Synthesis and properties of Polyurethane-imide elastomers.

Tomohiro UEDA (上田知宏), Shin-ichi INOUE (井上眞一)

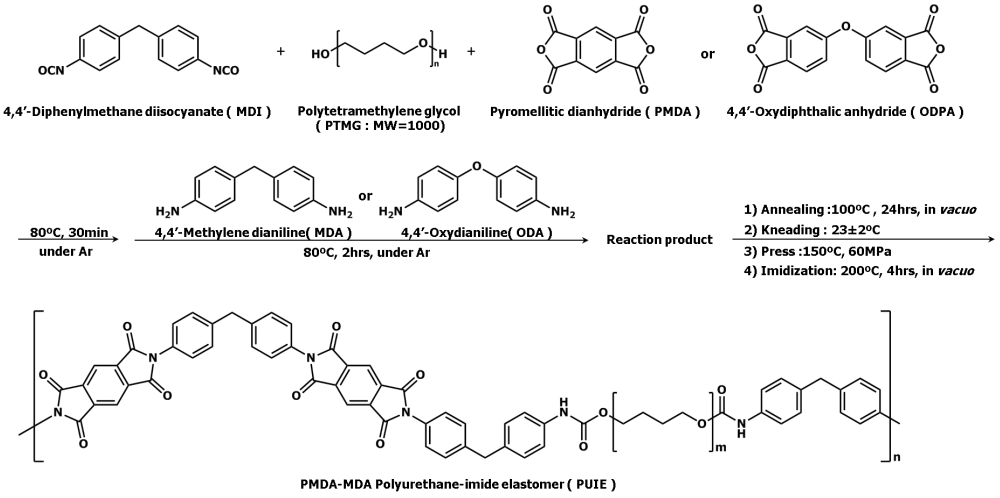
Aichi Institute of Technology
1247 yachigusa, yakusa-cho, toyota-shi, Aichi 470-0392, Japan

Abstract:A series of polyurethane-imide elastomers (PUIEs) were prepared from 4,4'-diphenylmethane diisocyanete (MDI), polytetramethylene glycol (molecularweight=1000) (PTMG1000), diamines, 4,4'-Methylenedianiline (MDA) or 4,4'-oxydianiline (ODA), and tetracarboxylic dianhydrides, pyromellitic dianhydride (PMDA) or 4,4'-oxydiphthalic anhydride (ODPA) by bulk polymerization. Flexible sheets were obtained by pressing at an appropriate temperature and Imidizaition of the sheets was completed at 200ºC for 4h in vacuo. The PUIEs were characterized by FTIR, and ^{13}C NMR spectra. The PUIEs synthesized from ODPA show thermoplasticity which caused by the structure of tetracarboxylic dianhydride.
Keywords: Polyurethane-imide / Polyurethane / Polyimide / Bulk method / Thermoplasticity /

1. Introduction

Polyurethane (PU) is a material widely used in our life. For PU material, most mentioned ones are elastomer, foam, resin, and coating. PUs are excellent at property, however, their heat resistance are not well. Therefore, The PUs with high heat resistance are required. In the past several years, we reported on the synthesis of Polyurethane-imide elastomer (PUIE) [(1)]. In that paper, PUIEs were prepared from *N*-methtyl-2-pyrrolidone (NMP) as solvent (Polyurea method). In the present study, PUIEs were prepared without solvent (bulk method) and thermoplasticity of these PUIEs and the relationships between structure and thermoplasticity are discussed.

2. Results and Discussion



Scheme 1. Synthesis of polyurethane-imide elastomer by bulk method.

Scheme 1 shows the preparation procedure for the PUIE by bulk method. MDI, PTMG1000 and tetracarboxylic dianhydrides, PMDA or ODPA were added to a 100 mL four-necked reaction flask

equipped with a stirrer, a gas inlet tube and a gas outlet tube, and were then stirred at 80℃ for 30 min under an Ar atmosphere. Then diamine, MDA or ODA were added and stirred at 80℃ for 2 h under an Ar atmosphere. The reaction product was obtained by annealing at 100℃ for 24 h in *vacuo*. Then it was kneaded by 3 inch roll. Flexible sheets were obtained by press at an appropriate temperature. Imidizaition of the PUIE sheets was completed at 200ºC for 4h in vacuo.

The FTIR spectra of PUIEs are shown in Figure 1. FTIR measurements gave the following results. The peak at 3311cm^{-1} (N-H stretching), 1779cm^{-1} (C=O stretching of imide), 1721cm^{-1} (C=O stretching of imide and urethane), and 1372cm^{-1} (C-N stretching).

The ^{13}C NMR spectrum of PMDA-MDA PUIE is shown in Figure 2. The Peaks at 164.3 ppm (imide) and 153.5 ppm (urethane) in the obtaining PUIEs were observed.

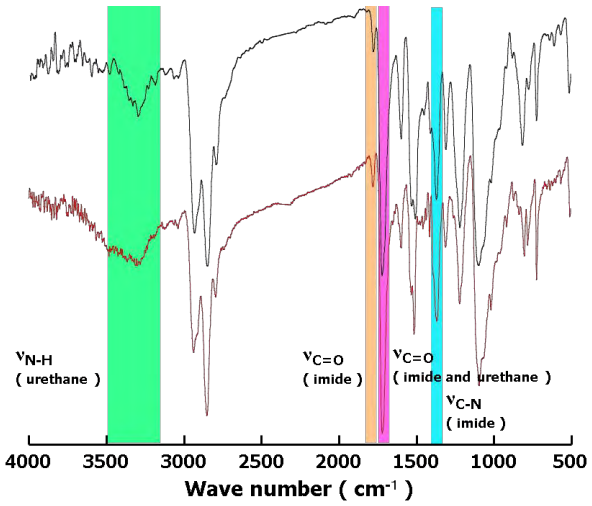


Figure 1. FTIR spectraof PUIEs, which were synthesized by a each method. ; Black line (Polyurea method), Red line (Bulk method)

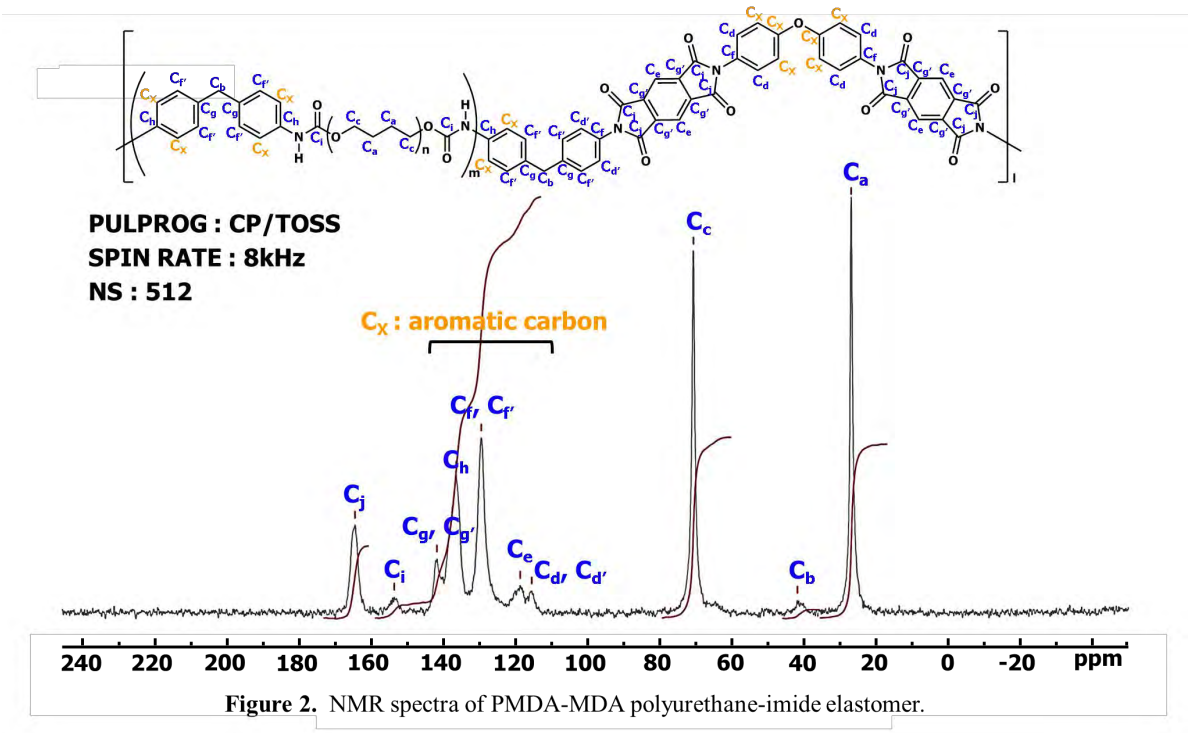


Figure 2. NMR spectra of PMDA-MDA polyurethane-imide elastomer.

The stress-strain curves are shown in Figure 3. The tensile strength and elongation at break of PUIEs prepared by polyurea method is 48MPa and 465%, respectively. On the other hand, the tensile strength and elongation at break of PUIE prepared by bulk method is 46MPa and 377%, respectively. Figure 4 shows the viscoelastic behavior of PUIEs through the storage modulus (E') and tan δ (tan δ ＝E''/E'). The glass transition temperature (Tg) of PUIE using PMDA is -70℃ and the Tg of PUIE using ODPA is -32℃. The PUIE using PMDA shows a long rubbery plateau up to approximately 225℃. However, the PUIE using ODPA do not shows rubbery plateau. This result suggested that the PUIE using ODPA has thermoplasticity.

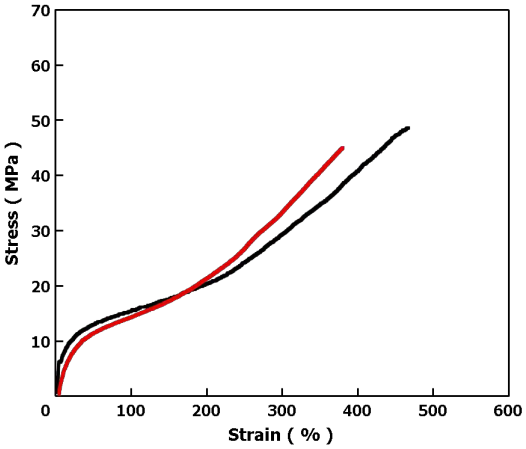


Figure 3. Tensile tests (Stress-Strain curves) of PUIEs, which were synthesized by a each method. ; Black line (Polyurea method), Red line (bulk method)

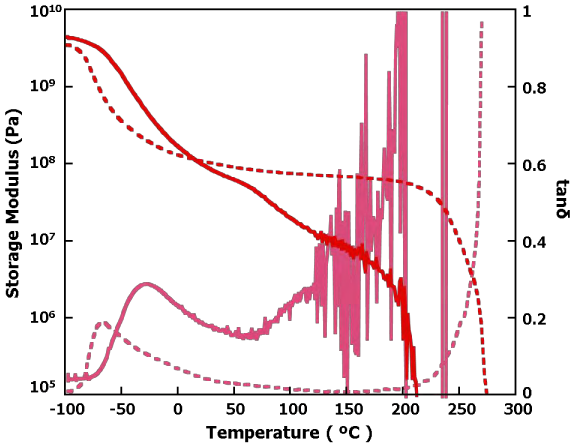


Figure 4. Dynamic mechanical analyses of PUIEs synthesized form MDI ,PTMG1000 and ODA, PMDA (dot line) and ODPA (solid line).

The Optimized structures of PUIEs using PMDA and ODPA are shown in Figure 5.The structure of the PMDA in PUIE is not flexibility. On the other hand, the structure of the ODPA in PUIE is flexibility. Thermoplasticity of PUIEs may be influenced to the structure of the ODPA strongly.

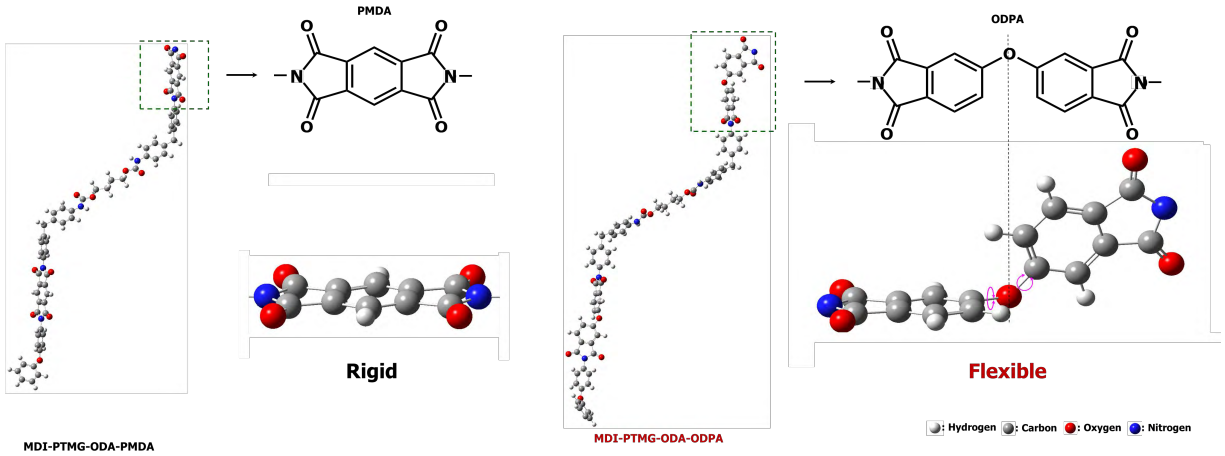


Figure 5. Optimized structure of PMDA-PUIE and ODPA-PUIE structures calcuated by Gaussian09W B3LYP/6-31G(d).

3. Conclusions

The PUIEs were successfully prepared by bulk method. The results of FTIR, tensile strength and elongation value at break for PUIEs obtaining by bulk method are similar to those of the PUIEs obtaining by the polyurea method. It was developed that thermoplasticity of PUIEs are strongly affected to the structure of tetracarboxylic dianhydride.

References

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[2] T. Kogiso and S. Inoue, J.Appl. Polym. Sci., 115, 2010, 242-248.