoe interface, can be of substantial preventive and/

or therapeutic value to a variety of patients. Common materials include foam rubbers, such as latex, and cellular polymers such as polyethylene (PE), ethylene vinyl acetate (EVA), PU, and polyvinyl chloride (PVC). Essentially solid materials such as viscoelastic polymers and natural cork are also used effectively. PU foam and viscoelastic PUs are offering good cushioning and shock absorption properties without suffering compression set. 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. 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

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TABLE I
Composition of Polyurethanes Developed in the Laboratory

Sample code	Isocyanate (NCO)	Polyol (OH)	Chain extender-1 (CE-1)	Chain extender-2 (CE-2)	NCO : OH : CE1 : CE2 mole ratio
PUSC-1	MDI	PTMG 1000	TDH	–	2 : 1 : 1 : 0
PUSC-2	MDI	PTMG 1000	TDH	1,4-BD	2 : 1 : 0.5 : 0.5
PUSC-3	MDI	PTMG 1000	OH-IDH	–	2 : 1 : 1 : 0
PUSC-4	MDI	PTMG 1000	OH-IDH	1,4-BD	2 : 1 : 0.5 : 0.5
PUSC-5	MDI	PTMG 1000	TDH	OH-IDH	2 : 1 : 0.5 : 0.5

mechanical properties. The physical and mechanical properties can be designed and controlled at various stages during synthesis. SPEU materials combine flexibility with high strength, wear resistance and a degree of hardness.

A common method for the preparation of porous PU film involves the phase inversion process.⁷ In the phase-inversion process, a homogeneous polymer solution in contact with a nonsolvent and the subsequent exchange of solvent and nonsolvent across the interface results in phase separation into a polymer-rich phase and polymer-poor phase. At high polymer concentration, phase separation is continued until the polymer-rich phase is solidified.⁸ The final morphology of PU films is strongly influenced by the solidification process of the polymer-rich phase, which can be achieved by either gelation or crystallization of the polymer-rich phase.^{9–11} The aim of this research work was to prepare viscoelastic PU materials and fabricate into sheets of 3–6-mm thickness for application in therapeutic footwear and accessories such as heel pad, metatarsal pad, etc. Polymer structures with a high concentration of amide groups that provides for the highest degree of phase separation can be made with the addition of hydrazine or a diacid hydrazide to a diisocyanate. In this paper we have reported the synthesis of various PUs by chain extending the isocyanate-terminated prepolymer with terephthalic dihydrazide (TDH), 5-hydroxy isothalic dihydrazide (OH-IDH), and 1,4-butanediol (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 and the solution mixture was developed into sheet by the same method. Further PU sheets based on only CPU were also developed with various concentrations. The synthesized PU and their blends with CPU were characterized by infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA), gel permeation chromatography (GPC), and dynamic mechanical analysis (DMA). Morphological characteristics of PU sheets were studied by scanning electron microscopy (SEM).

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, Boisar, India) and dibutyltin dilaurate (Sigma-Aldrich, Germany) were used as received. Polyester-based PU Desmopan 8078 (CPU) with Shore A hardness 70 was obtained from Bayer Science Materials (Mumbai, India).

METHODS

Terephthalic acid was converted to TDH by a procedure as reported elsewhere.^{12,13} Similarly 5-hydroxy isothalic dimethyl ester was converted to 5-hydroxy isophthalic dihydrazide (OH-IDH). These dihydrazides were used as chain extenders in PU synthesis either alone or in combination with 1, 4-BD. Prepolymers were prepared by the reaction of MDI with PTMG 1000 at 65–70°C for 3 h. Then the temperature was reduced to 0–10°C. Chain extenders suspended in dimethyl sulfoxide were added drop wise, followed by the addition of a drop of dibutyltin dilaurate, catalyst. The temperature was slowly raised, and the chain extension step was carried out at 65°C for 6 h. The polymeric solutions was cooled to room temperature and precipitated in water. The products were washed well in water to remove all the solvents and dried at 60°C for 2 days in oven. Table I shows the basic formulation for preparing samples with various hard segment contents.

Preparation of PU sheets

The processing method used to develop porous viscoelastic sheets from blends of synthesized PU and CPU and from commercial polyurethane (CPU) alone is phase inversion or coagulation method. DMF was

TABLE II
List of PU Sheets Developed in the Laboratory and their Composition

Sample no.	Sample code	Description
1	15-pusc-2	15% PUSC-2 (90 g in 600 mL of DMF)
2	15-cpu1-pusc-1	15% CPU 8078: PUSC-1 (45:45 g in 600 mL of DMF)
3	15-cpu1-pusc-1h	15% CPU 8078: PUSC-1 (75:75 g in 1000 mL of DMF)
4	20-cpu1-pusc-1	20% CPU 8078: PUSC-1 (60:60 g in 600 mL of DMF)
5	25-cpu1-pusc-1	25% CPU 8078: PUSC-1 (75:75 g in 600 mL of DMF)
6	15-cpu1-pusc-2	15% CPU 8078: PUSC-2 (45:45 g in 600 mL of DMF)
7	20-cpu1-pusc-2	20% CPU 8078: PUSC-2 (60:60 g in 600 mL of DMF)
8	25-cpu1-pusc-2	25% CPU 8078: PUSC-2 (75:75 g in 600 mL of DMF)
9	15-cpu1-pusc-3	15% CPU 8078: PUSC-3 (45:45 g in 600 mL of DMF)
10	20-cpu1-pusc-3	20% CPU 8078: PUSC-3 (60:60 g in 600 mL of DMF)
11	15-cpu1-pusc-5	15% CPU 8078: PUSC-5 (45:45 g in 600 mL of DMF)
12	15-cpu-1h	15% CPU 8078 (150 g in 1000 mL of DMF)
13	15-cpu-1	15% CPU 8078 (90 g in 600 mL of DMF)
14	20-cpu-1h	20% CPU 8078 (200 g in 1000 mL of DMF)
15	20-cpu-1	20% CPU 8078 (120 g in 600 mL of DMF)
16	25-cpu-1	25% CPU 8078 (150 g in 600 mL of DMF)
17	30-cpu-1	30% CPU 8078 (180 g in 600 mL of DMF)
18	35-cpu-1	35% CPU 8078 (210 g in 600 mL of DMF)
19	40-cpu-1	40% CPU 8078 (240 g in 600 mL of DMF)
20	45-cpu-1	45% CPU 8078 (270 g in 600 mL of DMF)
21	50-cpu-1	50% CPU 8078 (300 g in 600 mL of DMF)

used to prepare PU solution and distilled water was used as nonsolvent or coagulant. As per reported procedures in literature, the glass plate containing PU solution was immersed in coagulation medium and left for few hours to develop microporous PU membranes for biomedical applications.⁹⁻¹¹ In the present work, PU solution in room temperature was taken in polypropylene tray to a height of 3–6 mm and left for 15–20 min to allow evaporation of solvent and formation of microskin layer over the surface. Then the coagulant, water was sprayed uniformly over the surface to a height of 2 mm and left for 15–20 min to allow slow exchange of solvents. Then the tray was filled with water and left for over night.

PU sheets were prepared with blends of commercial PU and experimental PU in 1 : 1 ratio. Blends were prepared as homogenous solution in DMF and made into sheets as explained above. Further PU sheets were prepared with only commercial polyurethane 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 using water as nonsolvent. Table II shows the composition of all 21 sheets developed in the laboratory by phase inversion method using synthesized PU and commercial PU with different composition of polymer and volume of solvent.

Measurements

FTIR spectra were recorded with a Nicolet Avator 360 FTIR spectrophotometer with an attenuated total reflection accessory. Thermogravimetric analysis was

done with a Dupont 951 thermogravimetric analyzer at a heating rate of 20°C/min under a nitrogen atmosphere (flow rate = 50 mL/min). DSC was carried out under a nitrogen atmosphere with a Dupont differential scanning calorimeter at a heating rate of 10°C/min. The samples were first heated to 200°C to erase the thermal history, and then quenched to –100°C, and finally scanned up to +300°C. Gel permeation chromatography was carried out with Refractive Index Detector 2414, Waters India. Samples were dissolved in HPLC grade DMF and filtered before injection. About 50 µL of sample solution was injected and run time was set as 60 min. DMF was used as eluent. Calibration was performed using monodisperse polystyrene standard samples with narrow polydispersity. Dynamic mechanical analysis was carried out in the multifrequency mode using DMA 2980 dynamic mechanical analyzer with rectangular specimens of dimension (20 × 10 × 5 mm³) at 1-Hz frequency in the temperature range of –100–300°C with strain amplitude of 20 µm. Samples were scanned in FEI-Quanta 200 scanning electron microscope, after coated with gold in Edwards E-306 Sputter Coater. The density of the PU sheets were determined by SATRA TM 12, and then the porosity percentage of PU sheets were calculated using the following equation.¹⁴

$$\% \text{ Porosity} = [(1/D_s - 1/D_o)/(1/D_s)] \times 100$$

D_o = density of the pure PU

D_s = density of the PU sheets, where $D_o = 1.19 \text{ g/cm}^3$.

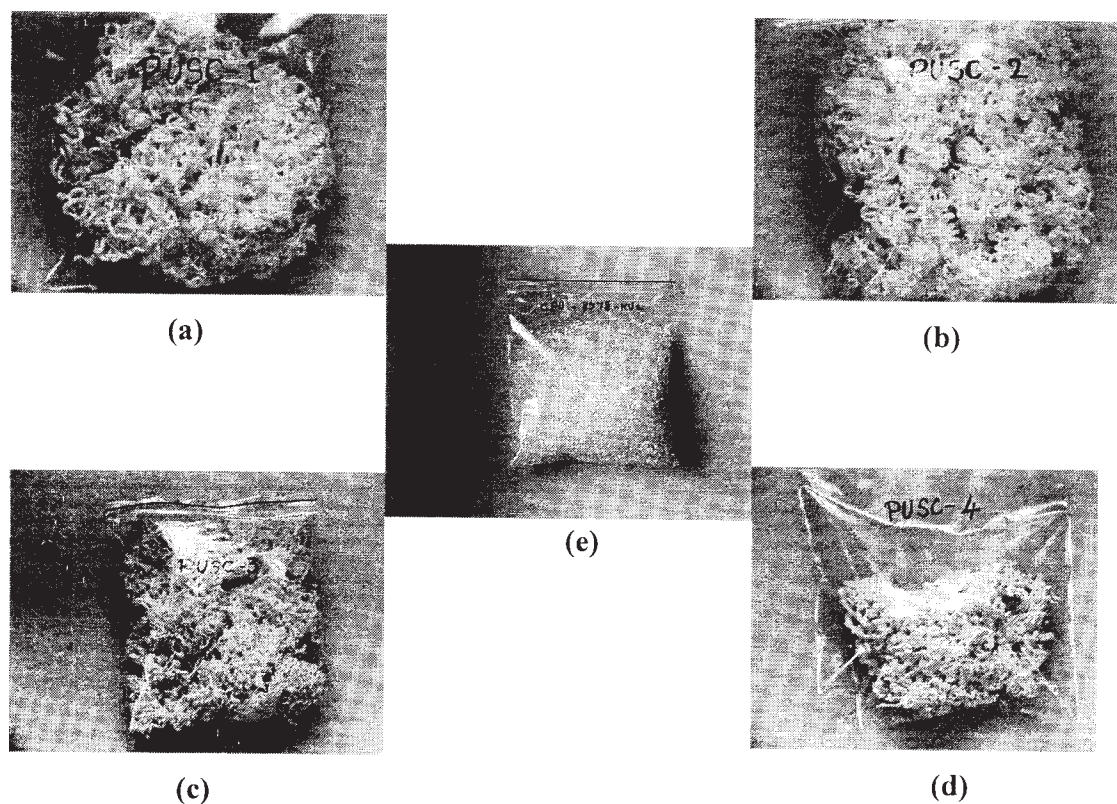


Figure 1 Fiber forming polyurethanes developed in the laboratory (a) PUSC-1, (b) PUSC-2, (c) PUSC-3, (d) PUSC-4, and (e) commercial polyesterurethane, Bayer Materials, India.

RESULTS AND DISCUSSION

Preparation of PU sheets

When the PU solution was precipitated in water all PU samples formed soft white fibrous materials, which are resilient in nature (Fig. 1). But the degree of resilience varied with type of hard segment content and CPU concentration. When the PU solution was fabricated into sheet by phase inversion method the sheet was formed with smooth surface on bottom side and porous surface on upper side, which was in direct contact with nonsolvent during fabrication.

It was found that the sheets that were developed after allowing for PU solution in the tray to evaporate for 15–20 min, had more uniform thickness and smoother surface than in those cases where the coagulant was sprayed immediately. Further it was found that when the tray was filled with water without allowing for 15 min standing after filling it for 2-mm thickness over PU solution, the sheet had formed with more macrovoids in upper layer. It may be due to the rate of water inflow that is greater than that of DMF outflow.

The mechanism of processing method is liquid-liquid separation. When the PU solution comes in contact with nonsolvent, exchange of solvent and nonsolvent takes place and forms polymer-rich

phase and polymer-poor phase; the former forms polymeric matrix and later forms macrovoids. Exchange of solvents is due to that the solution at interface becomes thermodynamically unstable and it exists till the nucleation and growth of polymeric matrix completes, that is till the polymer-rich phase solidifies. It was found that the PU solution of high molecular weight polymer or higher polymer concentrations had formed sheets with less macrovoids. It can be attributed to the fact that DMF outflow is greater than water inflow in case of higher polymer concentrations and water inflow is greater than DMF outflow in case of lower polymer concentrations. Further the processing method had resulted in the formation of asymmetric sheets. The increase of polymer content will lead to a much higher polymer concentration on the surface and restrict the movement of polymer chains, especially soft segment. On the other hand, increase in polymer concentration will decrease the demixing rate between polymer solution and coagulation medium, and hence increase the migration of soft segment toward surface. Thus, it is resulting in the formation of spongy upper layer and thick compactly packed bottom layer. Both are linked by open cellular structure through out the sheet. In literature,^{14,15} researchers have studied the effect of temperature and various coagulation mediums such as mixture of water and DMF,

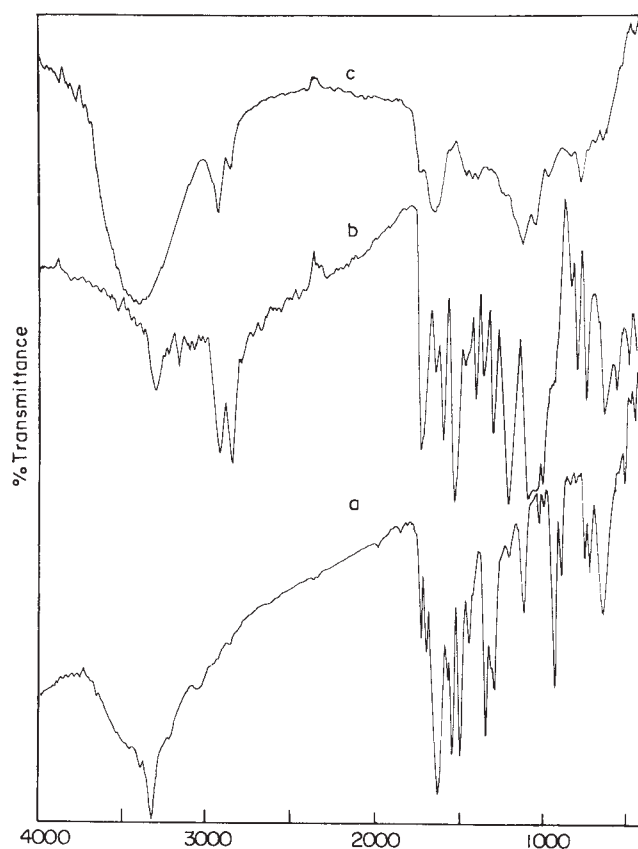


Figure 2 FTIR spectra of (a) TDH, (b) PUSC-1, and (c) blend of CPU: PUSC-1.

mixture of water and alcohol and alcoholic medium, on morphology of final PU membrane. Khorasoni et al.¹⁴ found that coagulation medium at 60°C and alcohol as nonsolvent for DMF had formed membranes with less macrovoids. But in our study we have used only distilled water at room temperature as coagulation medium since it required the development of large sheets of 30 cm × 16 cm × 5 mm size for making pair of insole and the presence of macrovoids provides more air to be occupied inside the sheet which can enhance the cushion properties of the material when used in therapeutic footwear.

FTIR spectroscopic analysis

FTIR spectra of synthesized PU are given in Figures 2-4. In Figure 2, the spectrum of PUSC-1 is compared with the spectrum of TDH (chain extender that was used in synthesis of PUSC-1) and spectrum of blend of PUSC-1 with CPU. In Figure 3, the spectrum of PUSC-3 is compared with the spectrum of 5-hydroxy isothalic dihydrazide (chain extender that was used in synthesis of PUSC-3) and spectrum of blend of PUSC-3 with CPU. In Figure 4, the spectrum of PUSC-2 is compared with the spectrum of blend of PUSC-2 with CPU. Spectrum of dihydrazide compounds had confirmed the conversion of

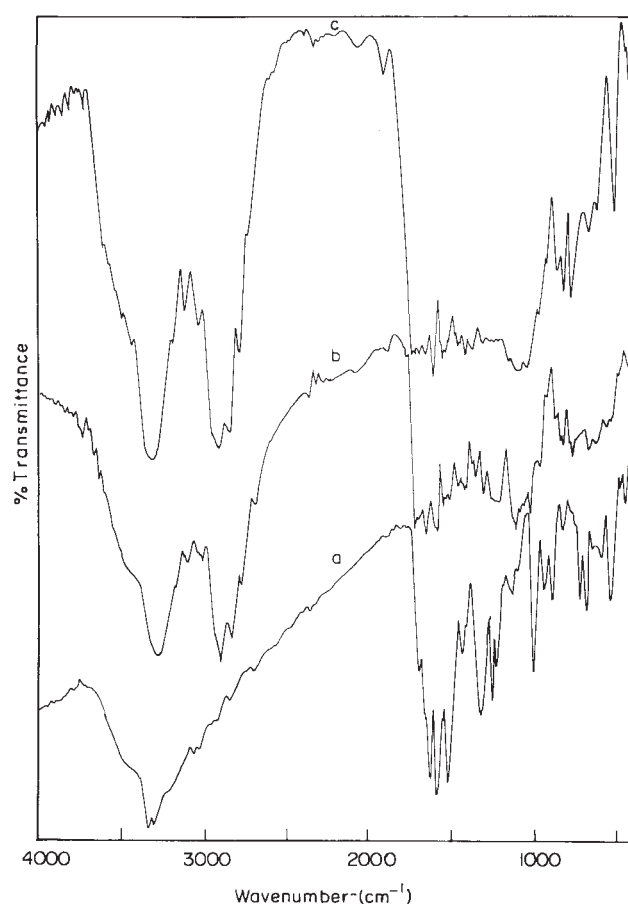


Figure 3 FTIR spectra of (a) OH-IDH, (b) PUSC-3, and (c) blend of CPU: PUSC-3.

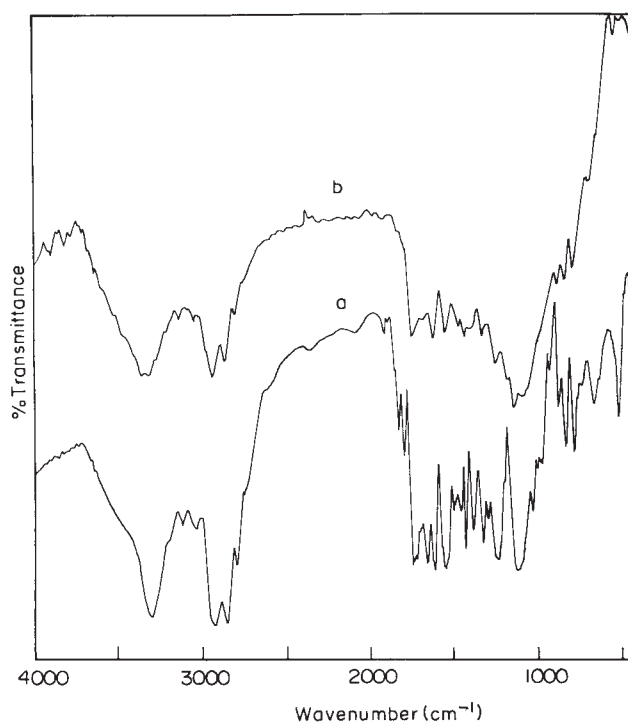


Figure 4 FTIR spectra of (a) PUSC-2 and (b) blend of CPU: PUSC-2.

TABLE III
Results of Thermogravimetric Analysis

Sample code	T1 (°C)	T2 (°C)	T3 (°C)	W1 (mg)	W2 (mg)	W3 (mg)
PUSC-1	350	396	445	7.688	6.311	4.932
PUSC-2	323	380	440	11.65	9.011	6.550
PUSC-3	365	410	456	6.924	4.695	2.468
PUSC-4	376	415	456	12.75	9.74	6.73
PUSC-5	365	404	452	9.259	6.899	4.543
CPU 1	323	355	386	8.418	6.962	5.5
CPU1: PUSC-1	342	395	455	10.34	8.22	6.11
CPU1: PUSC-2	309	387	436	11.48	9.07	6.66
CPU1: PUSC-3	323	395	445	10.39	8.07	5.74
CPU1: PUSC-5	318	390	453	11.21	9.00	6.8

ester into dihydrazide. All the PUSC exhibit characteristic peaks around 3300 and 1750 cm^{-1} corresponding to the $>\text{NH}$ and $>\text{C}=\text{O}$ stretching of the urethane linkage. The peak around 2950 cm^{-1} is due to the stretching of aliphatic $>\text{CH}_2$ groups, and that around 3000 cm^{-1} is due to the aromatic $>\text{CH}$ stretching, confirming the incorporation of the chain extender. The multiple peaks around 2940–2800 cm^{-1} correspond to CH_2 , which is very strong for polyether-based polymers. The peak at 1100 cm^{-1} corresponds to $\text{C}-\text{O}-\text{C}$ stretching of PTMG units. The presence of urethane linkages confirms the formation of the polymer. In the spectrum of blends, ester polyol-based CPU shows a $\text{C}=\text{O}$ peak that is due to the ester linkages in the polyol (soft segment). Further the spectrum of blends had confirmed that they are merely physical blends and there is no chemical interaction between polyester urethane and polyetherurethane.

Thermo gravimetric analysis

The thermal stability of the polymers was evaluated by the determination of the weight change with temperature, and the initial decomposition temperature was taken as the point of onset. The onset or first step (T1), midpoint or second step (T2), and end point (T3) of degradation of various compositions are given in Table III. The incorporation of semicar-

bazide linkages into the PU backbone leads to increased thermal stability, the variation in the composition seems to have little effect on the thermal stability of the systems. This behavior is due to the thermal stability being connected to the dissociation of the least thermally stable chemical groups, in this case urethane linkages, which dissociate around 200–250°C.¹⁶ PUSC-3, PUSC-4, and PUSC-5 had shown slightly higher T2 temperature comparing to PUSC-1 and PUSC-2. Further CPU, which is based on MDI, polyester polyol and 1, 4-BD had shown lower T2 temperature than PUSC. The results clearly show that presence of aromatic hydroxy group and large number of amide linkages in the hard segment domains of PUSC may have led to increased thermal stability due to increased phase separation. Blends of PUSC and CPU had shown T2 temperature significantly higher than CPU but lower than PUSC.

Differential scanning calorimetry

The results of DSC had shown in Table IV. In a DSC scan for PU, as many as five transitions can be observed. These include the glass transition temperature (T_g), short range and long-range order transitions, and finally the melting temperature of the hard segments. The variation of the T_g of the soft segment as a function of composition or segmental chemical structure has been used as an indicator of

TABLE IV
Results of Differential Scanning Calorimetry

Sample code	T_g (°C) (onset)	T_g (°C) (midpoint)	T_g (°C) (endpoint)	Del cp (J/g k)	Tm1 (°C)	Tm2 (°C)
PUSC-1	-83.2	-77.7	-72.2	0.36	56.9	185.4
PUSC-2	-81.7	-62.8	-61.7	3.11	33.3	203.5
PUSC-3	-79.4	-72.1	-64.7	0.08	61.1	203.8
PUSC-4	-69.5	-56.1	-42.7	0.63	73.7	226.7
PUSC-5	-81.2	-63.0	-44.8	1.54	50.9	-
CPU 1	-8.6	5.2	18.9	1.11	111.6	156.4
CPU1: PUSC-1	-65.5	-59.2	-53.3	0.08	55.7	211.9
CPU1: PUSC-2	-96.4	-90.9	-85.4	0.58	54.2	156.7
CPU1: PUSC-3	-94.4	-89.4	-84.5	0.40	70.4	220.5
CPU1: PUSC-5	-92.7	-76.8	-60.8	1.45	50.3	267.7

TABLE V
Results of Gel Permeation Chromatography

Sample code	Mn	Mw	Mp	Polydispersity
PUSC-1	154467	207330	184765	1.34
PUSC-2	155817	174219	201339	1.12
PUSC-3	168183	325135	615430	1.93
PUSC-4	90983	228872	311264	2.51
PUSC-5	301471	363286	402765	1.2
CPU1	278646	384796	444313	1.38
CPU1: PUSC-1	135343	280794	216723	2.07
CPU1: PUSC-2	124092	261934	211468	2.11
CPU1: PUSC-3	106728	248403	185902	2.32
CPU1: PUSC-5	155491	252290	216723	1.62

the degree of microphase separation. From the DSC thermograms of PUSC, the glass transition temperature (T_g) of soft segment was observed around -80°C . The decrease in T_g of soft segment shows the presence of microphase separation between the soft and hard segment of polymer that provides for the elastomeric nature of these PUs. The T_g of soft segment of CPU was observed at -8°C . The polyester-urethane materials show a greater tendency for the hard segment to be trapped in the polyester rich soft segment phase, owing to the greater polarity of the polyester segment. The T_g of the soft segment in the polyesterurethane thus increases due to phase mixing. Two distinct endotherms were observed in all the samples. The high temperature endotherm ($156\text{--}267^\circ\text{C}$) can be ascribed to melting of microcrystalline hard domains. A lower temperature endotherm ($33\text{--}73^\circ\text{C}$) may be assigned to the onset of microdomain mixing of noncrystalline hard and soft segments, i.e., the disruption of urethane-macroglycol bonds.¹⁷

Gel permeation chromatography

GPC was carried out for all the samples to find the molecular weight of the polymer. The results are shown in Table V. Among the synthesized polymers, PUSC-5 had given the highest molecular weight. This may be due to the presence of both 5-hydroxy isothalic hydrazide and terephthalic dihydrazide as chain extenders in that compound, whereas PUSC-3 had given comparatively high molecular weight. The weight average molecular weight (Mw) of CPU was found to be 384796 Da. Blends of CPU and PUSC had shown higher molecular weight than PUSC alone but lower than CPU alone in 1 : 1 ratio. So by increasing CPU ratio in blends, the molecular weight can be improved which will in turn improve the mechanical properties of the materials.

Dynamic mechanical analysis

DMA can be simply described as applying an oscillating force to a sample and analyzing the material

response to that force. From this, properties like the ability to lose energy as heat (damping) and the ability to recover from deformation (elasticity) can be calculated. Basically relaxation of the polymer chains or changes in the free volume of the polymer that occur on application of load at various temperatures is studied from dynamic mechanical analysis. One advantage of DMA is that modulus at each time sine wave is applied can be obtained, allowing to sweep across a temperature or a frequency range.

The dynamic mechanical results of polymers with various compositions are tabulated in Table VI. Among the polymer sheets developed, CPU: PUSC-3 had shown the highest storage modulus, E' . Presence of aromatic hydroxy group and dihydrazide linkages in the back bone of polymer chain had made the hard segment to act as filler in the matrix of polyol soft segment and resulted the polymer more viscoelastic. This is again proved by high value of E' for CPU: PUSC-5, which is based on OH-IDH and TDH. Further the results are in agreement with the fiber forming property of dihydrazide compounds.¹⁷ As the sheets are developed by phase inversion method, fibrous structures are formed within the sheets as seen in SEM micrographs. Presence of fiber like structures within the sheet makes the sheet more resilience in nature. The lower values of E' for CPU: PUSC-1 and CPU: PUSC-2 than other samples may be attributed to larger number of macrovoids. Formation of large number of macrovoids may be due to the low molecular weight of the polymers. As the molecular weight is low the viscosity of polymer solution was also low. Because of low viscous polymer solution the rate of flow of water into the polymer solution is higher than the rate of flow of DMF out of the solution. This resulted in formation of large number of macrovoids and sheets with low toughness. In case of CPU-based sheets, storage modulus (E') increases with increase in concentration of CPU. This is also in agreement with the fact that the concentration of polymer has effect on viscosity of the polymer solution, which in turn has effect on formation of macrovoids within the sheet. As the concentration of CPU increases sheets were formed with

TABLE VI
Results of Dynamic Mechanical Analysis

Sample code	E' (Mpa)	Tan δ
15 CPU1: PUSC-1	820	0.1947
15 CPU1: PUSC-2	885	0.1359
15 CPU1: PUSC-3	3525	0.1741
15 CPU1: PUSC-5	2225	0.3723
15 CPU1 8078	880	0.1932
25 CPU1 8078	2000	0.2310
30 CPU1 8078	900	0.2228
35 CPU1 8078	1330	0.1629
40 CPU1 8078	1900	0.2329

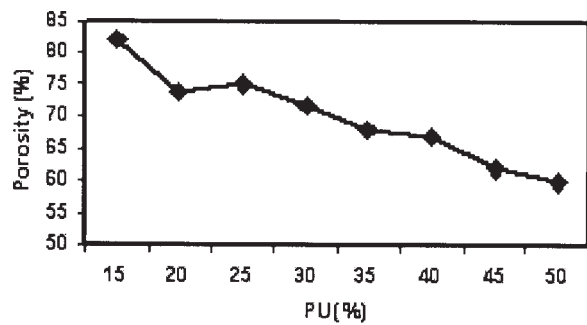


Figure 5 Porosity (%) of PU sheets vs. PU (%) in polymer solution.

less macrovoids and thus high toughness. But 25% of concentration of polymer had shown the higher value of E' . This is due to the fact that both density and porosity play important role in material toughness. In case of 15% PU sheets either CPU alone or CPU: PUSC blends the percentage porosity is higher and thus density is low comparing to higher concentrations. Because of the presence of large number of pores sheets become flexible. From 30% CPU, the percentage porosity of sheets decreases rapidly with increase in polymer concentration. In case of 25%

CPU, the percentage porosity (75%) is at optimum to make the sheet viscoelastic (Fig. 5). Therefore, 25% concentration of CPU could be the optimum concentration for development of porous viscoelastic sheets by phase inversion method.

The thermomechanical spectra had shown two distinct transitions as indicated by drastic drops in storage moduli. The low temperature transition is related to the T_g of the soft-segment phase (as observed in DSC). As the material becomes elastic, the phase angle δ becomes smaller. The low value of $\tan \delta$ (dissipation factor) for all the samples shows the elasticity of the sheets. The slight differences in $\tan \delta$ value among PUSC samples may be attributed to change in hard segment content.

Scanning electron microscopy

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. Figures 6 and 7 show the outer surface morphology of CPU: PUSC blends at lower and higher magnification respectively, whereas Figures 8

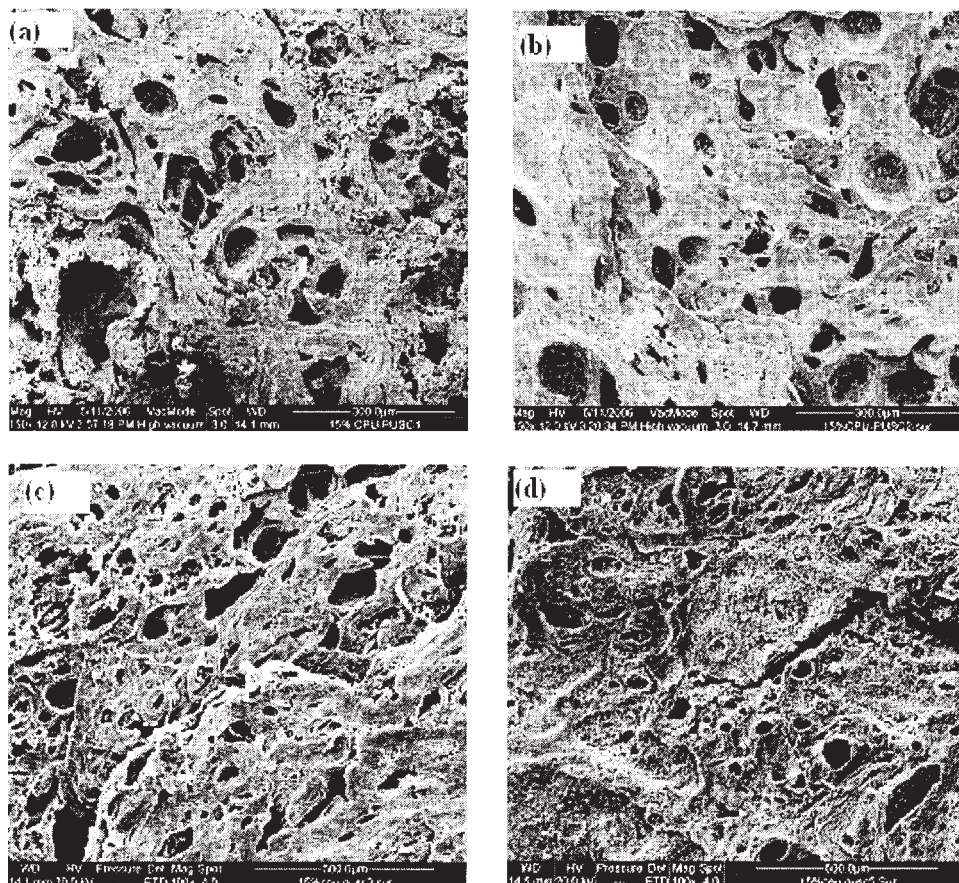


Figure 6 SEM micrographs of surface of 15% W/V CPU: PUSC blends (a) CPU: PUSC-1, (b) CPU: PUSC-2, (c) CPU: PUSC-3, and (d) CPU: PUSC-5 at $\times 150$ magnification.

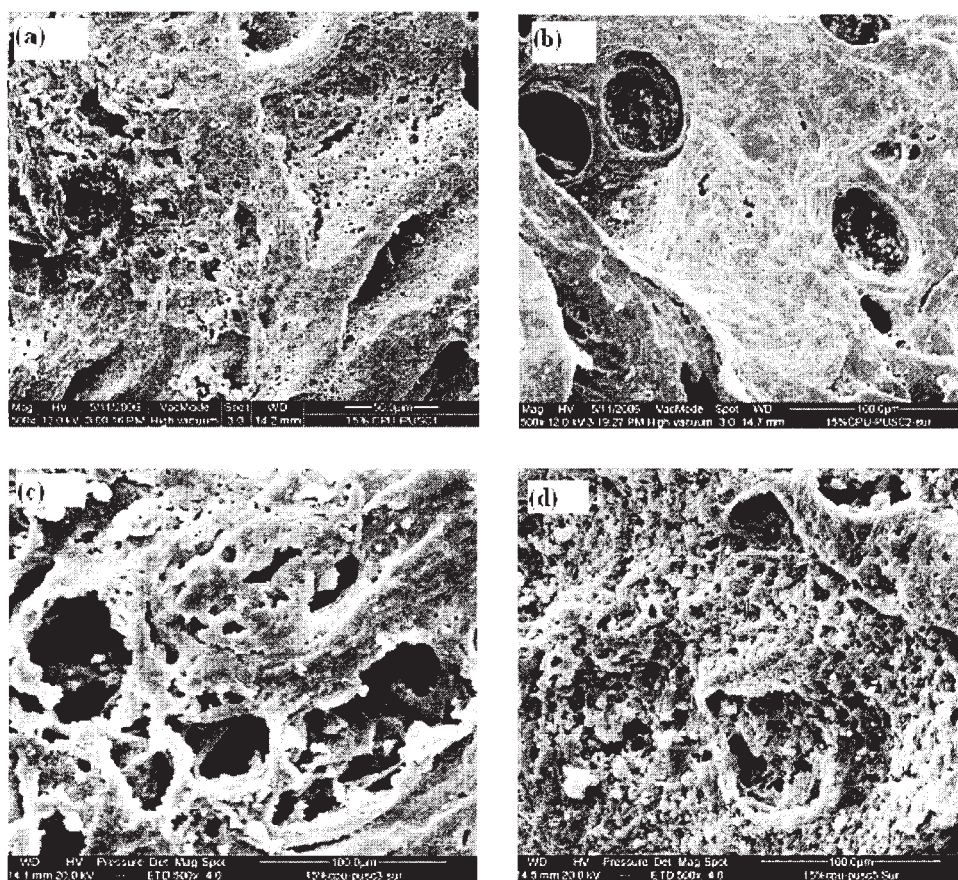


Figure 7 SEM micrographs of surface of 15% W/V CPU: PUSC blends (a) CPU: PUSC-1, (b) CPU: PUSC-2, (c) CPU: PUSC-3, and (d) CPU: PUSC-5 at $\times 500$ magnification.

and 9 show that of CPU sheets of various concentrations. The possible mechanism associated with the formation of cavities on surface is explained by many researchers.⁶ Once the PU solution comes in contact with the coagulant (water), the exchange of the nonsolvent water molecule and the DMF molecule occurs immediately. However, water is a nonsolvent for the PU solution the precipitation rate of the PU molecule is quite high. Hence, it is difficult to maintain a smooth exchange rate between water and DMF molecule. In this situation once the surface of the PU solution has some “defects” or “structural weak points,” the partial precipitated skin of the PU solution may rupture and subsequently the coagulant will penetrate into the PU solution or viscous substrate and form cavities.

SEM micrograph of 15% CPU: PUSC-1 shows more fibrous structure in cross section of upper side of the sheet, comparing to other blended polymer sheets [Fig. 10(a)]. This confirms the fiber forming property of aromatic dihydrazides (TDH) when used as chain extender in PU synthesis. Since the mole ratio of TDH is less in case of PUSC-2, the fibrous nature of the sheet is reduced in 15% CPU: PUSC-2 sheet but still cellular structure can be seen

from the SEM photograph [Fig. 10(b)]. The fiber forming capacity of dihydrazide group is confirmed from SEM pictures of cross section of 15% CPU: PUSC-3 and 15% CPU: PUSC-5 [Fig. 10(c,d)]. The SEM photographs of cross section of lower side of CPU: PUSC blends showed different cellular structure from that of upper side (Fig. 11). Because the mass transfer rate is high at the polymer solution and water interface, one may expect the appearance of an interconnected structure due to spinodal decomposition at the top surface when the coagulation bath contained pure water. 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. More dense and cellular structure is seen in CPU: PUSC-1 and CPU: PUSC-5 [Fig. 11(a,d)]. In case of CPU sheets of various concentrations there is no significant difference between the cross sections of upper and lower side of the sheet (Figs. 12 and 13). A higher polymer concentration is seemed to surpass the formation of macrovoids. Bigger pores in CPU: PUSC blended sheets are considered to result from the delayed solidification of polymer-rich phase

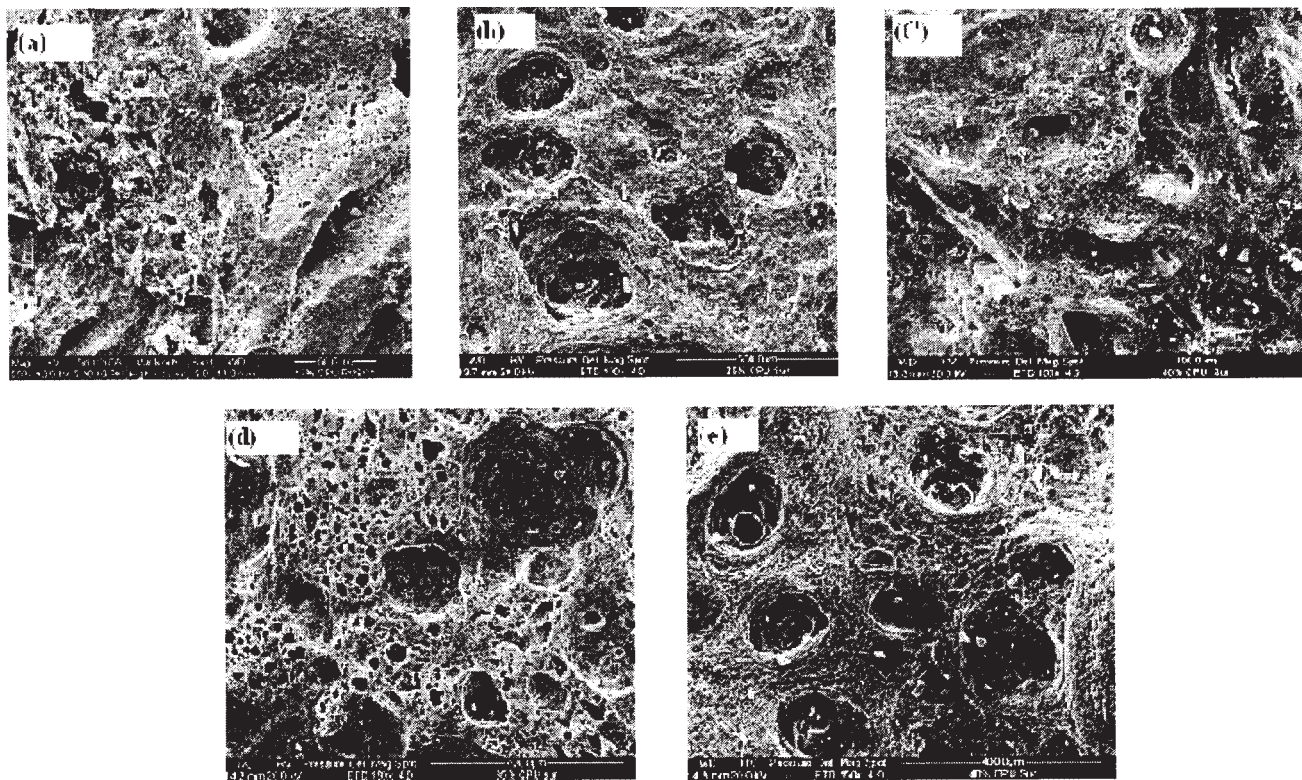


Figure 8 SEM micrographs of surface of CPU (a) 15% CPU, (b) 25% CPU, (c) 30% CPU, (d) 35% CPU, and (e) 40% CPU at $\times 150$ magnification.

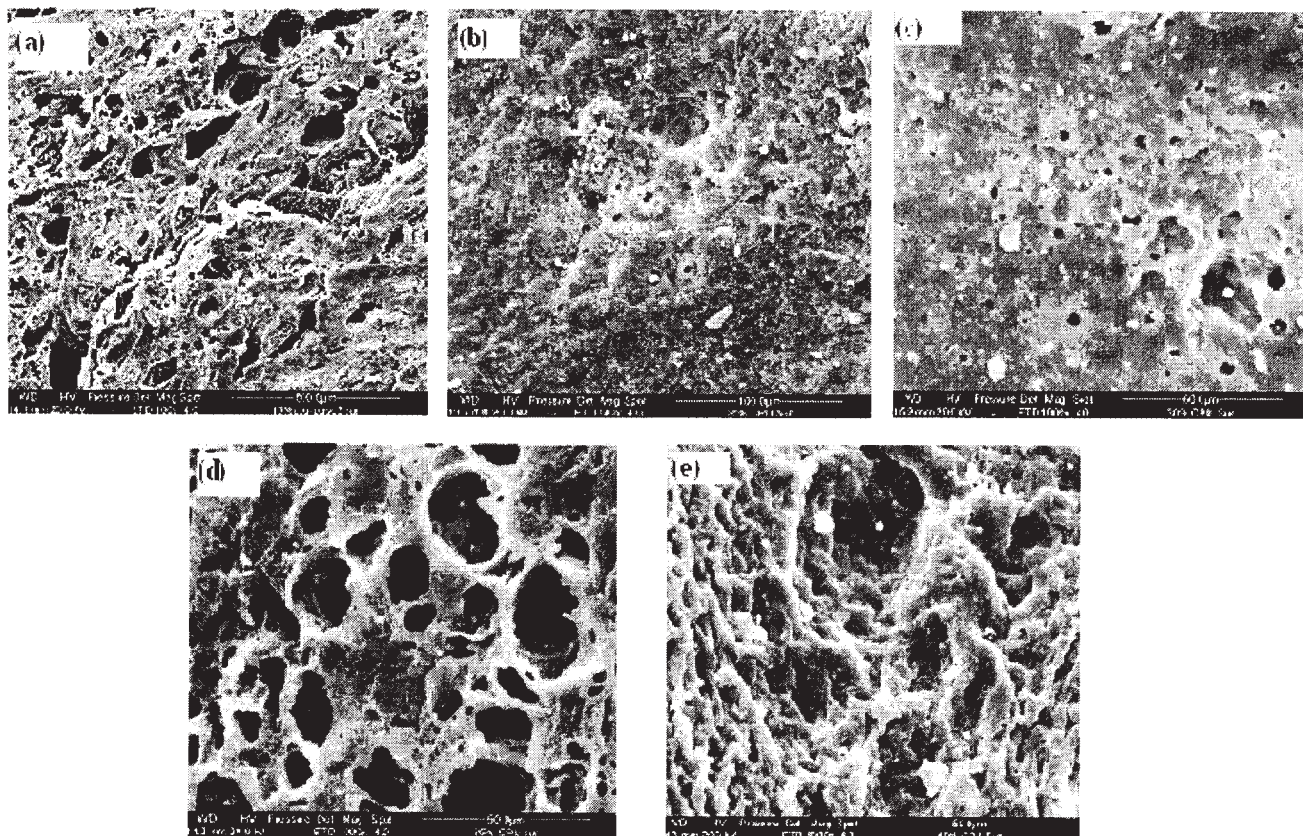


Figure 9 SEM micrographs of surface of CPU (a) 15% CPU, (b) 25% CPU, (c) 30% CPU, (d) 35% CPU, and (e) 40% CPU at $\times 500$ magnification.

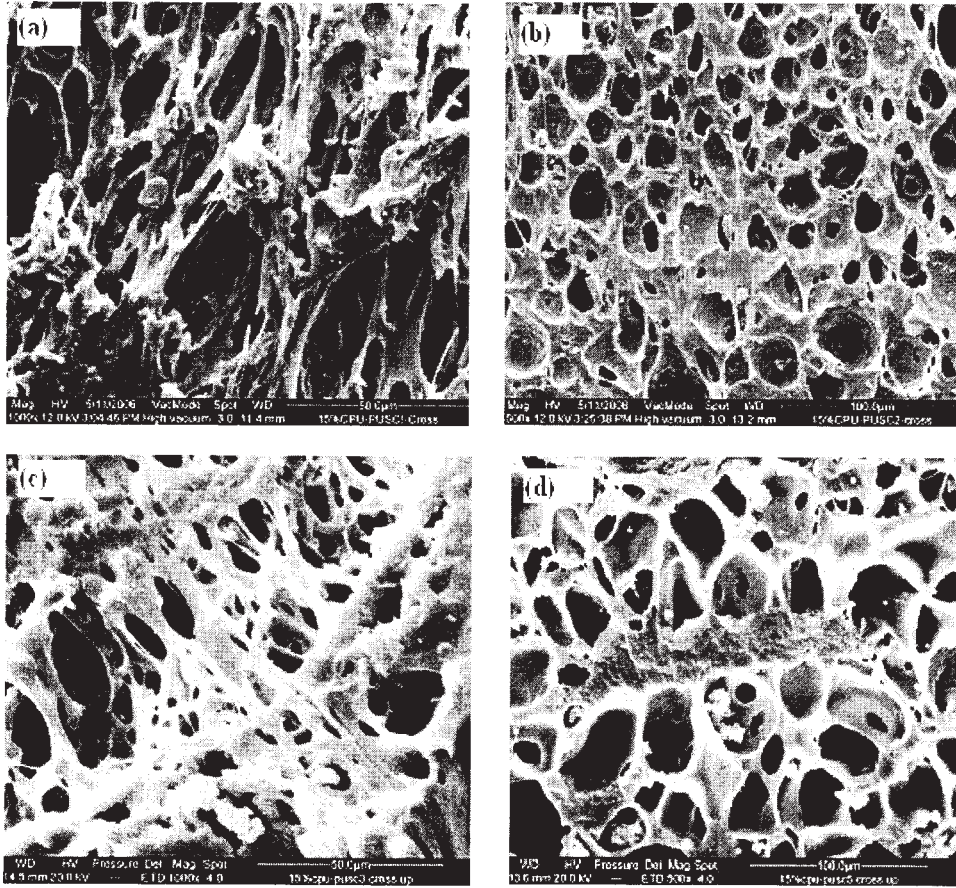


Figure 10 SEM micrographs of cross section of upper side of 15% W/V CPU: PUSC blends (a) CPU: PUSC-1, (b) CPU: PUSC-2, (c) CPU: PUSC-3, and (d) CPU: PUSC-5 at $\times 500$ magnification.

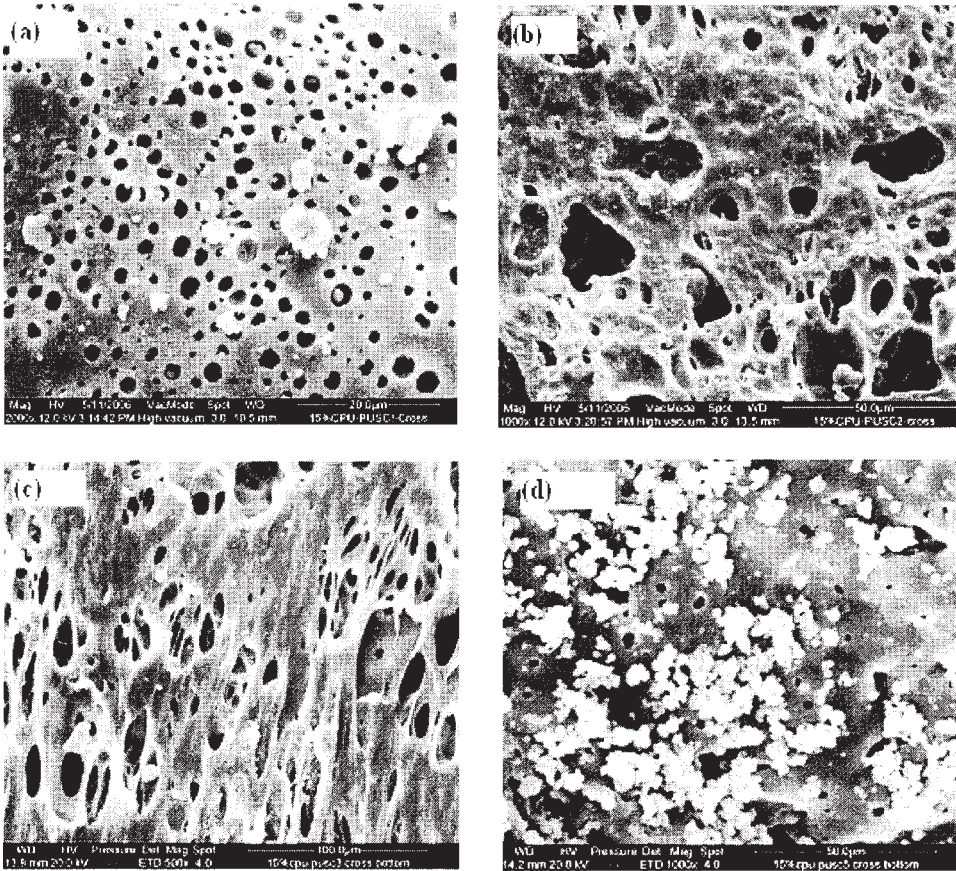


Figure 11 SEM micrographs of cross section of lower side of 15% W/V CPU: PUSC blends (a) CPU: PUSC-1, (b) CPU: PUSC-2, (c) CPU: PUSC-3, and (d) CPU: PUSC-5 at $\times 500$ magnification.

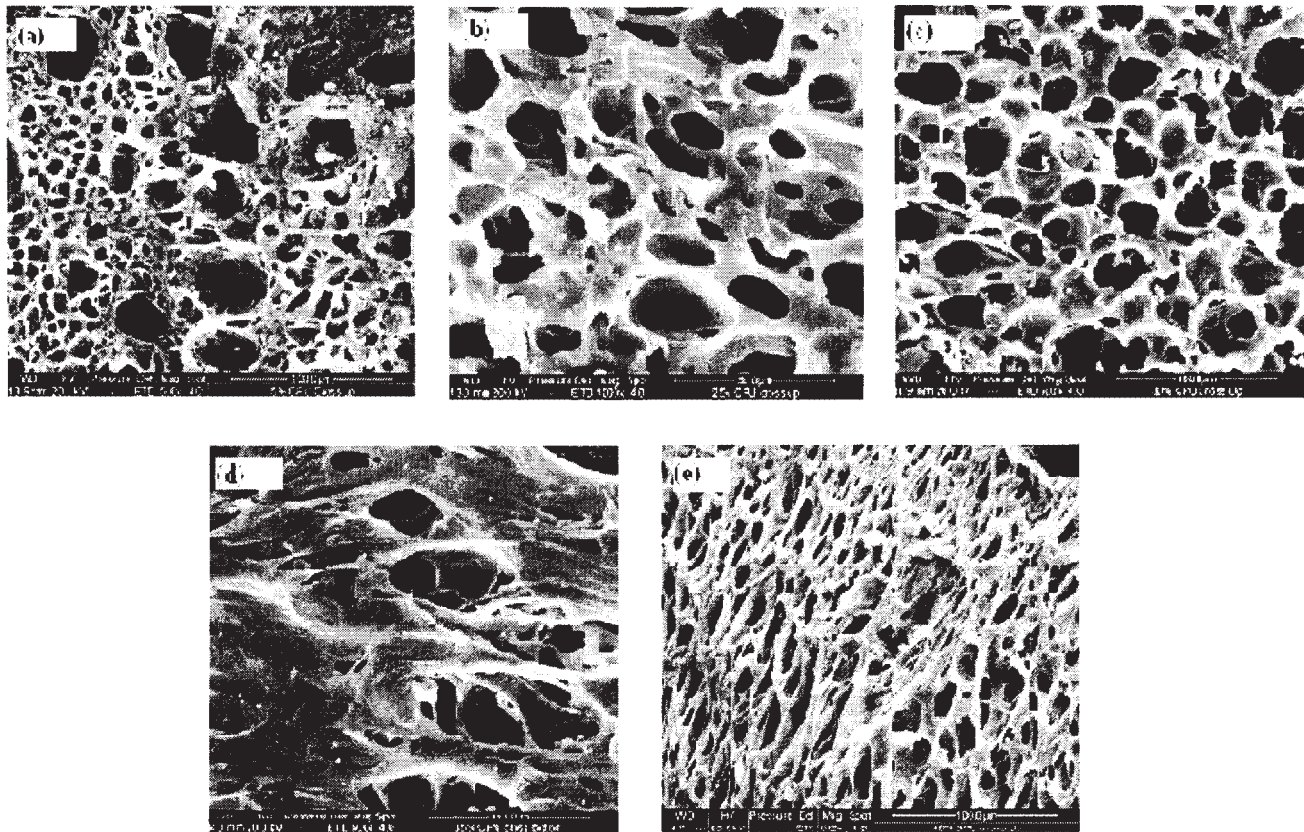


Figure 12 SEM micrographs of cross section of upper side of CPU (a) 15% CPU, (b) 25% CPU, (c) 30% CPU, (d) 35% CPU, and (e) 40% CPU at $\times 500$ magnification.

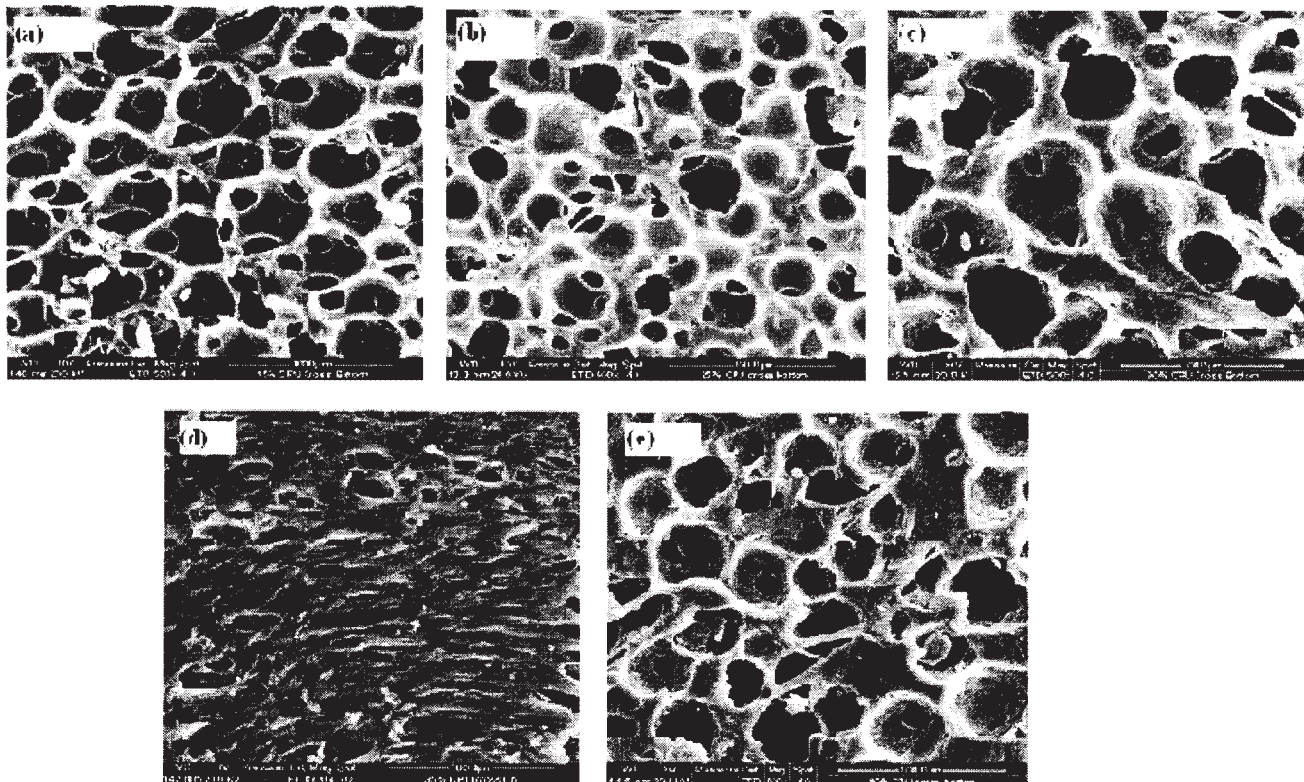


Figure 13 SEM micrographs of cross section of lower side of CPU (a) 15% CPU, (b) 25% CPU, (c) 30% CPU, (d) 35% CPU, and (e) 40% CPU at $\times 500$ magnification.

during the phase separation process. Further, from the Figure 12 where the cross section of lower side of CPU sheets of various concentrations is compared, it is found that as the concentration of CPU increases, porosity of the sheets decreases because a more irregular but interconnected cell form changed to an independent cell structures (Fig. 13).

CONCLUSIONS

Viscoelastic materials based on PUs having terephthalic dihydrazide, 5-hydroxy isothalic dihydrazide, and 1, 4-BD in hard segment were proved to have the highest degree of phase separation that provides for the elastomeric nature of these polymer sheets by DSC, TGA, DMA, and SEM analysis. SEM micrographs had shown the dependency of pore morphology on PU formulation, polymer concentration, rigidity, and molecular weight of polymer. Formation of fibrous structures through phase inversion method has contributed in formation of more flexible and soft sheets. They can be used in therapeutic footwear for diabetic patients who have neuropathic foot for uniform distribution of planter pressure that may lead to diabetic foot ulcers. On the other hand, presence of high molecular weight commercial polyesterurethane has contributed in the formation of micro porous cellular sheets. Further the presence of two layers within a sheet will also give more resilience nature for the insole material to be used in therapeutic footwear. Therefore, by increasing the ratio of CPU in polymer solution cellular sheets can be

developed and the formation of macrovoids can be reduced.

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