

Research Article

Preparation and Properties of DMF-Based Polyurethanes for Wet-Type Polyurethane Artificial Leather

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DMF-based polyurethanes for wet-type polyurethane artificial leather were prepared using 4,4'-diphenylmethane diisocyanate (MDI) as diisocyanate, 1,4-butanediol (BD)/1,6-hexanediol (HD) as chain extender, and four different macroglycols (MW: 2000): poly(butylene/3-methyl-pentylene adipate) glycol based on 1,4-butanediol/3-methyl-1,5-pentanediol (MPD), poly(butylene adipate) glycol based on BD, polycarbonate glycol based on HD/MPD, and polycarbonate glycol based on HD. The properties of the as-polymerized polyurethane solutions and their films and the size/uniformity of cells of the foam layer of the resulting artificial leather were investigated. The viscosities of as-polymerized polyurethane solutions were significantly high in the range of 7500–15,000 cps, indicating that the molecular weight of the obtained polyurethanes is high. The tensile strengths of polyurethane films based on carbonate-polyol and BD chain extender were found to be higher than those of polyurethane films based on ester-polyol and HD chain extender. The elongation at the break of polyurethane films with the MPD component were higher than that of polyurethane films without the MPD component. The artificial leather containing MPD had smaller cells than the artificial leather without MPD and had higher uniformity. From these results, DMF-based polyurethanes prepared by using MPD components containing polyols are found to be most suitable for wet-type artificial leather.

1. Introduction

Since polyurethane is excellent in abrasion resistance, flexibility, durability, and toughness, interest in various fields such as textile, leather, plastic, wood, concrete, glass- and metal-coating materials, adhesives, and binders is increasing [1, 2]. Generally, polyurethanes are made from long chain polyols with an average molecular weight (MW) of 200–10,000, chain extenders with a MW of 60–4000, and polyisocyanates. The long flexible soft segment chiefly controls the low temperature properties, the solvent resistance, and the weather resistant properties of polyurethanes. Meanwhile, the choice of chain extender and diisocyanate determines mainly the mechanical properties of polyurethanes [3, 4].

There are mainly two types of soft segments such as the hydroxyl-terminated polyesters and the hydroxyl-terminated polyethers. The typical polyester diol is made from adipic acid and an excess of glycol such as ethylene glycol, 1,4-butanediol (BD), 1,6-hexanediol (HD), neopentyl glycol, or mixtures of these diols. Generally, polycarbonate diols are generally made from 1,6-hexanediol and phosgene or by transesterification with low MW carbonates like diethyl or diphenyl carbonate. In general, a homopolyester diol with a molecular weight of 2000 or more is a crystalline material with a melting temperature of about 50–60°C, whereas a copolyester diol prepared from an acid and two or more diols has no crystallinity. The branched chain structure such as 3-methyl-1,5-pentanediol (MPD) instead of the linear chain

diol such as BD and HD in the polyol component interferes with the packing of the molecule, so the polyol cannot have crystallinity. The resulting polyurethane is amorphous and can have properties such as excellent softness, excellent durability, broad solvent compatibility, good transparency, excellent stain resistance, and improved mold resistance. The characteristics of the soft segment are determined according to the kind and content of the constituent, which is an important factor determining the properties of the resulting polyurethane. In particular, polycarbonate-based polyurethanes are superior in hydrolytic stability, mechanical properties, durability, and transparency to conventional polyol-based polyurethanes. Therefore, polycarbonate-based polyurethanes are widely applied to automotive coatings, dry coatings, and UV-curing resins [5–10].

Generally, artificial leather is prepared by impregnating a nonwoven fabric/knitted goods with a polyurethane resin dissolved in an organic solvent. In this case, artificial leather is made by wet process with dimethylformamide (DMF) as the main organic solvent. In particular, wet process polyurethane synthetic leather has the advantage of being lightweight, durable, sewable, and washable by using synthetic fibers (nonwoven fabric, knitted fabric). Synthetic leather is a substitute material of natural leather [11–13]. In the 1970s, Toray of Japan developed suede artificial leather called Ecsaine (trade name) using ultrafine fiber-nonwoven fabric and solvent-based polyurethane. Kuraray has developed Clarino (trade name) using microfiber fibers, and it was spotlighted not only for shoes but also for automotive interiors and interior materials [14, 15]. Generally, artificial leathers based on nonwoven support materials coated with poly(vinyl chlorides) or polyurethanes are used for apparels and shoe upper materials [16].

Research on polyurethanes containing MPD component has been done at many company laboratories, but it is hardly found in the open literature. Studies on artificial leather using such polyurethane could not be found in the open literature. There is little systematic academic study of the relationship between the structure and properties of polyurethanes with these various molecular structures. Therefore, in this study, the DMF-based polyurethanes were synthesized using four different types of polyols with/without MPD component, 1,4-butanediol and 1,6-hexanediol as chain extenders, and MDI as diisocyanate. The wet process artificial leathers based on nonwoven fabrics coated with DMF-based polyurethanes were prepared. The thermal properties, dynamic mechanical thermal properties, and mechanical properties of the eight polyurethane film samples were compared. The cell-forming properties of wet process artificial leather were also investigated.

2. Materials and Methods

2.1. Materials. Four different polyols used in this study are shown in Table 1: polycarbonate diol (MW: 2000, C2090, Kuraray, Japan) based on 1,6-hexanediol/3-methyl-1 and 5-pentane diol (MPD) and polyester diol (polyadipate diol, MW: 2000, P2010, Kuraray, Japan) based on 1,4-butanediol/MPD were used as polyols containing 3-methyl-1,5-

pentanediol (MPD). And polycarbonate diol (MW: 2000, T6002, Asahi Kasei) based on 1,6-hexanediol and polyester diol (MW 2000, HP1020, Heung Il Polychem) based on 1,4-butanediol were used as polyols. All polyols used in this study were dried at 100°C under 65 mmHg for 3 hours until no bubbling was observed. Methylene diphenyl diisocyanate (MDI, BASF), dibutyltin dilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI), 1,4-butanediol (Aldrich Chemical, Milwaukee, WI), 1,6-hexanediol (Aldrich Chemical, Milwaukee, WI), dimethylformamide (DMF, Junsei, Japan), and antioxidant (Irganox 1010, SA) were used without further purification. The characteristic of nonwoven fabric (HDF 3310, HACO, Korea) used in this study is as follows: method: needle punching, composition: PET/nylon (30/70 wt%), weight: 330 g/m², thickness: 1.30 mm, and width: 1410 mm.

2.2. Preparation of DMF-Based Polyurethane Solutions. Polyurethanes were synthesized by solution polymerization using DMF as a solvent (Scheme 1). The polyols (140 g), DBTDL (catalyst, 0.03 wt% based on solid content), and DMF (solvent, 30 g) were placed in a four-necked flask that was equipped with a thermometer, a stirrer, a condenser, an inlet and outlet for dry nitrogen, and a heat jacket, and then the system was degassed under vacuum at 80°C for 1 h to obtain stable solution. The mixture was allowed to cool to 45°C with moderate stirring (175–200 rpm). MDI was then slowly dropped into the flask, and the reaction mixture was allowed to react at 85°C under stirring (125–150 rpm) until the theoretical NCO content was reached. The change in the NCO value during the reaction was determined using standard dibutylamine back-titration method (ASTM D 1638). The prepolymer was chain-extended by dropping 1,4-butanediol/1,6-hexanediol at room temperature for 2 h, and the reaction continued until the NCO peak (2170 cm⁻¹) in the IR spectrum had completely disappeared. The solid content of the polyurethane solution was fixed at 30 wt%. The molar ratio of MDI/polyol/diol was fixed at 0.2/0.07/0.13. The sample designation and composition are shown in Table 2.

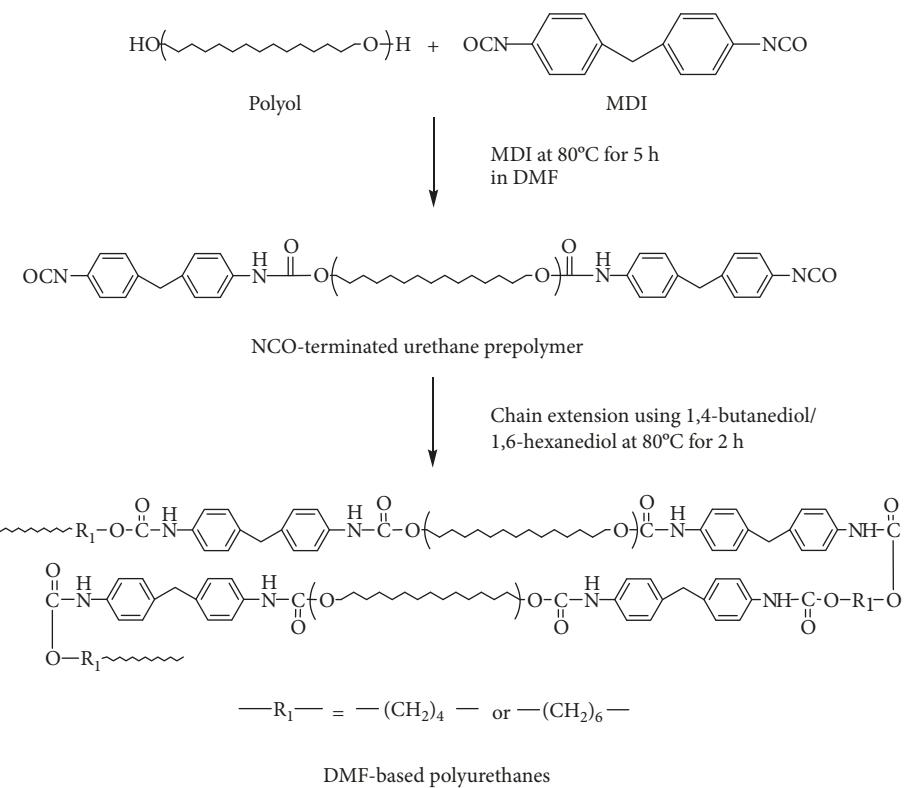
2.3. Preparation of Polyurethane Film and Wet Process Artificial Leather. The release paper (RP film) was coated with DMF-based polyurethane and dried in a dry oven at 80°C for 12 h in order to volatilize the solvent DMF. In this study, wet-type artificial leather was manufactured as follows: after coating DMF-based polyurethane on the nonwoven fabric, DMF was extracted by the osmotic principle using the coagulation of polyurethane and the solubility of DMF in water, so that continuous cells were formed in the polyurethane layer. The DMF-based polyurethane prepared in this study was coated to nonwoven fabrics and then coagulated for 8 minutes in a water bath containing 10% DMF solution at 25°C and washed in a 50°C water bath for one hour to remove residual DMF. Finally, it was dried in a dryer at 60°C for 3 h to produce artificial leather.

2.4. Characterization

2.4.1. Viscosity Measurement. A Brookfield digital viscometer (Brookfield LVDVII+, USA) was used to measure the

TABLE 1: Four different macroglycols used in this study.

Macroglycols		
PE/B/M	P2010	Polyadipate diol based on 1,4-butanediol/3-methyl-1,5-pentandiol (MPD)
PE/B	HP1020	Polyadipate diol based on 1,4-butanediol
PC/H/M	C2090	Polycarbonate diol based on 1,6-hexanediol/3-methyl-1,5-pentandiol (MPD)
PC/H	T6002	Polycarbonate diol based on 1,6-hexanediol



SCHEME 1: Preparation process of DMF-based polyurethanes.

TABLE 2: Sample designation and composition of wet-type PU.

Sample designation	Isocyanate MDI	Composition (molar ratio)						Chain extender BD diol	Chain extender HD diol
		PE/B/M	PE/B	Polyol	PC/H/M	PC/H			
B-PE/B/M	0.2	0.07	—	—	—	—	0.13	—	
B-PE/B	0.2	—	0.07	—	—	—	0.13	—	
B-PC/H/M	0.2	—	—	0.07	—	—	0.13	—	
B-PC/H	0.2	—	—	—	0.07	0.07	0.13	—	
H-PE/B/M	0.2	0.07	—	—	—	—	—	0.13	
H-PE/B	0.2	—	0.07	—	—	—	—	0.13	
H-PC/H/M	0.2	—	—	0.07	—	—	—	0.13	
H-PC/H	0.2	—	—	—	—	0.07	—	0.13	

viscosity of DMF-based polyurethane solutions (solid content: 30 wt%) at 25°C. The measurements were performed at 10 rpm using a LV-3 spindle.

2.4.2. FTIR Analysis. FTIR spectroscopy was used to confirm the chemical components of the CWPU/P samples by Fourier transform infrared spectrometer (FT-IR 3D analysis system, MB 104, BOMEM). For each sample, 8 scans at 4 cm⁻¹ resolution were collected in the transmittance mode and recorded in the range of 4000–650 cm⁻¹.

2.4.3. Mechanical Test. The tensile properties were measured at room temperature using a universal testing machine (UTM, Model M-130, Instron Co., USA) with a 5582 system according to ASTM D412. A cross-head speed of 100 mm/min was used throughout these investigations to determine the ultimate tensile strength and elongation at break for all samples. The values quoted are the average of three measurements.

2.4.4. Differential Scanning Calorimetry Analysis. Differential scanning calorimetry (DSC, Model Q-25, TA Instruments) was used for thermal characterization. The sample (10.0 ± 1.5 mg) was placed in an aluminum pan and quenched to -80°C, and then the change in calories was measured while raising the temperature from -80°C to 100°C at a rate of 10°C/min under nitrogen atmosphere at 50 ml/min of N₂ flow rate.

2.4.5. Dynamic Mechanical Thermal Analyzer Analysis. The dynamic mechanical properties of film samples were measured at 1 Hz using dynamic mechanical thermal analyzer (DMA, Q800, TA Instruments, USA) with a heating rate of 5°C/min in the temperature range from -80 to 150°C.

2.4.6. Scanning Electron Microscope (SEM) Observation. In order to confirm the cell shape of the polyurethane film layer of the artificial leather produced by the wet process, the cross section of the film was cut and analyzed by a field-emission scanning electron microscope (SEM, Hitachi TM-1000, Japan).

3. Results and Discussion

3.1. Analysis of Chemical Structure of Polyurethane Films. The results of the qualitative analysis of the synthesized polyurethane structure using FT-IR are shown in Figure 1, since the content of polyols acting as a soft segment in the polyurethane structure is relatively larger than that of the other components. The peaks of the polyol component were found to be very large in the spectroscopic analysis. As shown in Figure 1, B-PE/B/M, B-PE/B, H-PE/B/M, and H-PE/B samples are polyurethanes synthesized using ester polyols as polyols. It can be seen that a characteristic peak appeared at 2800–3000 cm⁻¹ corresponding to CH stretching vibrations of asymmetric and symmetric stretching modes of methylene groups and a characteristic peak due to stretching vibration of the ester carbonyl group at 1733 cm⁻¹ is observed. Typical peaks of polyadipate were also observed at 1200 and 1300 cm⁻¹. It was found that the

characteristic absorption peaks of the carbonate group (-O-COO-C) were observed at around 1250 cm⁻¹ in the polyurethane B-PC/H/M, B-PC/H, H-PC/H/M, and H-PC/H samples synthesized by using polycarbonate diol as the polyol. Based on the results of the IR analysis, it was confirmed that polyester polyol and polycarbonate polyol components were well incorporated in the polyurethane synthesized in this study. In addition, it was confirmed that the NCO absorption peak at 2270 cm⁻¹ disappears as the reaction progresses. The urethane group formed was identified from NH peaks at 3200 and 1500 cm⁻¹.

3.2. Viscosity of As-Polymerized Polyurethane Solutions. Figure 2 shows the viscosity measured using a Brookfield viscometer of DMF solutions of polyurethanes synthesized with the same solid content (30 wt%). Generally, the viscosity of a polymer solution is proportional to the molecular weight and polarity of the polymer. The viscosities of as-polymerized polyurethane solutions were in the range of 7500–15,000 cps at 25°C. This very high viscosity value means that the molecular weight of the obtained polyurethane is considerably high. The viscosity of the polyurethane solution containing MPD was slightly lower than that without MPD. This can be attributed to the fact that the methyl groups present in the MPD structure interfere with intermolecular forces. The viscosity of the as-polymerized polyurethane solution was found to be higher in the case of BD as a chain extender than in HD. Also, the viscosity of the carbonate-polyol-based polyurethane solution was higher than that of the ester-polyol-based polyurethane solution. The higher viscosity of BD/carbonate-polyol-based polyurethanes might be due to the higher molecular weight or higher polarity.

3.3. The Glass Transition Temperature/Storage Modulus of Prepared Polyurethane Films. Figure 3 shows the DSC curves of the synthesized polyurethane films. The dynamic mechanical thermal analysis curves are shown in Figures 4 and 5. The soft segment glass transition temperature (T_{gs}) of the polyurethane films determined by DSC and DMA is summarized in Table 3. The DSC analysis showed that the melting temperature (T_m) was not observed. The T_{gs} change tendency of polyurethanes according to the composition measured by DSC and DMA was the same. The DSC-T_{gs} of B-PE/B/M, B-PE/B, B-PC/H/M, and B-PC/H samples was observed respectively at -40.1, -42.4, -10.9, and -14.0°C, and the DSC-T_{gs} of H-PE/B/M, H-PE/B H-PC/H/M, and H-PC/H samples appeared respectively at -35.2, -31.9, -13.11, and -7.6°C, while the T_{gs} of B-series samples measured by DMA was observed at -37.4, -40.2, -11.5, and -15.1°C and the T_{gs} of H series samples appeared at -37.6, -36.9, -15.8, and -12.8°C. In the case of chain extender BD-based polyurethane films, the T_{gs} of polyurethane films containing the MPD component was a little higher than that of polyurethane films without MPD. This is presumed to be attributable to the limited segment motion of MPD-contained polyurethanes due to the side chain methyl group of MPD. However, in the case of chain extender HD, polyurethane films with the MPD component showed lower T_{gs} than polyurethane films

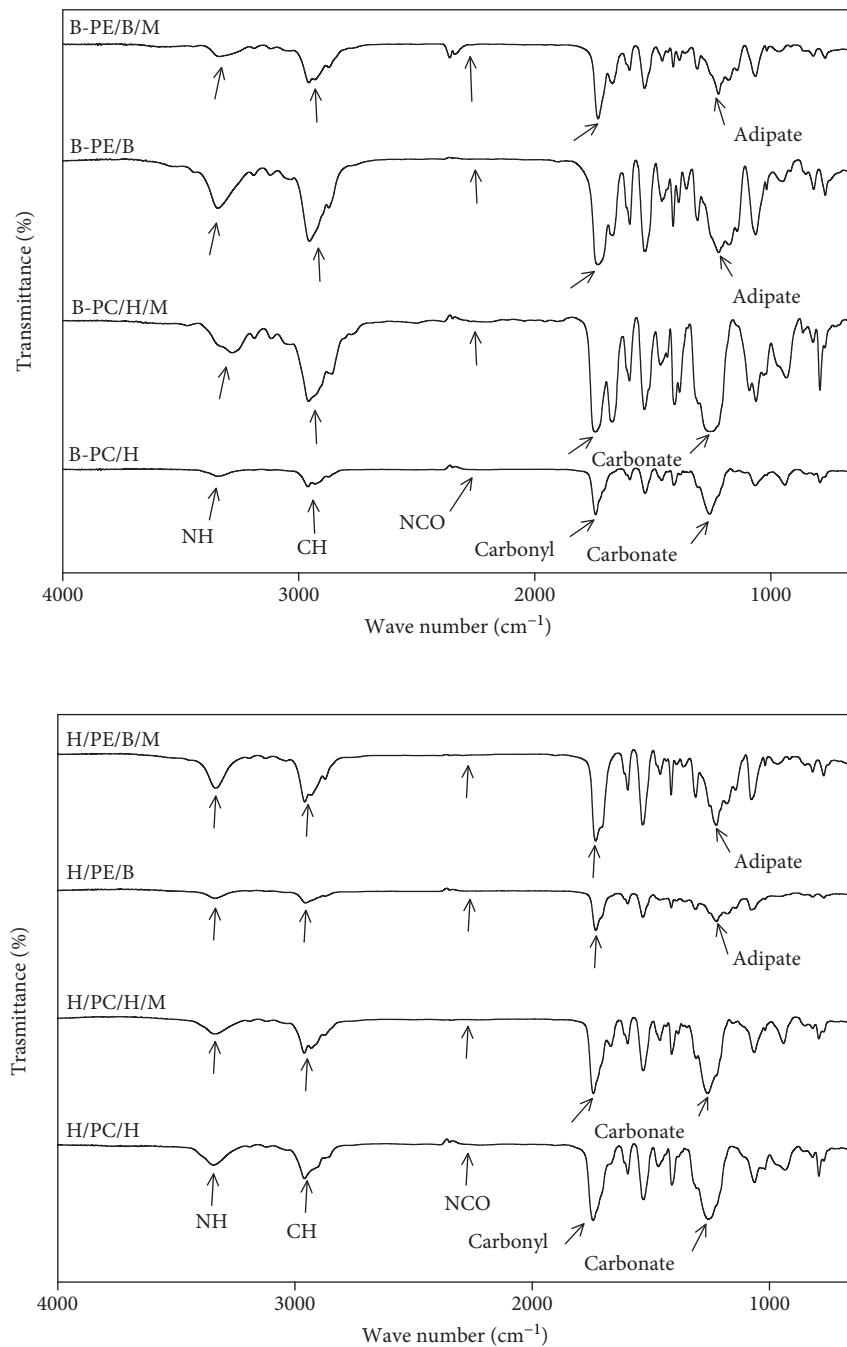


FIGURE 1: FT-IR spectra of polyurethane films.

without MPD. This might be due to the number of carbons in the HD of 6 more than the 4 carbons in BD. The carbonate-polyol-based polyurethane films showed the higher Tgs than ester-polyol-based polyurethane films. It was found that the polyurethane film containing the MPD component had a higher storage modulus value than the corresponding polyurethane film without the MPD component. The glassy plateau region of carbonate-polyol-based polyurethane films was found to be wider than that of ester-polyol-based polyurethane films. This should be due to the higher polarity of carbonate-glycol than ester-glycol.

3.4. Mechanical Properties of Prepared Polyurethane Films. Figure 6 shows the stress-strain curves of polyurethane films. The tensile strength (kgf/cm²) and elongation (%) at the break of samples are summarized in Table 3. The tensile strength of the polyurethane film containing no MPD component was higher than that of the film containing the MPD component. In the same series, the tensile strength of carbonate-polyol-based polyurethane was higher than that of ester-polyol-based polyurethane. It was found that the tendency of the change in tensile strength of the polyurethane film was almost consistent with the change in

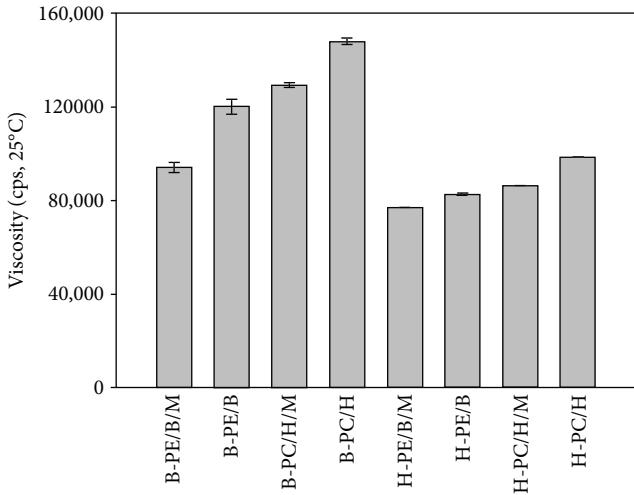


FIGURE 2: Viscosity of DMF-based polyurethane solutions (average value of five tests).

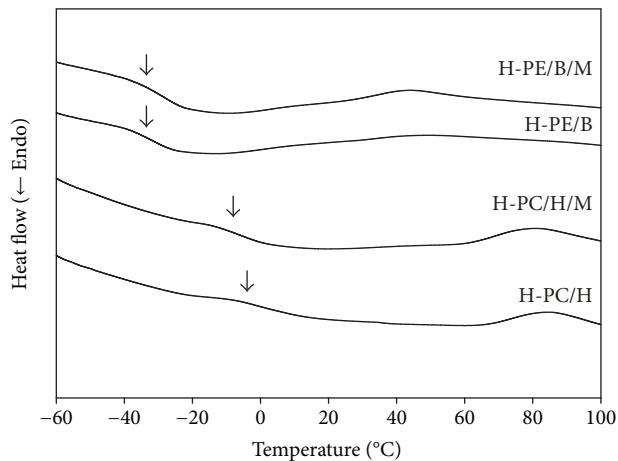
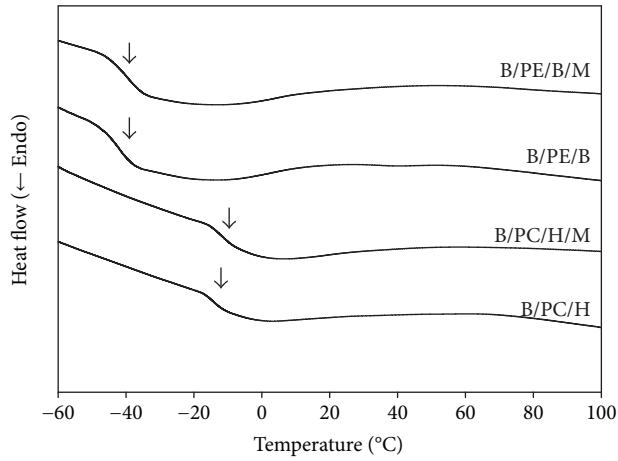


FIGURE 3: DSC thermograms of polyurethane films.

viscosity of the DMF-polyurethane solution. These results are in good agreement with the fact that strength depends on molecular weight. The elongation at the break of the

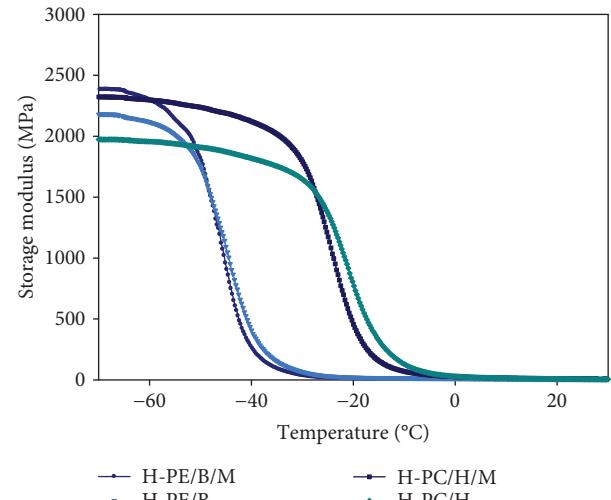
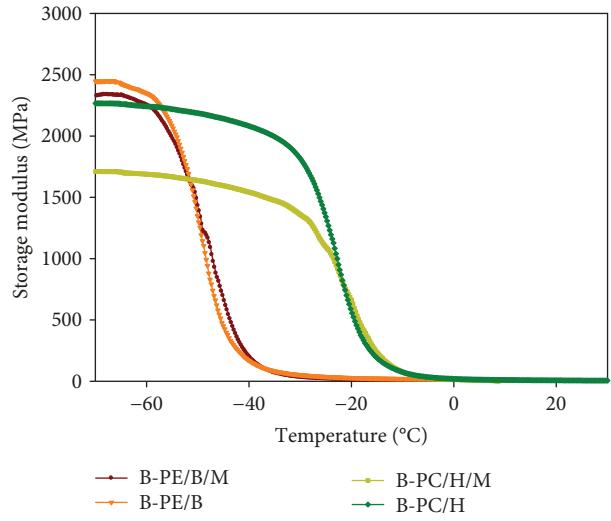


FIGURE 4: Storage modulus of polyurethane films.

polyurethane film with the MPD component was larger than that of the film without the MPD component. And the ester-polyol-based polyurethane film showed higher elongation at the break than the carbonate-polyol-based film. This is thought to be due to both the branched structure in the MPD component and the ester group with lower polarity than the carbonate group.

3.5. Cross Sections of Wet Process Artificial Leathers Based on Nonwoven Fabrics Coated with DMF-Based Polyurethanes. Figure 7 shows the cross-sectional SEM micrographs of the wet process artificial leathers based on nonwoven fabrics coated with DMF-based polyurethanes prepared in this study. Generally, artificial leather having a large number of cells per unit volume, a small cell size, and a uniform distribution is preferable. This is because such a characteristic can impart an excellent tactile touch to the synthetic leather. In this study, wet process artificial leathers based on nonwoven fabrics coated with DMF-based polyurethanes are prepared for shoe upper materials. The polyurethane-based artificial leather containing the MPD component prepared

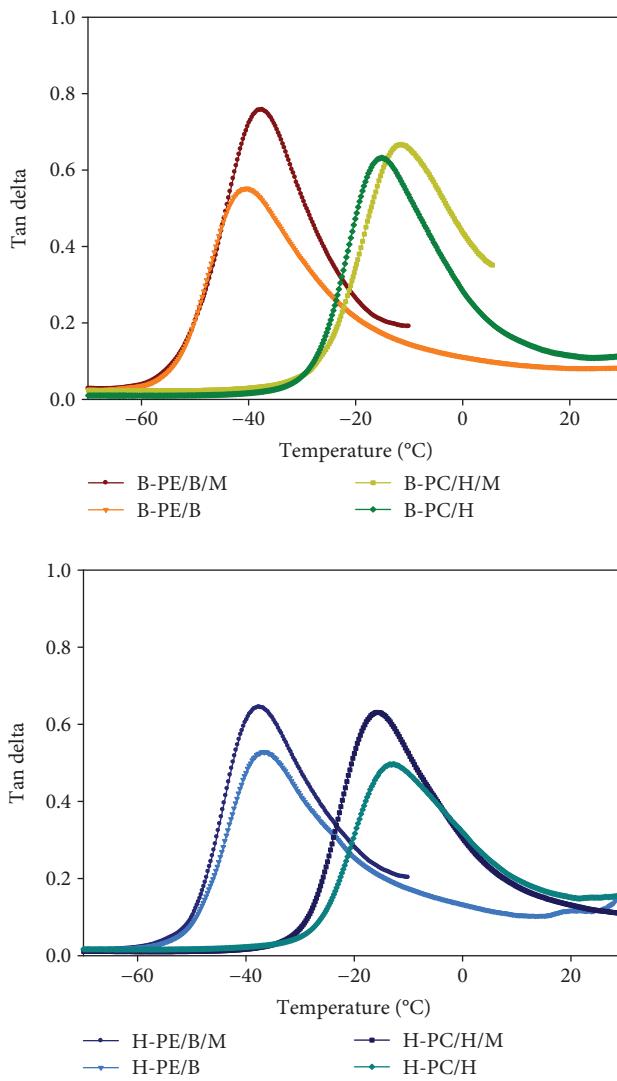


FIGURE 5: Tan delta of polyurethane films.

TABLE 3: Thermal and mechanical properties of wet-type PU films.

Sample designation	DSC result Tgs (°C)	DMA result Tgs (°C)	Mechanical properties	
			Tensile strength (kgf/cm ²)	Elongation at break (%)
B-PE/B/M	-40.1	-37.4	41	483
B-PE/B	-42.4	-40.2	62	391
B-PC/H/M	-10.9	-11.5	68	342
B-PC/H	-14.0	-15.1	101	162
H-PE/B/M	-35.2	-37.6	39	669
H-PE/B	-31.9	-36.9	46	346
H-PC/H/M	-13.1	-15.8	61	429
H-PC/H	-7.6	-12.8	96	218

under the same coating conditions was found to have a large coating layer and a large number of cells and a uniform distribution. In general, the ester-polyol-based polyurethane has a slightly higher cell layer than the

carbonate-polyol. In the case of using BD as a chain extender, the coating layer was thicker than that of using HD, and the number of cells per unit volume was larger than HD. From these results, it was found that DMF-

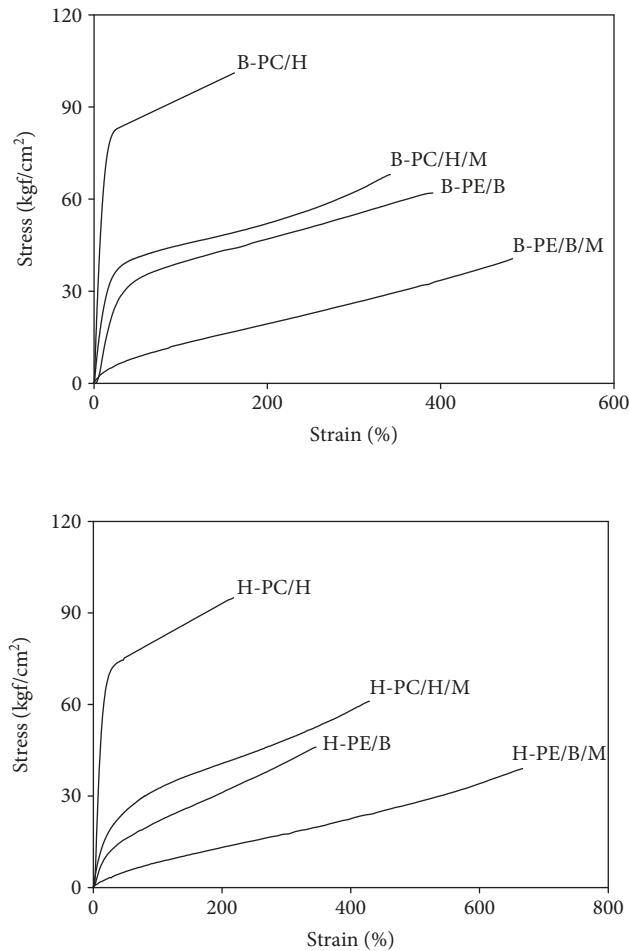


FIGURE 6: Stress-strain curves of polyurethane films.

based polyurethanes prepared by using MPD component-contained polyols are most suitable for the production of wet-type artificial leather.

4. Conclusions

In this study, DMF-based polyurethanes for wet process artificial leather were prepared by using 1,6-hexanediol/1,4-butanediol as chain extender and polycarbonate diol and polyester diol containing 3-methyl-1,5-pentanediol (MPD) component, which is known to give excellent adhesion, durability, low temperature flexibility, and transparency. The effects of these compositions on the physical properties of polyurethane films and the cell-forming properties of wet-type artificial leather were investigated. The viscosities of as-polymerized polyurethane solutions were significantly high in the range of 7500–15,000 cps, indicating that the molecular weight of the obtained polyurethanes is high. It was confirmed that the Tgs obtained from the peak of tan delta and the Tgs obtained by DSC were almost the same. The tensile strength of the polyurethane film containing no MPD component was higher than that of the film containing the MPD component. In the same series, the tensile strength of carbonate-polyol-based

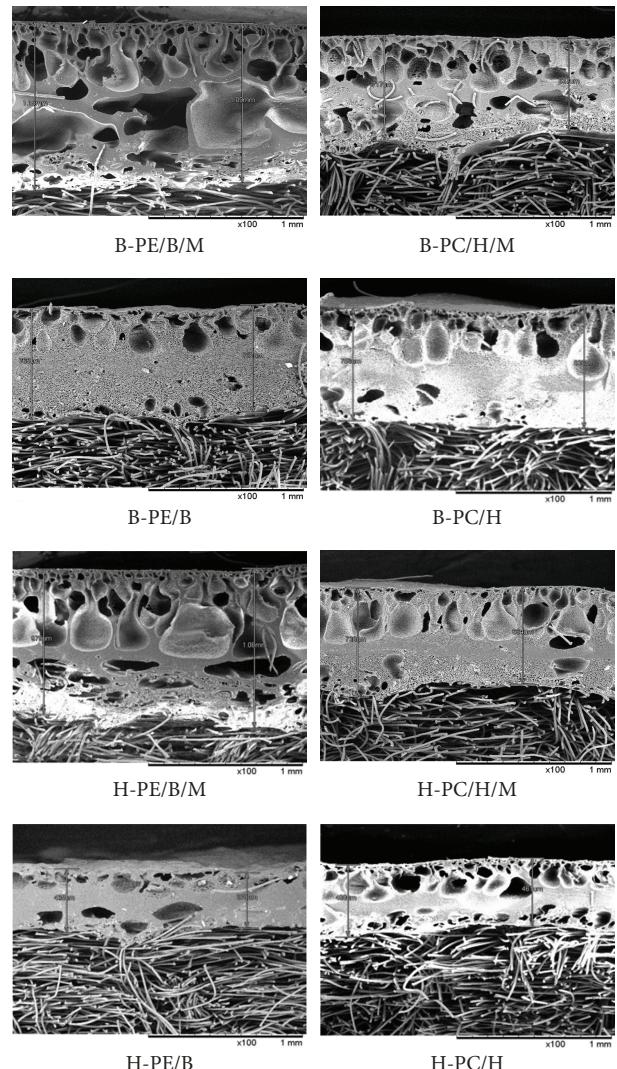


FIGURE 7: SEM micrographs of wet-type artificial leathers based on nonwoven fabrics coated with various DMF-based polyurethanes.

polyurethane was higher than that of ester-polyol-based polyurethane. The MPD component-contained synthetic leather prepared under the same coating conditions was found to have a large coating layer and a large number of cells and a uniform distribution. These results indicate that MPD component-contained polyurethane prepared in this study is most suitable for the production of wet-type artificial leather.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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