Preparation and Properties of New Polyurethane Gels with a Stress-Distributing Function for Medical Applications

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ABSTRACT: The purpose of this study is to prepare new polyurethane gels that can be used as stress- or pressure-distributing materials, particularly by being combined with selective plasticizers for medical or clinical applications. Because low-molecular-weight plasticizer molecules in polymer gels intrinsically tend to migrate to the surface of the gels by the so-called entropy effect in polymer miscibility, the stress-distributing function may decrease gradually after a certain amount of time. Correspondingly, both the chemical nature of the plasticizer and polymer gels and the compatibility between the polymer segments and plasticizer should be deliberately considered as important factors in determining the thermophysical properties and stress-distributing performance of polymer gels. New polyurethane gels comprising separated phases of soft and hard segments, the glass-transition temperature of which was around the ambient temperature, were prepared, and selective plasticizers were combined to obtain an optimized formulation of gels for stress-relieving properties. The glassy-to-rubbery transition of semicrystalline hard segments occurring around the ambient temperature caused the rearrangement of chain conformations, leading to the reduction of the pressure applied to the surface; this indicated that the pressure buildup or loss was somewhat related to the heat regulation by thermal absorption and release in the phase-transition range. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2750–2758, 2006

Key words: compatibility; gelation; polyurethanes; stress

INTRODUCTION

Polyurethanes are used in a wide range of applications,[1–8] such as resins, gels, and foams, because they can be synthesized into materials with a variety of functions from various combinations of diisocyanate and diol monomers depending on the applications. Polyurethane gels have many advantageous properties, such as good pressure-distribution capacity, high shock and shearing-force absorption, and high elasticity and recoverability.

Particularly related to the purpose of this study, there is a tendency for an increase in spinal or other clinical problems resulting from the human posture due to human sedentary lifestyle in modern times.[9] As for medical or clinical applications, materials with the function of dispersing or reducing pressure have continuously been developed, and a polyurethane gel is well known to be one of the materials used widely. For

higher functionality, good heat-transfer behavior is an advantageous characteristic that can be added to the properties of polyurethane gels. The thermal conductivity of polyurethane gels, about 0.410 W/mK, which is high for polymers, permits very good heat transport between hard- and soft-segmented phase-separated polymers and their surroundings.[10]

In this study, we prepared new polyurethane gels combined with selected plasticizers and investigated the gel properties to optimize the relationship between the plasticizer migration and stress–strain behavior of the gels. Di-*n*-butyl phthalate as a plasticizer for toluene diisocyanate derived polyurethane gels is most preferable for the aspect of stress distribution, whereas it may be less favorable for long-term properties because the gradual migration of plasticizers to the bulk outside following total weight loss is quite large. The long-chain ester that we used shows the opposite trend. The elasticity of the gels controlling stress buildup is related to the chemistry of the hard segment of polyurethane gels and its compatibility with the plasticizer molecule. The viscosity governing the stress distribution is related to the soft and flexible segments of the gels and the phase separation between the polyurethane and plasticizers. The new polyurethane gels obtained in this study show an improved

Composition (wt %) of P and R Mixtures for the Synthesis of Polyurethane Gels Including (A) Acetyl Tributyl Citrate,
(B) Di-n-butyl Phthalate, (C) TOTM, (D) an Ester, or (E) an Ester Oil (5 wt %)

	A	B	C	D	E
P liquid					
toluene 2,4-diisocyanate (TDI), polyol (M_w = 6000), polyol (M_w = 2000), and NCO % = 5% prepolymer	100.0	100.0	100.0	20.0	15.0
Plasticizer	90.0	90.0	90.0	80.0	85.0
Total	100.0	100.0	100.0	100.0	100.0
R liquid					
Polyol					
Polyol (M_w = 6000)	30.0	30.0	40.0	70.0	50.0
Polyol (M_w = 2000)					
Plasticizer	69.4	69.4	59.4	29.4	49.4
Catalyst	0.4	0.4	0.4	0.4	0.4
Pigment	0.2	0.2	0.2	0.2	0.2
Total	100.0	100.0	100.0	100.0	100.0

M_w = weight-average molecular weight.

stress-distributing function and durability of the gel performance. These polymer gels will be employed for various applications in medical and rehabilitation fields, including bedsore-prevention-position materials in future studies.

EXPERIMENTAL

Materials

The poly(propylene glycol) (molecular weight = 2000 or 6000; Korea Polyol Co., Ulsan, Korea), toluene 2,4-diisocyanate (DC Chemical Co., Incheon, Korea), and oil (industrial soy bean oil) were commercial grades, and dibutyltin dilaurate as a catalyst was obtained from Aldrich Chemical Co. Various plasticizers of a long-chain ester (a polyester of aliphatic dicarboxylic acid; Pallamol 858, BASF, Ulsan, Korea), trioctyl trimellitate (TOTM; Aekyung Chemical Co., Ulsan, Korea), di-n-butyl phthalate (Daejung Chemical Co., Shi-

huang, Korea), and acetyl tributyl citrate (Uniplex, Unitex Chemical Co., Greensboro, NC) were employed.

Synthesis of the polyurethane gels

The polyurethane gels were synthesized in two steps. In the first step, the urethane prepolymer[7,8] was made from the reaction of a polyol [poly(propylene glycol); 20–40 wt %], an isocyanate (1–3 wt %), a trace of di-butyltin dilaurate as a catalyst, and a plasticizer (80–60 wt %) for 3 h at 50°C; gelation as the second step of the curing reaction was carried out for 2 h at the ambient temperature. The formulations are summarized in Table I. To improve the gel performances for the pressure-distributing function, various polyurethane gels, including selected ester plasticizers and oil (Table II), were prepared in the same way mentioned previously.

TABLE II
Composition (wt %) of P and R Mixtures for the Synthesis of Polyurethane Gels Including an Ester and oil (5%) and
(A) Acetyl Tributyl Citrate, (B) di-n-butyl Phthalate, (C) TOTM, (D) an Ester, or (E) an Ester and Oil (5 wt %)

|	A	B	C	D	E
P liquid					
toluene 2,4-diisocyanate, polyol (M_w = 6000), polyol (M_w = 2000), and NCO % = 5% prepolymer	10.0	10.0	7.0	8.0	7.0
Plasticizer and oil	90.0	90.0	93.0	92.0	93.0
Total	100.0	100.0	100.0	100.0	100.0
R liquid					
Polyol					
Polyol (M_w = 6000)	40.0	40.0	50.0	60.0	80.0
Polyol (M_w = 2000)	5.0	5.0	—	—	—
Plasticizer and oil	54.4	54.4	49.4	19.4	19.4
Catalyst	0.4	0.4	0.4	0.4	0.4
Pigment	0.2	0.2	0.2	0.2	0.2
Total	100.0	100.0	100.0	100.0	100.0

M_w = weight-average molecular weight.
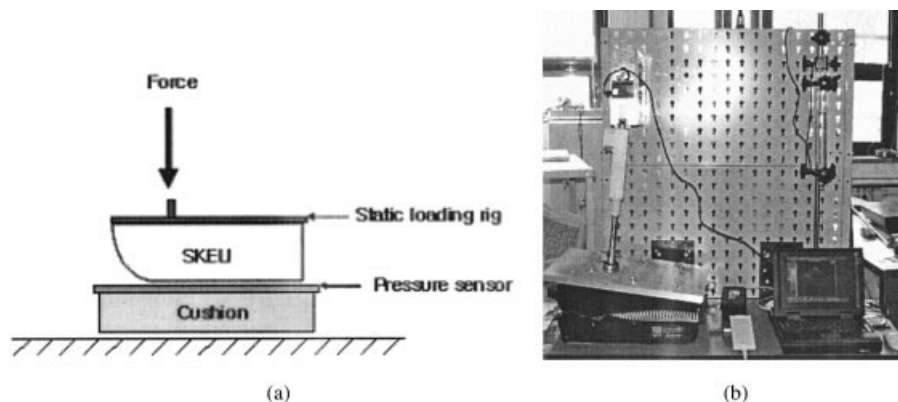
Figure 1 (A) Schematic layout and (B) real image of the apparatus for the pressure-distribution test with SKELI.

Measurements of the various properties

We determined the change of the cure rates of the gel as a function of the catalyst weight after selecting the D type as an optimized formulation on the basis of the preliminary results from the pressure measurements. The hardness was also measured with an F-type durometer for the D-type gels with the settling equivalent ratio of isocyanate to polyol as the isocyanate index. The migration of plasticizers to the surface was accelerated by the exposure of the gels under heating at 70°C in a convection oven for 7 days. The extent of migration of the plasticizers was evaluated by the measurement of the weight losses of the specimens.

The compression–strain behavior of the polyurethane gels was analyzed with an Instron 8544 (Boston, MA) to determine the stress distribution and stiffness. The strain was fixed at a value of 20 mm. The compression rate was 0.5 mm/s. The thermal and mechanical properties were also measured to analyze the migration and gel properties. The size of the speci-

mens was $3 \times 3 \times 3$ cm^3. The glass-transition temperature (T_g) of the synthetic polyurethane gels combined with various plasticizers was measured with the temperature increasing at a rate of 10°C/min from -50 to 100°C by a DSC 2010 (Thermal Analysis Co., New Castle, DE). The thermogravimetric analysis (TGA) of the polyurethane gels was carried out with an SDT 2960 (Thermal Analysis) at a heating rate of 10°C/min between 30 and 500°C. For pressure-distribution measurements, pad specimens ($430 \times 430 \times 2$ mm^3) were prepared from the gels of the ester plasticizer and oil formulation shown in Table II. We also studied the body pressure distribution of males and females as well as a skeletal embedded loading indenter (SKELI; ISO 16840-1 and 16840-2) with a Tekscan model 5315 (Boston, MA) map and sensor, in which the measurable pressure limit was 200 kPa and the total number of sensors for measuring pressure in the arrays was 2016. The schematic layout and real image of the apparatus for measuring the pressure buildup and distribution are shown in Figure 1.
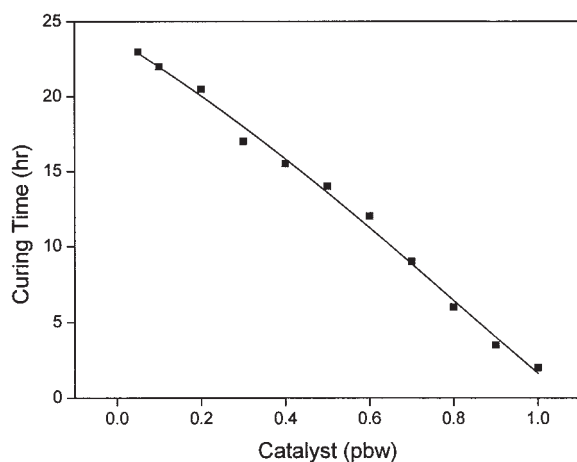

Figure 2 Curing time change according to the different catalyst ratios in the gelation reactions of polyurethanes.
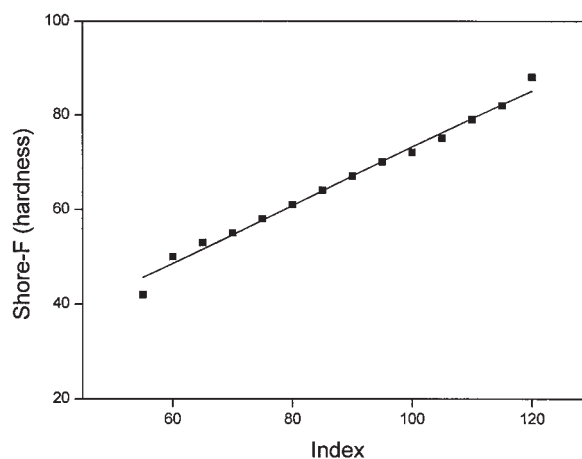

Figure 3 Hardness change according to the isocyanate index in the gelation reaction of polyurethanes.
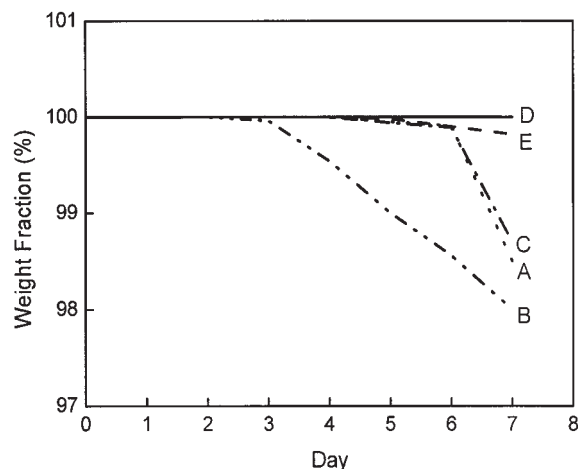
Figure 4 Weight loss of the polyurethane gels when annealed at 70°C to accelerate the migration of the plasticizer: (A) acetyl tributyl citrate, (B) di-*n*-butyl phthalate, (C) TOTM, (D) an ester, and (E) an ester and oil (5 wt %).
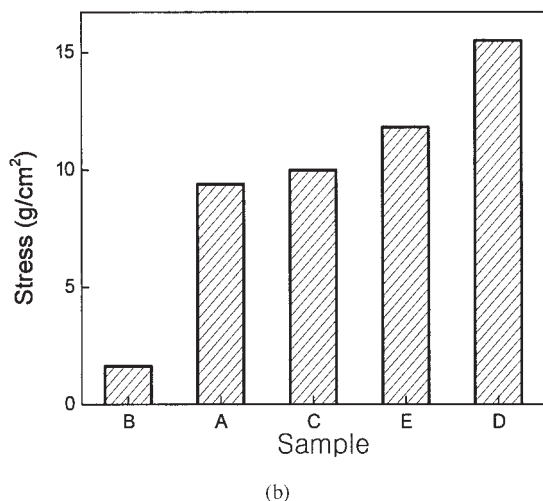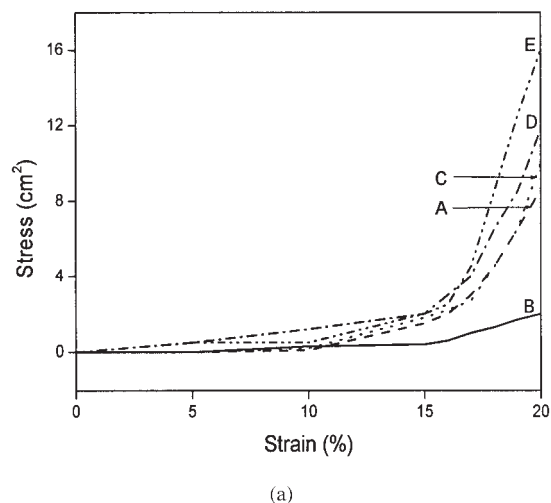

(a)

(b)

Figure 5 (A) Strain–stress curves and (B) stress buildup of the polyurethane gels plasticized with (A) acetyl tributyl citrate, (B) di-*n*-butyl phthalate, (C) TOTM, (D) an ester, or (E) an ester and oil (5 wt %) when compression was applied at a strain rate of 0.25 mm/s with a strain of 20 mm.
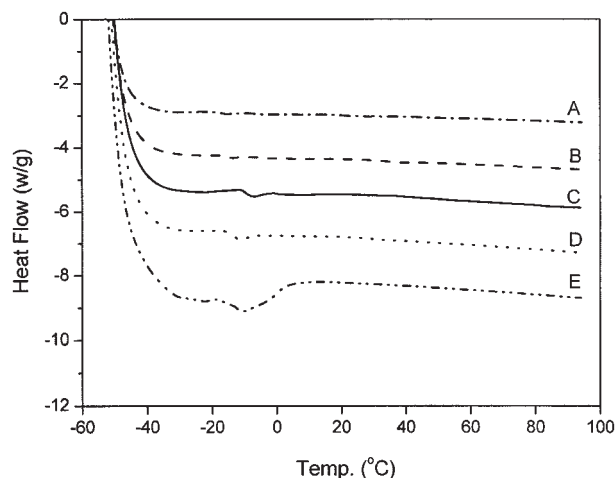

Figure 6 Differential scanning calorimetry thermograms of polyurethane gels (heating rate = 10°C/min) plasticized with (A) acetyl tributyl citrate, (B) di-*n*-butyl phthalate, (C) TOTM, (D) an ester, or (E) an ester and oil (5 wt %).

RESULTS AND DISCUSSION

The gel properties of polyurethanes depend on the gelation condition as well as the composition determining the soft-segment/hard-segment ratio.[7,8] The overall gelation rate, depending on the catalyst ratio, influences the final gel properties, and the curing conditions for gelation can be adjusted to obtain an optimized relationship between the curing gelation rate, catalyst, and gel properties. As shown in Figure 2, as the amount of di-butyltin dilaurate, used as a catalyst, increases, the curing time decreases gradually in a reverse linearly proportional pattern. Under the gelation conditions that we chose for the curing time and temperature, the curing rate and time thus could be controlled by a change in the catalyst ratio.
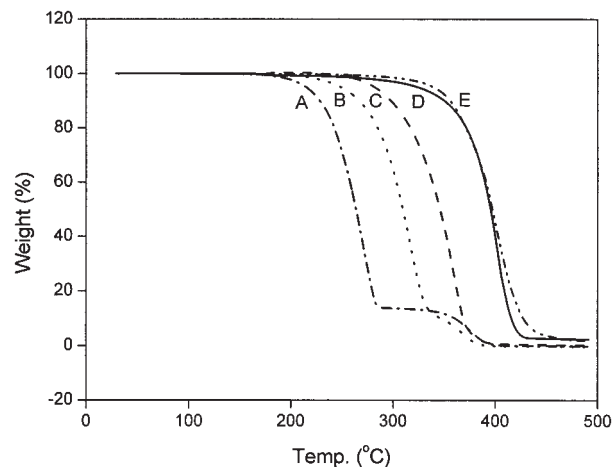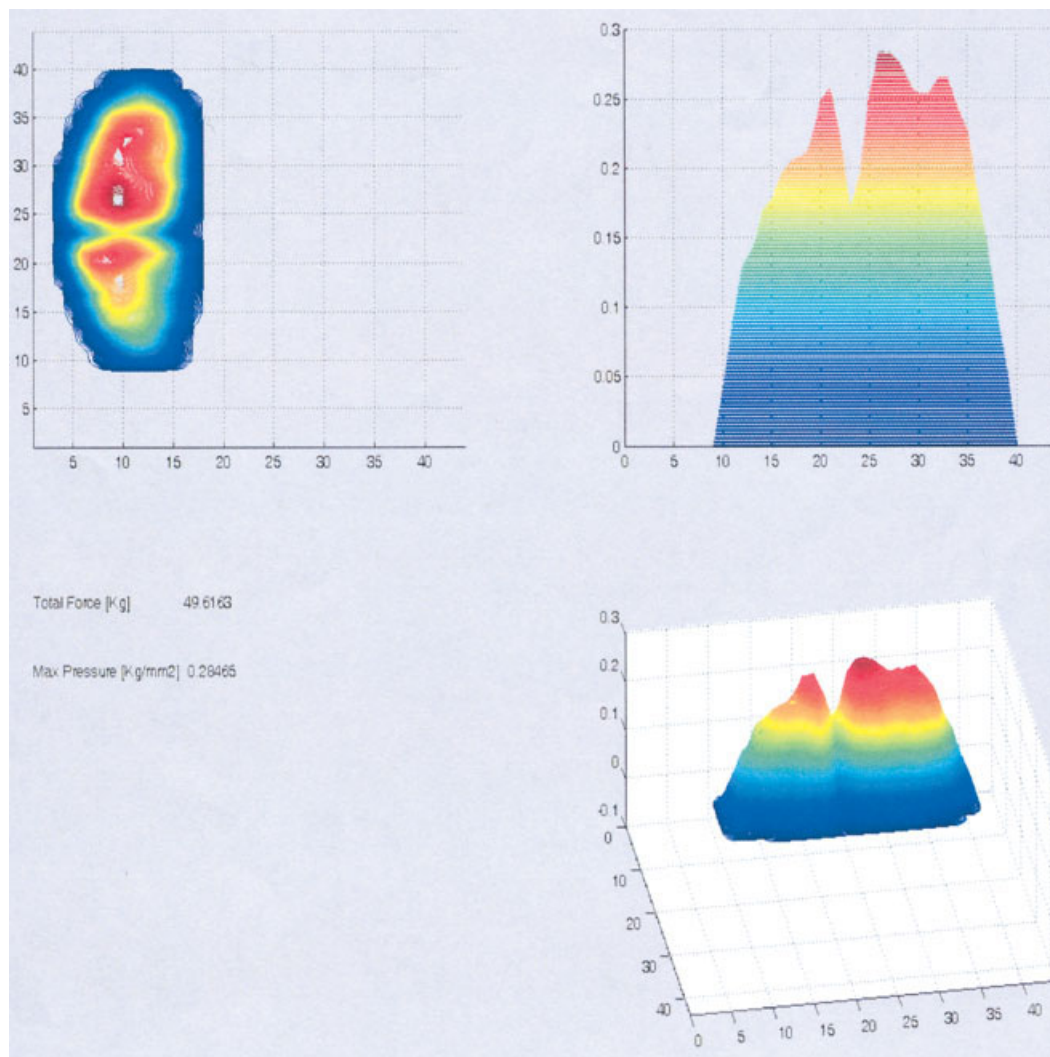

Figure 7 TGA thermograms of polyurethane gels (heating rate = 10°C/min) plasticized with (A) acetyl tributyl citrate, (B) di-*n*-butyl phthalate, (C) TOTM, (D) an ester, or (E) an ester and oil (5 wt %).

(A)

Figure 8 Results of pressure-distribution measurements in the human sedentary posture: (A) a man (before use), (B) a man (after use), (C) a woman (before use), and (D) a woman (after use). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3 shows the relationship between the hardness of the gels and the isocyanate index (NCO index = isocyanate equivalents/polyol equivalents). The isocyanate index can usually be used to give an indication of the hard-segment ratio in gels. If the isocyanate index increases, that is, the isocyanate ratio over polyol in polyurethane increases, the gel hardness also increases in a linear pattern. The relationship curve that we obtained could be used to predict and estimate the final hardness of the gel from the hard-segment/soft-segment composition ratio for particular applications.[7]

Long-term gel stability is a very important factor for determining gel performance, such as the pressure/stress-distributing or -relieving function. The long-term property is strongly dependent on how effi-

ciently the migration of plasticizer molecules existing in the bulk of the gel to the surface is inhibited. Figure 4 shows the weight loss of various gel samples caused by the loss of plasticizers gradually migrating outside the bulk. The migration of plasticizers is known to be greatly dependent on the chemophysical compatibility between the polyurethane segments and plasticizers as well as the molecular size and mobility of the plasticizer itself. The mobility may be influenced by the linearity and flexibility of the plasticizers.

The migration test was carried out under well-designed accelerated conditions at elevated temperatures to obtain the results in a shorter period. The overall weight loss by migration was less significant until 5 days, except with di-*n*-butyl phthalate as a
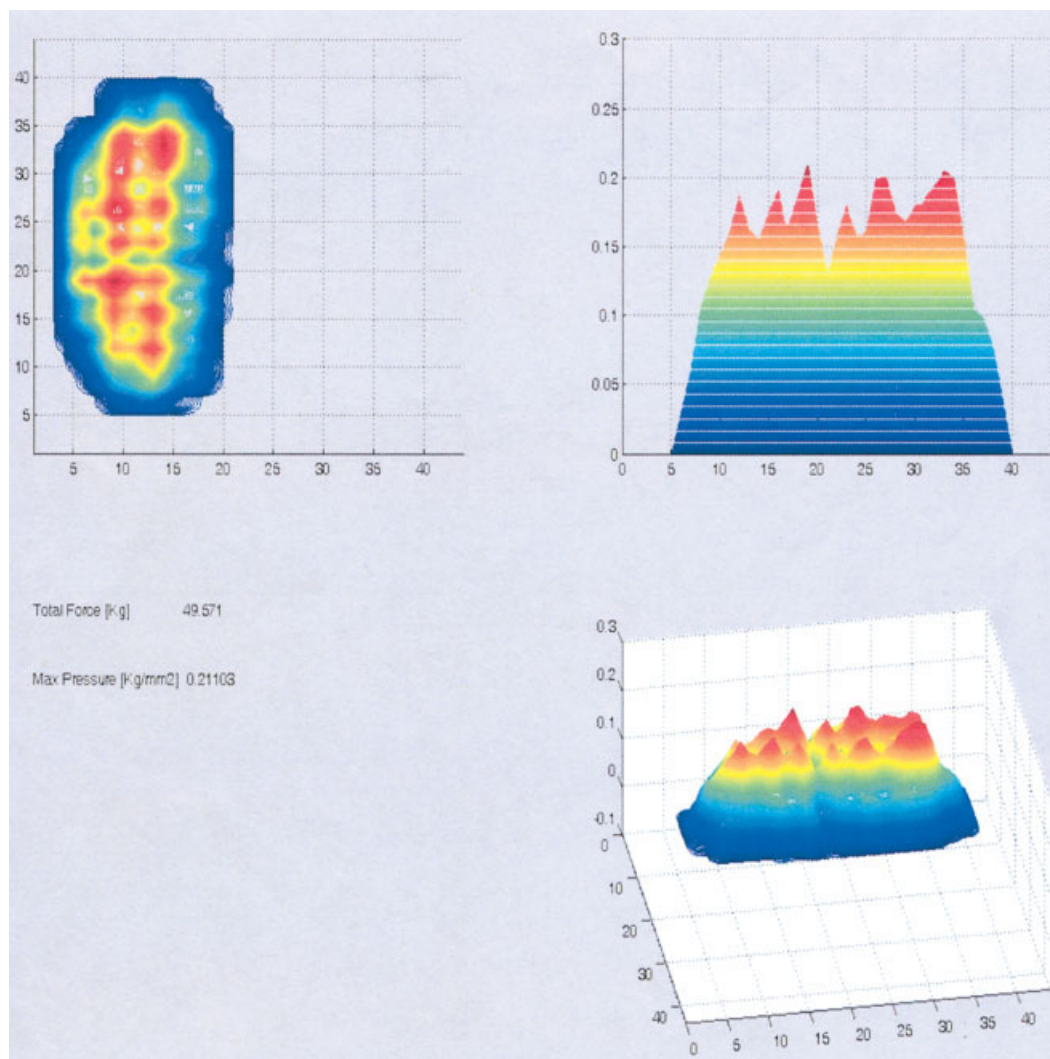
(B)

Figure 8 (*Continued from the previous page*)

plasticizer, which began to show weight loss at the 3rd day of the test. Di-*n*-butyl phthalate generally shows relatively great weight loss by severe migration, which is primarily due to its aromatic character and less favorable compatibility with polyurethane segments. The plasticizer (sample D) of an aliphatic long-chain ester is considered to be most compatible with the hard segment of polyurethane.

Figure 5 shows the stress built when a compressive strain of 20 mm was applied to specimens at a strain rate of −0.25 mm/s. It indicates the degree of the reduction of the stress applied to various specimens as prepared. The stress distribution by the reduction of the pressure was greatest among the specimens when di-*n*-butyl phthalate was used as a plasticizer, whereas the aliphatic ester induced a lower stress-distribution degree. On the other hand, the migration of phthalate

molecules to the surface of the gels was most noticeable because of the aromatic shape and size of the molecules as well as the lower compatibility with gel segments. On the basis of both aspects, di-*n*-butyl phthalate shows the most preferable performance in stress distribution at the initial state but the least favorable for the migration determining long-time properties, whereas the long-chain ester shows the opposite. Because the stress distribution may also depend on the mobility of the plasticizer as well as the compatibility[2,3] between the polymer segment and plasticizer molecule, when the stress builds up during compression, the less compatible and more flexible molecules of the plasticizer tend to make chain motions rapidly relax the stress. Phenomenologically, the polyurethane gel plasticized with di-*n*-butyl phthalate shows softer material behavior in a stress–strain plot

Total Force [Kg]   49.6163

Max Pressure [Kg/mm2] 0.28465
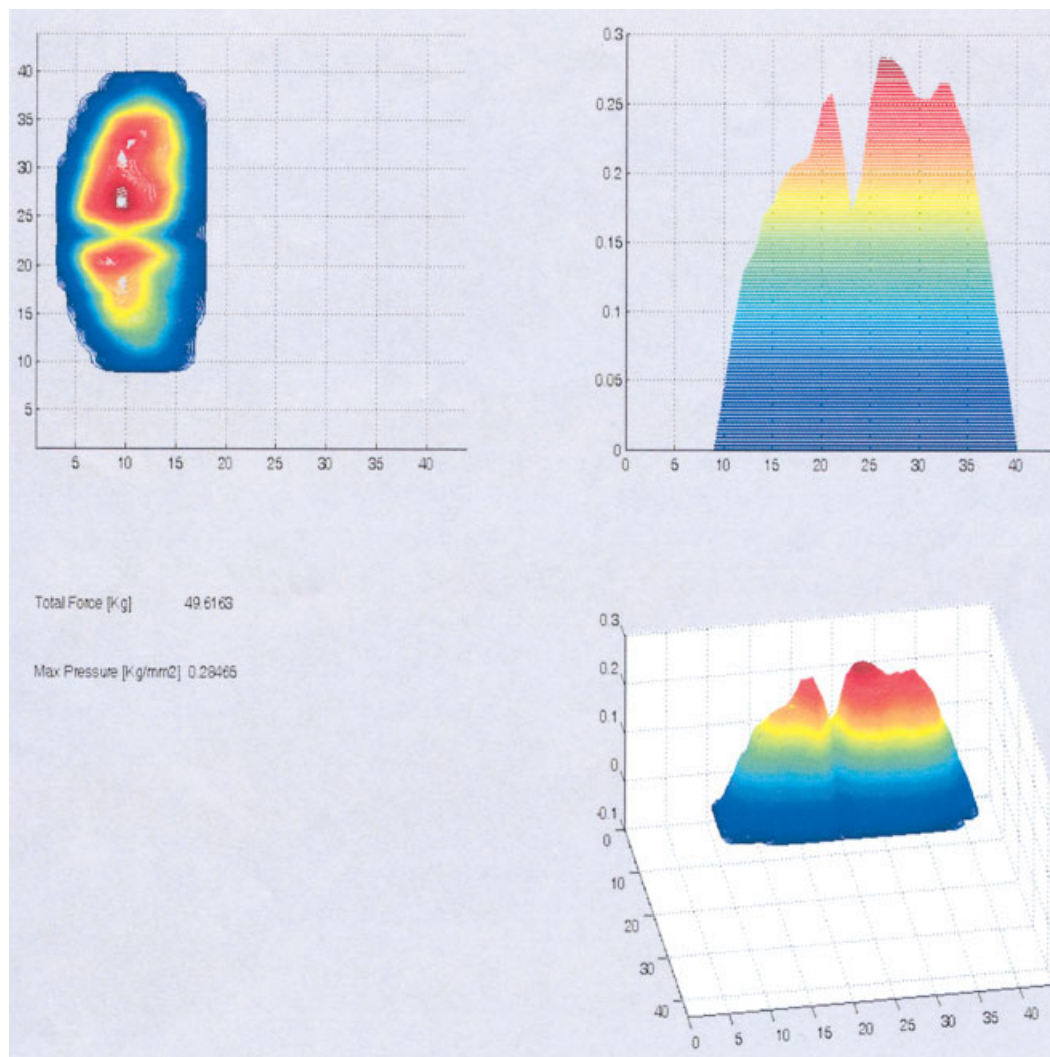
(C)

Figure 8 (*Continued from the previous page*)

than a gel plasticized with the long-chain ester. Meanwhile, embedded oil makes a contribution to reduce the stress buildup, whereas it sacrifices the long-term stability of the gel, as shown in Figure 4. Conclusively, two major factors governing the performance of stress distribution should be considered in an optimizing way, but when final applications are being considered, the migration is conjectured to be more crucial as an important factor when the long-term stability of polymer gels is considered to be a critical factor.

The thermal behaviors of polyurethane gels with various plasticizers are shown in Figure 6. The thermal behavior due to the glassy-to-rubbery transition of the gel's soft segment can be observed between -20 and $0°C$ for the plasticized gels, whereas their heat flux is very small and almost undetectable with our instrumentation, particularly in the case of polyure-thane gels plasticized with acetyl tributyl citrate or TOTM. This means that the thermal difference between the molecular motions of the polymer gel segments induced thermally before and after T_g is trivial and that the noticeable change of the gel structure is not induced in these cases. Through compression–strain testing, the polyurethane gel with di-n-butyl phthalate plasticizer was found to be excellent in dispersing pressure, and thermal analysis shows that structural changes by thermal induction can lessen pressure buildup. From the heat flux of T_g in the polyurethane gel with the ester plasticizer, the same as that in the polyurethane gel with the di-n-butyl phthalate plasticizer, the thermally induced structural change can possibly disperse pressure. For the gel with the ester and oil (5%), two broad T_g's can be assigned to the polymer segments plasticized with

Total Force [Kg]   49.803

Max Pressure [Kg/mm2] 0.23634
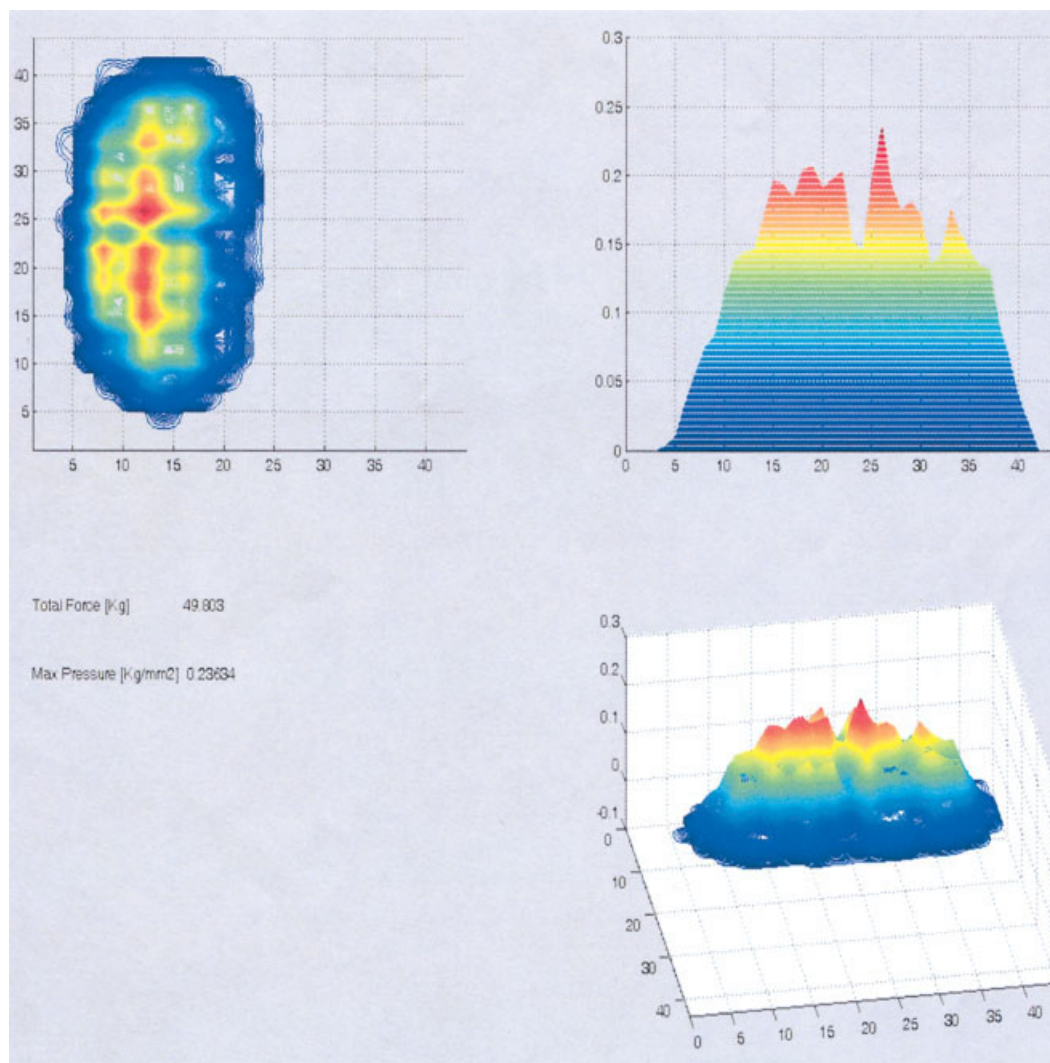
(D)

Figure 8 (*Continued from the previous page*)

esters and those less plasticized with esters in the presence of oil. In other words, the oil incorporated into the esters acts to isolate the plasticizer from the polymer segment because of the greater compatibility between the oil and ester than that between the ester and polymer segments. The higher T_g represents the polymer unplasticized or less plasticized with esters. Thus, excessive oil causes the facilitation of the migration of the plasticizer to that surface.

The trend of weight loss as the temperature increases, as shown in Figure 7, explains why the polyurethane gels with the ester plasticizer or ester and oil (5%) show the most retarded reduction of the weight. This is probably due to the better compatibility between the esters and polymer segment because the initiation of weight loss depends on the compatibility between the polymer and plasticizers as well as the

thermal stability of the plasticizer of a lower molecular weight, which usually shows thermal degradation at a lower temperature.

Gels with a phthalate-type plasticizer show an earlier start of weight loss but have a good capacity for pressure dispersion, whereas gels with an ester type show the opposite trend. Also, the elasticity necessary to create the pressure buildup of a polyurethane gel is related to the compatibility between the hard segment of the polyurethane gel and the plasticizer molecule, whereas the viscosity for dispersing pressure is related to the incompatibility between the hard and soft segments of the gel as well as that between the gel and the plasticizers. How efficiently we adjust these two factors will lead to the optimization of the gel function in the pressure distribution. Consequently, along with the fact that the combined employment of an ester

plasticizer and the proper amount of oil improves the thermal stability and pressure-distribution capability, the D type shows the best results in this study from human model testing, as shown in Figure 8.

This corresponds to the results that we obtained from preliminary calibration testing with a SKELI standard indenter. For SKELI, it represents a typical type of pressure builder for stress-relieving tests in various medical or rehabilitative applications, with the purpose of enabling a comparison between products as well as different test environments.[9,10] For both the real human male and female tests, noticeable effects on the relief of stress built by the buttocks of a human sedentary posture were observed when a pad made of polyurethane gel that we made was introduced. Peak pressures, as shown in Figure 8, were diminished, and the pressure contour was wide spread all over the pressed area. The pressure relief was directly related to the rearrangement of the entangled gel chains, along with the thermal relocation of the thermal motion of the gel segments.

This study shows that the new composition of the polyurethane gels provides much improved comfort and performance when the gel material is used in items such as shoe soles, bicycle seats, chair cushions, and position pads in medical and rehabilitation applications.

CONCLUSIONS

We investigated the effects of various plasticizers to obtain the pressure-distributing function of polyurethane gels. The phthalate type shows earlier weight loss because of migration but is better in pressure dispersion for short-time performance, whereas the ester type of long aliphatic chains shows no weight loss within the time of the test and less efficiency in pressure dispersion. The elasticity necessary to create the pressure buildup of a polyurethane gel is related to the compatibility between the hard segment of the polyurethane gel and the plasticizer molecule, whereas the viscosity for dispersing pressure is related to the incompatibility between the hard and soft segment of the gel as well as that between the gel and the plasticizers.. Therefore, an important factor for designing a pressure-distributing gel is to optimize these two factors. Another factor is to adjust migration through effective design of packing, and thus packing materials are also recognized as an important factor.

The polyurethane gel synthesized with the ester plasticizer and oil shows improved performance in pressure dispersion, and the polyurethane gel properties have been determined by the relationship between the plasticizers and polyurethane gel segment, the curing rate by the catalyst weight, and the isocyanate index (isocyanate equivalent/polyol equivalent).

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