Effect of Hot Pressing/Melt Mixing on the Properties of Thermoplastic Polyurethane

Young-Hee Lee, Bo-Kyung Kang, and Han-Do Kim*

Department of Organic Material Science and Engineering, Pusan National University, Busan 609-735, Korea

Hye-Jin Yoo

POSCO Technical Research Laboratories, Gwangyang 545-090, Korea

Jung-Soo Kim

Korea Institute of Footwear & Leather Technology, Busan 614-100, Korea

Jae-Ho Huh

Busan Branch of Korea Apparel Testing & Research Institute, Busan 1191-6, Korea

Young-Jin Jung

Department of Biomaterials Engineering, Pusan National University, Miryang 627-706, Korea

Dong-Jin Lee

Korea Institute of Ceramic Engineering and Technology, Seoul 153-801, Korea

Abstract: In-depth understanding of the influence of hot pressing and melt processing on the properties of thermoplastic polyurethane (TPU) is critical for effective mechanical recycling of TPU scraps. Therefore, this study focused on the effects of hot pressing and melt mixing on molecular weight (MW), polydispersity index (PDI), melt index (MI), characteristic IR peaks, hardness, thermal degradation and mechanical properties of TPU. The original TPU pellet (o-TPU) showed two broad peaks at lower and higher MW regions. However, four TPU film samples, TPU-0 prepared only by hot pressing of o-TPU pellet and TPU-1, TPU-2 and TPU-3 obtained by hot pressing of melt mixed TPUs (where the numbers indicate the run number of melt mixing), exhibited only a single peak at higher MW region. The TPU-0 film sample had the highest M_n and the lowest PDI and hardness. The TPU-1 film sample had the highest M_w and tensile modulus. As the run number of melt mixing increased, the peak-intensity of hydrogen bonded C=O stretching increased, however, the free C=O peak intensity, tensile strength/elongation at break and average MW decreased. All the samples showed two stage degradations. The degradation temperatures of TPU-0 sample (359 °C and 394 °C) were higher than those of o-TPU (342 °C and 391 °C). While all the melt mixed samples degraded at almost the same temperature (365 °C and 381 °C). The first round of hot pressing and melt mixing was found to be the critical condition which led to the significant changes of M_n/M_w/PDI, MI, mechanical property and thermal degradation of TPU.

Keywords: thermoplastic polyurethane (TPU), TPU scrap, melt mixing, recycle, thermal degradation.

Introduction

Large amounts of scrap arise at the end of the service-time of polymer articles such as pipes, profiles, floor coverings, cable insulation, roofing sheets, package foils, bottles, airbags and medical products. Therefore, the question of disposal of used polymer has gained increasing importance in the public discussion because of the environmental problems resulting from the rapid increase of plastic wastes. At present, the recycling method mainly include the reuse of the original plastic waste, chemical recycling (cracking, gasification, hydrogenation, pyrolysis),[1] mechanical recycling,[2,3] and energy recovery by incineration.[4] Among these methods, mechanical recycling is a viable option both economically

*Corresponding Author. E-mail: kimhd@pusan.ac.kr

and environmentally.

Generally, recycled polymers show unsatisfactory mechanical properties because of their degradation during reprocessing. The reprocessing involves several high temperature shearing cycles that facilitate (1) the occurrence of thermal and/or mechanical degradation, (2) the consequent chemical and physical changes, and (3) a detriment of final properties. Therefore, the knowledge of the nature and intensity of such degradation is important in choosing a stabilizer and determining the maximum amount of recycled material without significant losses in the final properties of polymer blend products.

The thermoplastic polyurethane (TPU) is one of the most versatile engineering thermoplastics with elastomeric properties.[5-7] The TPU elastomers play an important role within the rapidly growing family of thermoplastic elastomers. They can be processed, shaped and formed upon heating via numerous industrial processes. The TPUs possess higher tensile modulus, abrasion resistance and oil/solvent resistance compared to rubber. They are becoming more and more important as engineering materials.[8,9]

Generally, the FTIR spectroscopy has been used to confirm the chemical structure of synthesized products and to detect the change of chemical/physical structure due to chemical/physical modification and heat treatment. Several studies[10-14] have examined the hydrogen bonding characteristics of phased segregated polyurethanes by FTIR. The main regions of interest are the carbonyl region which is defined by three carbonyl stretching vibrations [the non-hydrogen-bonded(free) C=O at 1732 cm^{-1} and two stretching vibration associated with disordered hydrogen-bonded C=O at 1712 cm^{-1} and ordered hydrogen-bonded C=O at 1700 cm^{-1}.[7,15,16] There have been many studies on different amide types of urethane/urea/peptide groups such as amide I, amide II and amide III, etc.[15,17-20] In the IR spectra of all amides types, there are absorption bands called amide I (near 1650 cm^{-1}), associated with CO stretching vibrations, and amide II (near 1550 cm^{-1}), associated with stretching vibrations of the C-N and deformation vibrations of N-H. It is generally accepted that the frequency shift and change in peak intensity in IR spectra take place because of the changes of type, extent and strength of competitive hydrogen bonding, and the shift in equilibrium of conformations caused by hydrogen bonds in TPU, polyurea and polyurethane-urea. There is a report on the appearance of NCO groups observed at around 200 °C with IR spectra.[21] The NCO peak reaches its maximum at 300 °C, and further increases in temperature results in a decrease of the NCO peak, which may be caused by the formation of carbodiimide, or reaction with newly formed diamine to generate urea.

The thermal stability of polyurethanes and poly(urethane-urea)s has been extensively studied because of their great importance and their wide range of applications. Several studies[22-25] have regarded TPUs as undergoing two-stage degra-

dations. The first stage degradation that occurs between 200 and 370 °C is a de-polycondensation process associated with urethane hard segment degradation. The second stage degradation that occurs between 370 and 500 °C is the degradation of soft segment by depolycondensation of polyol. Chuang[26] proposed the three-stage degradation of diacetylene-containing polyurethane copolymers under various annealing conditions at different heating rates. The thermal degradation mechanism of polyurethane is very complex due to the variety of products formed in the process. It has been suggested that polyurethanes break down by a combination of three independent pathways:[27-30] (1) dissociation to the original polyol and isocyanate, (2) formation of a primary amine, an alkene, and a carbon dioxide in a concerted reaction involving a six-membered cyclic transition state, and (3) formation of secondary amine and carbon dioxide through a four-membered ring transition state.[27-30] The resulting primary degradation products, e.g. diisocyanate and diol which begin to form at 150-160 °C, have been identified through FTIR. These products at higher temperatures can give rise to secondary decomposition products, such as carbodiimides.[30-32] These primary degradation products can form urethane and allophanate(or biuret) groups and exchanged reaction products at adequate conditions. These changes can consequently affect the average molecular weight, molecular weight distribution and thermal/mechanical properties.

Hence, understanding the influence of hot pressing and melt mixing on the MW/PDI and properties of TPU is very important to reusing, and either to choosing a stabilizer or to determining the optimum content of recycled TPU without significant losses in the final properties. However, studies on the effect of such heat treatments especially on the molecular weight (MW) and PDI of TPU can hardly be found. In this context, this study explores the effect of hot pressing/mixing on MW/PDI, MI, characteristic IR peak, thermal degradation, hardness and mechanical properties of TPU.

Experimental

Material, Hot Pressing/Melt Mixing and Film Formation. The raw material (original TPU pellet: o-TPU pellet) [Hosung Chemex Co. MDI/Polyester polyol/BD based TPU, hard segment content: 28 wt%] was vacuum-dried at 110 °C for 24 h before being used. The TPU-0 film sample was prepared only by hot pressing of o-TPU pellet, and four film samples TPU-1, TPU-2 and TPU-3 were obtained by hot pressing of melt mixed TPUs, where the numbers indicate the run number of melt mixing. Hot pressing was done at 190 °C under 100 kg$_f$/cm^2 pressure for 4 min. The melt mixing of TPU was carried out at 190 °C and 50 rpm for 10 min using Haake Rheocord-90.

Characterization. Gel permeation chromatography (GPC) analysis was conducted at a flow rate of 0.4 mL/min in THF at 35 °C using a GPC (Waters Co., Singapore) that was

equipped RI detector and Syragel TM HR4 column. Poly-styrene standards were employed for molecular weight cali-bration. Melt mass-flow rate (MI) measurements of samples were carried out on a Melt Indexer CS127-604(CSI Ltd., U.S.A) according to ISO 1133:1999 standard. The test tem-perature was set 190 °C and the nominal load was 2.16 kg. Measurements on each sample were repeated five times and the average was considered as the characteristic value. Thermogravimetric analysis was done using TGA Q800 (TA Instrument, USA). All film samples (5-7 mg) were measured over a temperature range of 25 to 700 °C at heat-ing rates of 100 °C/min under N_2 atmosphere using the TA Instruments Hi-Res., dynamic rate TGA (DRTGA), which differs from previous control techniques in that the heating rate of the sample material is dynamically and continuously modified in response to changes in the rate of decomposi-tion of the sample so as to maximize weight change resolu-tion. This technique allows the use of very high maximum heating rates during Hi-Res ramp segments while avoiding transition temperature overshoot. During the heating period, the weight loss% and derivative weight% (%/min) were recorded as a function of temperature. The mechanical properties were measured in simple extension on dumbbell specimens with crosshead speed of 500 mm/min using a tensile tester (Instron 5582, Instron, Co. LTD, U.S.A.). The Shore A hardness was measured by ASTM D2240. These values quoted are the average of five measurements.

Results and Discussion

Gel Permeation Chromatography (GPC) Analysis. The GPC analysis is the most useful method to determine the average molecular weight (MW) and the extent of molecu-lar weight distribution [polydispersity index (PDI=M_w/M_n)] of polymers. Generally, the heat treatment of TPU induced not only the increases of MW and branching/cross-linking con-tent through the reactions of remained and new produced reactive functional groups but also the decrease of MW by the thermal degradation of polymer chains. The treatments also increase hydrogen bonds caused by phase separation. Therefore, the properties changes of TPU following hot pressing and melt mixing are dependent on these subse-
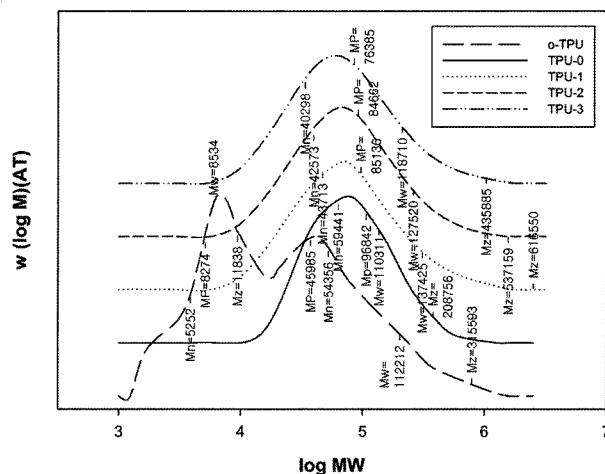

Figure 1. Molecular weight distributions of TPU samples.

quent reactions and their relative magnitude.

Figure 1 shows the molecular weight distribution curves of o-TPU pellet and TPU films samples (TPU-0, TPU-1, TPU-2 and TPU-3). Sample designation, average molecular weights (M_n and M_w) and polydispersity index (PDI) are shown in Table I. The o-TPU pellet sample showed a par-tially overlapped peak pair (two peaks) consisted of lower and higher MW peaks. The M_n and M_w of the lower peak of o-TPU pellet were 5,300/54,400, but those of higher MW peak were 8,500/112,200. However, all the film samples had a single peak at higher MW region. The M_n/M_w/PDI values of TPU-0 film sample prepared only by hot-pressing were found to be 59,400/110,300/1.86. While the M_n of TPU-0 markedly shifted to higher value compared to that of o-TPU, the M_w of TPU-0 was almost the same as that of the higher MW peak of o-TPU. This behavior indicated that the lower-MW polymer chains of o-TPU transformed into higher-MW polymer chains during hot-pressing at 190 °C under 100 kg$_f$/cm² pressure for 4 min. One could see that these results suggested that the hot pressing only could sharply give to increase the M_n of TPU. The highest M_n of TPU-0 might be attributable more to the larger amount of reactions of reactive functional groups than to the degrada-tion of polymer chains by thermal degradation during hot

Table I. Sample Designation, Average Molecular Weight, Polydispersity Index and MI of TPU Samples

Sample Designation	State	Treatment	$M_n{}^a$	$M_w{}^b$	PDI^c	MI^d
o-TPU	Pellet	-	(5,300)54,400	(8,500)112,200	-	7.01
TPU-0	Film	Hot Pressing (H)	59,400	110,300	1.86	7.70
TPU-1	Film	H/One Times Melt Mixing	43,700	137,400	3.14	6.63
TPU-2	Film	H/Two Times Melt Mixing	42,600	127,500	3.00	6.07
TPU-3	Film	H/Three Times Melt Mixing	40,300	118,700	2.95	5.78

$M_n{}^a$: Number average molecular weight. $M_w{}^b$: Weight average molecular weight. PDI^c: Polydispersity index (M_w/M_n). MI^d: Melt mass-flow rate (g/10 min).

pressing. Among all the samples, the TPU-1 sample had the highest M_w, indicating that it had the highest fraction of high molecular weight polymer. The M_n and M_w decreased significantly with increasing run number of melt mixing. These decreases might be due more to the thermal degradation than to reactions of functional groups during melt mixing process. The peak of o-TPU pellet sample was too broad to determine PDI, however, the PDI of TPU-0 film sample was the lowest value. The TPU-1 showed the highest PDI value (3.14). The PDI value decreased a little with increasing run number of melt mixing, indicating the lower decrease of M_n and higher decrease of M_w with run number of melt mixing. This result showed that the excessive melt mixing led to the higher decrease of higher molecular weight TPU polymers.

Melt Index. The melt index [MI, the mass rate (g/10 min) of flow of polymer through a specified capillary under controlled conditions (temperature: 190 °C, the nominal load: 2.16 kg)] of TPU samples was measured to investigate the structure change of TPU during hot pressing/melt mixing. Generally, the MI of polymer is directly related with melt viscosity which depended on MW, MW distribution and structure (polar/nonpolar, branching/cross-linking structure). Especially, in case of practical application, MI is a critical factor deciding the melt processibility and the usability requirements of customers of a TPU. The MIs of o-TPU, TPU-0, TPU-1, TPU-2 and TPU-3 film samples were found to be 7.01, 7.70, 6.63, 6.07 and 5.78 (g/10 min), respectively (see Table I). The TPU-0 film sample prepared only by hot pressing of o-TPU pellet had higher MI value than that of o-TPU pellet. The increase of MI of TPU-0 sample might be attributable more to the decrease of M_w in higher molecular region of o-TPU than to the increase of M_n and the change of structure during hot pressing. However, the MI was sig-

nificantly dropped at first run of melt mixing and then decreased a little with increasing run number of melt mixing. This might be due more to the change of structure (branching/cross-linking structure) than to the change (decrease) of MW during melt mixing. The first round of hot pressing and melt mixing was found to be the critical condition which led to the significant changes of MI of TPU. Anyway, rheological data such as complex viscosity/melt viscosity is also indeed important to get specific information of processed TPUs, therefore, the investigation of their rheological behaviors should be made in further research.

FTIR Analysis. It is well known that the TPU are extensively hydrogen bonded, which involves the N-H groups as proton donor and the urethane/urea/ester carbonyl groups as proton acceptor. There are some absorption of carbonyl bands of urethane groups reported by Srichatrpimuk,[10] Camargo,[11] Born[12] and Zharkov.[14] The peak at 1730 cm^{-1} was a characteristic of carbonyl group remaining free, and the peaks at 1702 cm^{-1} and 1713 cm^{-1} were assigned to the absorption of urethane groups involved in the strongest ordered hydrogen bonds and less ordered hydrogen bonds, respectively.[10-12,14] The peaks at 3300-3500, 2949, 2859, 1729, 1710, 1650 and 1530 cm^{-1} are attributed to hydrogen bonded NH stretching, asymmetric CH$_2$ stretching, symmetric CH$_2$ stretching, free C=O, hydrogen bonded C=O, amide I stretching C=O and amide II bending N-H/stretching C-N, respectively.[15]

The FTIR spectra of original TPU pellet (o-TPU) and film samples (TPU-0, TPU-1, TPU-2 and TPU-3) are shown in Figure 2. In contrast to the big difference in M_n, M_w and PDI between o-TPU and TPU-0 samples, the IR spectrum of o-TPU pellet was almost the same as that of TPU-0 film sample prepared by hot-pressing only. Such difference between MW and IR results might be attributed to the limited accuracy of quantitative analysis using IR spectroscopy. In the o-
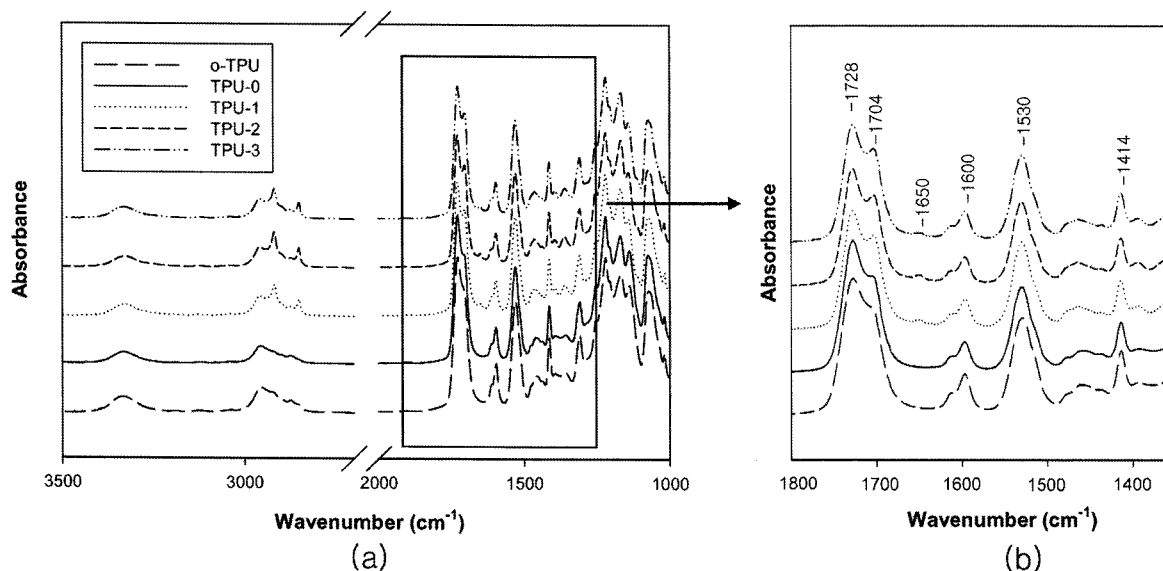

Figure 2. The FTIR spectra of TPU samples in the range of (a) 3500-1000 cm^{-1} and (b) 1800-1350 cm^{-1}.

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TPU pellet and TPU-0 film samples, the peak at 3332 cm^{-1} due to the N-H stretching(H-bonded to carbonyl), the peak at 2956-2850 cm^{-1} due to the asym and sym CH$_2$ stretching, the peak at 1728 cm^{-1} due to the free C=O stretching, the peak at1704 cm^{-1} due to hydrogen bonded C=O stretching, the peak at 1530 cm^{-1} due to amide II NH bending/CN stretching, and the peaks at 1600 cm^{-1}/1414 cm^{-1} due to C=C/C-C absorption bands of phenyl ring of MDI, were observed indicating the MDI based TPU. There was no distinct peak assigned to NCO group at about 2230 cm^{-1} for all samples, suggesting that the NCO group failed to reach a detectable level. As the run number of melt mixing increased, the peak-intensity of free carbonyl at near 1728 cm^{-1} decreased, but the peak-intensity at 1704 cm^{-1} due to the strong hydrogen bonded urethane carbonyl groups increased. This indicated that free urethane groups transformed into the strong hydrogen bonded urethane groups as a result of melt mixing. This might be due to the origination of phase separation between hard and soft segments during melt mixing process. Melt-mixing did not lead to any notable change in the intensity of amide II (NH bending/CN stretching) peak at 1530 cm^{-1} in all the film samples. However, the amide I peak (C=O stretching at 1650 cm^{-1}) appeared only in the melt mixed samples (TPU-1, TPU-2 and TPU-3), while o-TPU pellet and TPU-0 film sample did not have the amide I peak. The amide I peak increased slightly with increasing run number of melt mixing. This new amide I peak of melt mixed film samples might also be attributable to the conformational change of urethane groups caused by melt mixing process. Further research will be required to investigate the specific reason for such structure changes by using solid-state NMR analysis.

Thermal Degradation. Generally, the thermal degradation of polymers is determined at heating rates of 1~20 °C/ min, and the thermal degradation is dependent on the heating rate. In the case of lower heating rate, the thermal degra-

dation of TPU is continuously occurred during heating process. In this study, to prevent the continuous thermal degradation of TPU during heating process, we analyzed the thermal degradation of TPU at a high heating rate (100 °C/min) using high-resolution TGA, which facilitates rapid increase up to the degradation point and then holds the temperature to the end of the degradation process. During the heating period, the weight loss% and derivative weight% (DTG, %/min) were recorded as a function of temperature.

High resolution TGA and DTG curves of TPUs are shown in Figure 3(a) and (b). It was found that the o-TPU pellet sample showed two stage degradations [the first stage at 342 °C assigned to urethane hard segment degradation (de-polycondensation) and the second stage at 391 °C assigned to the degradation of soft segment polyol]. These two stage degradation temperatures of TPU-0 film sample had higher values (359 and 394 °C) than those of o-TPU. The increases of both two stage degradations of TPU-0 might be attributed to rapid increase of MW caused by the reactions of remained and produced reactive functional groups during hot pressing. The melt mixed film samples (TPU-1, TPU-2 and TPU-3) had almost the same degradation temperatures at near 365 and 381 °C. The first stage degradation of melt mixed film samples occurred at a higher temperature, and their second stage were exhibited at a lower temperature compared to those of TPU-0 film sample. The DTG peak intensity of first stage degradation of melt mixed samples showed higher value, but the DTG peak intensities of second stage degradation showed lower values, compared to those of TPU-0 film sample. The higher values of first stage degradation temperature and DTG peak intensity of melt mixed film samples might be due to the increase of strong hydrogen bonded urethane carbonyl group intensity at 1704 cm^{-1} (see Figure 2) caused by phase separation between hard and soft segments during melt mixing. The large decreases of second stage degradation tem-
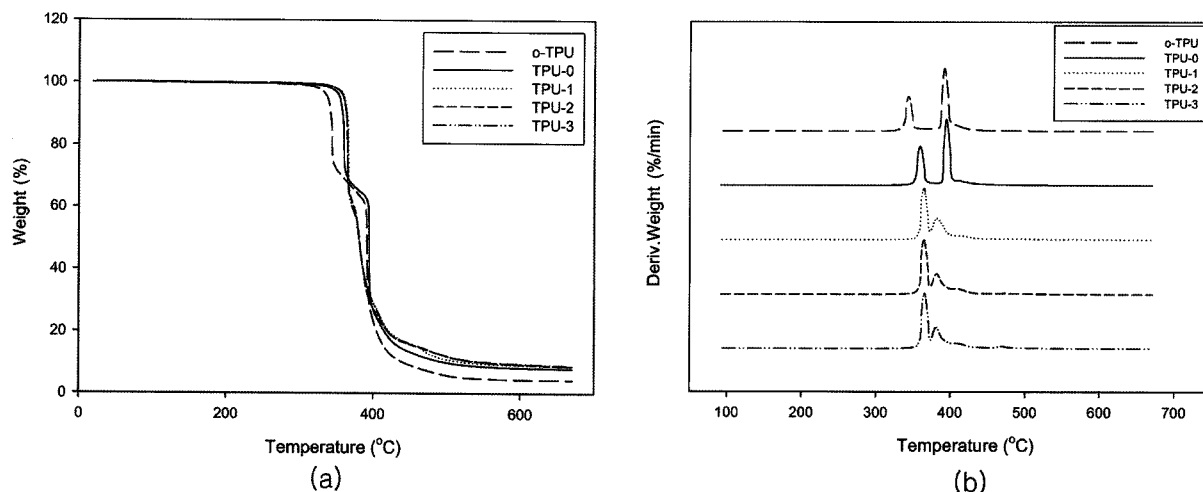

Figure 3. TGA curves (a) and differential weight loss (DTG) curves (b) of TPU samples.

perature and DTG peak intensity of melt mixed film samples might be attributed to the thermal and mechanical degradations during melt mixing process. The TGA ash content at 570 °C increased with increasing run number of melt mixing. The increase of ash content might be due to the little branching/cross-linking caused presumably by the side reaction of produced reactive functional groups and urethane groups during excessive melt mixing.

Hardness. The shore A hardness of TPU-0, TPU-1, TPU-2 and TPU-3 films prepared in this study are shown in Table II. The shore A hardness of TPU-0 sample was 84, but the hardness of TPU-1, TPU-2 and TPU-3 were in the range of 86~87. In spite of decreasing MW with increasing run number of melt mixing, the hardness of film samples increased a little. This little increase of hardness might be due more to the increases of hydrogen bonds and branching/cross-linking than to the decrease of MW during excessive melt mixing.

Mechanical Properties. Generally, a decrease in tensile strength and elongation at break is a usual consequence of reprocessing of polyamide,[33-35] high density polyethylene[36] and polypropylene,[37] as all degradation processes have negative influence on the tensile properties. Generally multiple melt processing of polymers causes molecular chains to undergo chain scissions and leads to formation of free radicals during the auto-oxidations of melting. Scission of the larger molecular chains increases the fraction of shorter chains of the respective polymers, which would lead to fewer entanglements and thereby decrease the tensile strength and elongation at break.[37,38] The changes of the mechanical properties of TPU following hot pressing and melt mixing is dependent on the changes of MW and hydrogen bonds and the formation of rigid structure having branching/cross-linking structure and their relative magnitude.

The stress-strain curves and the tensile properties are shown in Figure 4 and Table II. The highest tensile strength and elongation at break of TPU-0 film sample was also due to the increase of MW resulting from reactions of reactive functional groups. The tensile strength and elongation at break of TPU film sample decreased with increasing run number of melt mixing, as expected from the description above. The decrement percentages of tensile strength/elongation at break (based on TPU-0 sample) with the run number of melt mixing was found to be 13/16%, 17/17%, 32/
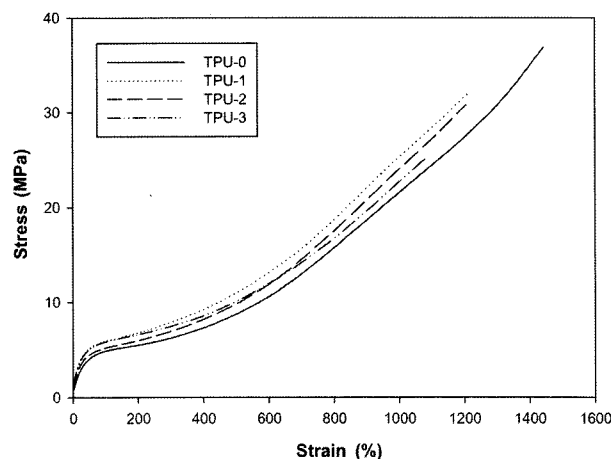

Figure 4. Stress-strain curves of TPU samples.

25%, respectively. The tensile modulus of all melt mixed film samples was higher than that of TPU-0 film sample prepared only by hot pressing. Among the melt mixed film samples, the TPU-1 had the highest modulus. This might be due more to the higher M_w than to the amount of hydrogen bonds. The tensile modulus of melt mixed sample decreased slightly with increasing run number of melt mixing. This behavior might be attributable more to the decrease of MW than to the increase of hydrogen bonds during excessive melt mixing. While it is very difficult to pin-point exactly why these trends occur in the mechanical properties, it certainly seems attributable to the multiple changes that occur simultaneously as a result of hot pressing/melt mixing, such as rapid increase of M_n and rapid decrease of PDI after hot pressing only, rapid increase of M_w after first melt mixing, and decrease of M_n and M_w and increase of total hydrogen bond with increasing run number of melt mixing.

Conclusions

Understanding the influence of hot pressing and melt processing on the properties of thermoplastic polyurethane (o-TPU, Hosung Chemex Co., MDI/Polyester polyol/BD based TPU) is very important to obtaining optimal results from mechanical recycling of TPU scraps. In this context, this study focused on the effects of hot pressing and melt mixing

Table II. TGA Data, Mechanical Properties and Hardness of TPU Samples

Sample Designation	TGA Data			Tensile Strength (MPa)	Elongation at Break (%)	Modulus (MPa)	100% Modulus	Hardness (Shore A)
	1st peak	2nd peak	Ash(%) at 570 °C					
o-TPU	342	391	4.5	-	-	-	-	-
TPU-0	359	394	8.4	36.9±1.8	1,442±22.3	8.7±1.0	4.1±0.1	84
TPU-1	365	381	9.3	32.1±3.1	1,217±34.6	12.1±1.3	4.5±0.3	86
TPU-2	364	382	9.6	30.8±1.6	1,204±45.6	11.0±1.5	4.1±0.5	86
TPU-3	364	381	9.8	25.1±2.5	1,097±40.7	11.0±1.4	4.4±0.2	87

on molecular weight (MW), PDI, MI, characteristic IR peak, hardness, thermal degradation and mechanical properties of thermoplastic polyurethane (TPU). While the original TPU pellet (o-TPU) showed a partially overlapped peak pair at lower/higher MW regions, the four TPU film samples, TPU-0 prepared by hot pressing of o-TPU pellet and TPU-1, TPU-2 and TPU-3 obtained by hot pressing of melt mixed TPUs, where the numbers indicate the run number of melt mixing, exhibited only a single peak. The TPU-0 film sample prepared only by hot pressing showed the highest M_n and the lowest polydispersity index (M_w/M_n) and hardness. The TPU-1 film sample exhibited the highest M_w and tensile modulus. The MIs of o-TPU, TPU-0, TPU-1, TPU-2 and TPU-3 film samples were found to be 7.01, 7.70, 6.63, 6.07 and 5.7 8(g/10 min), respectively. As the run number of melt mixing increased, the peak-intensity of free carbonyl at near 1728 cm^{-1} decreased, but the peak-intensity of strong hydrogen bonded urethane carbonyl groups at 1704 cm^{-1} increased, indicating that free urethane groups transformed into the strong hydrogen bonded urethane groups. The tensile strength/elongation at break and average M_n and M_w decreased significantly with increasing run number of melt mixing. The two stage (first: urethane/second: polyol) degradation temperatures of TPU-0 sample at both the first and second stages (359 °C and 394 °C) were higher than those of o-TPU (342 °C and 391 °C). While all the melt mixed film samples degraded at almost the same temperatures, the first stage degradation occurred at a higher temperature (about 365 °C) and the second stage degradation was exhibited at a lower temperature (about 381 °C) compared to TPU-0. From these results it was found that the first round of hot pressing and melt mixing was the critical condition which led to the significant changes of M_n/M_w/PDI, MI, mechanical property and thermal degradation behavior of TPU. It was concluded that hot pressing and melt mixing notably affected the molecular weight/PDI, MI and properties of TPU, which highlights the importance of providing adequate conditions of hot pressing and melt processing to obtain satisfactory results for mechanical recycling of TPU scraps.

References

(1) P. T. Williams and R. Bagri, *Int. J. Energy Res.*, **28**, 31 (2004).

(2) S. Jonna and J. Lyons, *Polym. Test.*, **24**, 428 (2005).

(3) N. T-Dintcheva, F. P. La Mantia, F. Trotta, M. P. Luda, G. Camino, M. Paci, L. DiMaio, and D. Acierno, *Polym. Adv. Technol.*, **12**, 552 (2001).

(4) F. Perugini, M. L. Mastellone, and U. Arena, *Environ. Progr.*, **24**, 137 (2005).

(5) C. H. Sung, K. S. Lee, K. S. Lee, S. M. Oh, M. S. Kim, and H. M. Jeong, *Macromol. Res.*, **15**, 443 (2007).

(6) Y. H. Kim, S. J. Choi, J. M. Kim, M. S. Han, W. N. Kim, and K. T. Bang, *Macromol. Res.*, **15**, 676 (2007).

(7) A. Ferry, P. Jacobsson, J. D. van Heumen, and J. R. Stevens, *Polymer*, **37**, 737 (1995).

(8) S. H. Kim, B. K. Kim, and H. Lim, *Macromol. Res.*, **16**, 467(2008).

(9) J. H. Saunder and K. C. Frisch, in *Polyurethane: Chemistry*, Interscience, New York, 1962.

(10) V. W. Strichatrapimuk and S. L. Cooper, *J. Macromol. Sci. Phys.*, **B15**, 267 (1978).

(11) R. E. Camargo, C. W. Macosko, M. Tirrell, and S. T. Wellinghoff, *Polym. Commum.*, **24**, 314 (1983).

(12) L. Born and H. Hespe, *Colloid Polym. Sci.*, **263**, 335 (1985).

(13) R. W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).

(14) V. V. Zharkov, A. G. Strikovski, and T. E. Verteletskaya, *Polym. Sci.*, **34**, 142 (1992).

(15) L. D'Orazio, G. Gentile, C. Mancarella, E. Martuscelli, and V. Massa, *Polym. Test.*, **20**, 227 (2001).

(16) F. M. B. Coutinho and M. C. Delpech, *Polym. Degrad. Stabil.*, **70**, 49 (2000).

(17) L. J. Bellamy in *The Infrared Spectra of Complex Molecules*, Chapman and Hall, New York, 1980.

(18) C. Zhang, Z. Ren, Z. Yin, H. Qian, and D. Ma, *Polym. Bull.*, **60**, 97 (2008).

(19) V. P. Pshenitsyna, N. N. Molotkova, M. P. Noskova, and B. Ya. Aksel'rod, *Zhurnal Prikladnoi Spektroskopii*, **29**, 486 (1977).

(20) S. Zhang, Z. Ren, S. He, Y. Zhu, and C. Zhu, *Spectrochim. Acta Part A*, **66**,188 (2007).

(21) F. Wang, Ph. D. Dissertation, Blacksburge, Virginia, 1998.

(22) N. Grassie and M. Zulfiqar, *J. Polym. Sci.: Polym. Chem. Ed.*, **16**, 1563 (1978).

(23) M. Herrera, G. Matuschek, and A. Kettrup, *Polym. Degrad. Stabil.*, **78**, 323 (2002).

(24) P. S. Wang, W. Y. Chiu, L. W. Chen, B. L. Denq, T. M. Don, and Y. S. Chiu, *Polym. Degrad. Stabil.*, **66**, 307 (1999).

(25) M. Thorn, *Can. J. Chem.*, **45**, 2537 (1967).

(26) F. S. Chung, *Polym. Degrad. Stabil.*, **92**, 1393 (2007).

(27) E. Dyer and G. E. Newborn, *J. Am. Chem. Soc.*, **80**, 5495 (1958).

(28) E. Dyer and R. E. Reed, *J. Org. Chem.*, **26**, 4388 (1961).

(29) J. R. Saunders, *Rubber Chem. Technol.*, **32**, 337 (1959).

(30) N. Grassie and M. Zulfiqar, *J. Polym. Sci.: Polym. Chem. Ed.*, **18**, 265 (1980).

(31) D. Joel and A. Hauser, *Die Angewandte Makromolekulare Chemie*, **217**, 191 (1994).

(32) K. Herzog, *Makromol. Chem. Macromol. Symp.*, **52**, 307 (1991).

(33) F. P. La Mantia, D. Curto, and R. Scaffaro, *J. Appl. Polym. Sci.*, **86**, 1899 (2002).

(34) M. A. J. Lozano-Gonzalez, M. A. T. Rodriguez-Hernandez, E. A. Gonzalez-De los Santos, and J. Vilapando-Olmos, *J. Appl. Polym. Sci.*, **76**, 851 (2000).

(35) M. L. Maspoch, H. E. Ferrando, and J. I. Velasco, *Macromol. Sym.*, **194**, 295 (2003).

(36) N. Ahmed, J. H. Khan, I. Hussain, and S. H. Hamid, *J. Polym. Mater.*, **16**, 341 (1999).

(37) N. Rust, E. E. Ferg, and I. Masalova, *Polym. Test.*, **26**, 130 (2006).

(38) H. Hinsken, S. Moss, J. R. Pauquet, and H. Zweife, *Polym. Degrad. Stabil.*, **34**, 279 (1991).