EUROPEAN JOURNAL OF MATERIALS SCIENCE AND ENGINEERING
Volume 1, Issue 1, 2016: 39-46 | www.ejmse.tuiasi.ro | ISSN: 2537-4338
EJMSE

STUDY ON SYNTHESIS AND CHARACTERIZATION OF POLYURETHANE CONTAINING SILVER NITRATE

Cheng-Lung WU[1], Chih-Yuan TSOU[1], Shih-Hsuan CHIU[1*],
Maw-Cherng SUEN[2], Chien-Hao KAO[3]

[1] Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taiwan, R.O.C.
[2] Department of Creative Fashion Design, Taoyuan Innovation Institute of Technology, Taiwan, R. O. C.
[3] Graduate School of Materials Applied Technology, Taoyuan Innovation Institute of Technology, Taiwan, R. O. C.

Abstract

In this study, the polycaprolactone diol (PCL), 4,4'-diphenylmethane diisocyanate (MDI) and 2,6-Pyridimthanol (2,6-PDM) were reacted in the N,N-dimethyl acetamid (DMAc) solvent to form the polyurethane (PU). Finally, the silver nitrate was added into the polyurethane. The silver ion was reacted with 2,6-Pyridimthanol to form the metal coordinate bond in PU/$AgNO_3$. Various addition ratios of silver nitrate were studied to understand the influence on the properties of polyurethane containing the pyridine ring. The characteristic peak was identified to determine the structure of polyurethane. The residue of thermal decomposition could be used to determine the addition of silver nitrate, and the variation of degradation temperature could be observed. When the content of silver nitrate was increased, the glass transition temperature (Tg) would be increased significantly. The stress-strain test showed that when the content of silver nitrate was increased, the elongation at break of PU/$AgNO_3$ would be reduced significantly. The NaOH aqueous solution was used to decompose PU/$AgNO_3$, and the degradation rate of PU/$AgNO_3$ was observed in a short time. The scanning electron microscope (SEM) was used to observe the pore and crack of PU/$AgNO_3$ after hydrolytic reaction.

Keywords: *polyurethane; polyurethane; silver nitrate; pyridine; hydrolytic*

Introduction

The polyurethane (PU) has many excellent properties, such as elasticity, ductility, tensile strength, wear resistance and possesses the properties of both plastics and elastomer [1]. It is comprehensively applied in fiber, artificial leather, adhesive, foam plastics, and painting etc., so it occupies a very important position in industry [2-4]. However, the heat resistance of polyurethane is quite poor, so its application will be limited in some fields.

In order to improve the heat resistance of polyether type polyurethane, the heterocyclic compound with higher thermal stability can be introduced by chemical synthesis, and the ratio of hard section and soft section can be adjusted to prepare high-performance PU elastomer. For example, Tsou et al. [5] used the pyridine as a chain extender to improve the thermal stability and mechanical property of polyurethane. In fact, the pyridine improved the thermal stability of PU, and the nitrogen atom on pyridine can be used for other application. For example, in the paper of Chiu et al. [6], 2,6-pyridinedimethanol (2,6-PDM) was used as a chain extender to prepare a novel shape-memory polyurethane, PDM/PUs. Lee et al. [7] used 2,6-

* Corresponding Author: schiu@mail.ntust.edu.tw

pyridinedimethanol (2,6-PDM) to react with silver nitrate to form PU with antibacterial property. Chen et al. [8] used N,N-bis(2-hydroxyl ethyl) isonicotinamide (BINA) to synthesize the moisture-sensitive polyurethanes.

The biodegradable polyurethane is generally mixed by the water soluble soft section, such as polycaprolactone diol (PCL), polyadipic acid (PAA), polylactic acid (PLA) and polyglycolic acid (PGA) etc. The biodegradable material has good biological compatibility, biodegradation, solvent solubility, high crystallinity and low melting point etc. [9-14], which can be decomposed by biological degradation, hydrolysis, and photodissociation etc. The material used for hard, soft tissue in human body shall have good biological compatibility and biodegradation [15]. In order to heal the tissue naturally, the medical ossicle transplant flawed or damaged substitution must be a porous support [16]. Due to the price of biodegradable material, the starch has been studied. But because of the water sensitivity and brittleness, the application of material is limited [17]. The chitosan can promote the regeneration of skin to accelerate the heal of wound, which is one of biomedical materials [18]. So, the addition of biodegradable PCL into PU can improve the hard degradation problem of disposal PU. The polycaprolactone diol (PCL) is a semi-crystalline material with good biodegradability, biological compatibility, hydrophobicity, and thermal property, and its crystallinity is decreased with molecular weight [19].

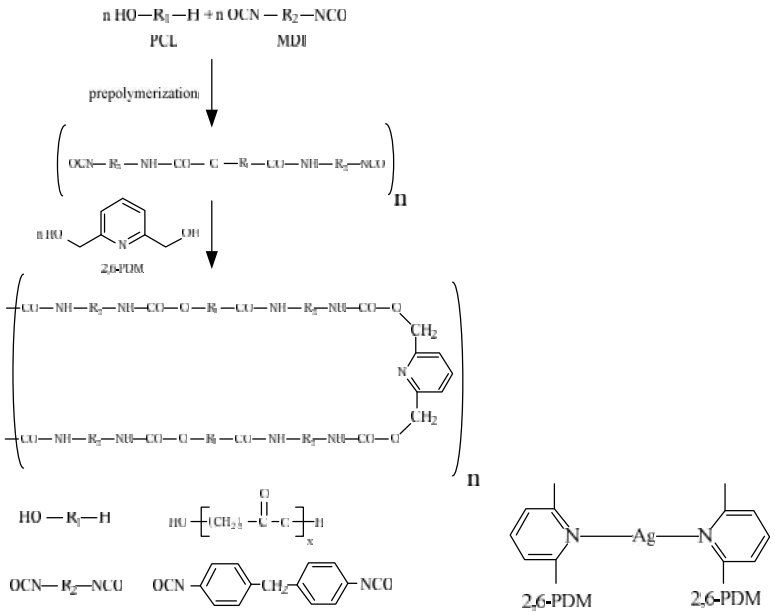
The silver metal has supreme electric conductivity and thermal conductivity, and possesses the best corrosion resistance and oxidization resistance [20]. The silver has comprehensive application on basic medical apparatus, such as support and bandage of external plaster medicine [21]. The polyurethane nanomembrane has good mechanical properties, which is thought to be the best nanomembrane. It can be applied in the antibacterial nanofilter [22] through the synthetic preparation of nano silver ion. The nanofiber doped with nanoparticles (NPs) receives great concern [23]. It is valid in verifying silver material to heal the burning and scalding effectively and can inhibit bacterium and inflammation [24]. These materials containing nanosilver can delay the release of ion, so that the material more effective long-term antibacterial property [25-26].

From the above-mentioned description, the polyurethane with metal addition has better properties compared with traditional PU. So this study used 2,6-pyridinedimethanol as a chain extender and various ratio of silver nitrate to synthesize PDM-PU/Ag to improve the properties of traditional polyurethane. And the polycaprolactone diol (PCL) was used as the soft section of PU, to make polyurethane with better hydrolysis properties.

Materials and Synthesis

4,4'-Diphenylmethane diisocyanate (MDI), poly(ε-caprolactone) diol (PCL Mw=530 g/mole), silver nitrate, and 2,6-pyridinedimethanol (2,6-PDM) were purchased from Aldrich. N,N-dimethylacetamide (DMAc) was bought from Mallinckrodt Chemicals.

Appropriate amounts of MDI, PCL, and DMAc were added to a 500 mL three-necked and flat-bottomed flask. The reaction proceeded by heating the mixture at 80°C and stirring at 200 rpm. After reacting for 2 h, PU prepolymer was formed. Then, certain amount of 2,6-PDM in DMAc was added to the flask and the reaction proceeded for another 2 h (Scheme 1). The PU solution was further mixed with various amounts of $AgNO_3$ in a flask at 70 °C for 1 h to form PU/$AgNO_3$ complexes. Then the PU/$AgNO_3$ complex solutions were dried in an oven at 70 °C for 2 days to form PU/$AgNO_3$ complex films. The PU, PU/$AgNO_3$-01, PU/$AgNO_3$-02, and PU/$AgNO_3$-03 represent the complexes with the $AgNO_3$/2,6-PDM molar ratio of 0, 10, 50, and 90 % respectively and list Table1.



Scheme 1. Synthesis formula for the PU/$AgNO_3$

Table 1. Formulas of the PU/$AgNO_3$

Designation	MDI (moles)	PCL (moles)	2,6-PDM (moles)	$AgNO_3$ (wt%)
PU	4	3	1	0%
PU/$AgNO_3$-01	4	3	1	10%
PU/$AgNO_3$-02	4	3	1	50%
PU/$AgNO_3$-03	4	3	1	90%

Results and Discussions

FT-IR Spectra

Fig. 1 shows the FTIR absorption spectra of PU/$AgNO_3$. There is a wide and weak absorption band at 3400-3200cm^{-1}, which is the vibration absorption band of N-H group. It is the product combined by isocyanate-NCO and alcohol-OH, representing the main reference functional group of urethane synthesized successfully. The double peaks at 3000-2800cm^{-1} are the vibration absorption peaks of alkyl group-CH. The peak at 2400-2300cm^{-1} is the vibration absorption band of isocyanate-NCO. The appearance of isocyanate-NCO absorption peak represents the existence of synthetic end group. The gentle peak area represents that the synthetic reaction of polyurethane has been completed. Due to the resonance of carboxyl group C=O, two absorption peaks will be appeared at 1800-1650 cm^{-1} and 1630-1570 cm^{-1} for the characteristic peak of PCL. At 1570-1480 cm^{-1}, there is a vibration absorption band of C=C. At 1220~1160 cm^{-1}, there is a vibration absorption band of C-O group. At 1100~1030 cm^{-1}, there is a vibration absorption band of ether group C-O-C. At 850~790 cm^{-1}, there is a deformed absorption band of cyclic-CH.

Thermal Properties

The Thermogravimetry Analysis (TGA) of PU/$AgNO_3$ is shown in Fig. 2 and Fig. 3, and its thermal decomposition temperature is shown in Table 2. Fig. 2 shows that the decomposition temperature is increased with the content of silver nitrate. In PU and PU/$AgNO_3$-01, the decomposition temperature is about 250 °C. In PU/$AgNO_3$-02 and PU/$AgNO_3$-03, the

decomposition temperature is about 150°C~250°C. It is known when more silver nitrate is added, a few irregular molecular chains will be appeared on PU chain section, so that a few molecular chains with poor heat resistance will be appeared. At 600°C, the residue is 4.5%, 5.7%, 14.7% and 22.9%, respectively, and the residue is increased with the content of silver nitrate.

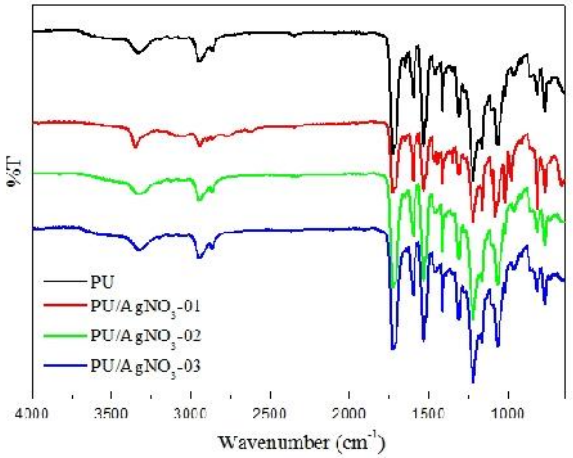


Fig. 1. FT-IR spectra of the PU/$AgNO_3$

The Differential Scanning Calorimetry (DSC) analysis is shown in Fig. 4. In PU to PU/$AgNO_3$-03, Table 2 shows the Tg is -6.6°C, -4.1°C, 2.9°C and 0.9°C, respectively. The Tg is increased by 7.6°C totally. It is known when more silver nitrate is added, the Tg will be increased.

Table 2. Thermal properties of the PU/$AgNO_3$

Designation	TGA		DSC
	Td(°C)	**Residue at 600**°C	**Tg** (°C)
PU	242.7	4.5 %	-6.7
PU/$AgNO_3$-01	215.0	5.7 %	-4.1
PU/$AgNO_3$-02	151.0	14.8 %	-2.9
PU/$AgNO_3$-03	138.2	23.0 %	1.0

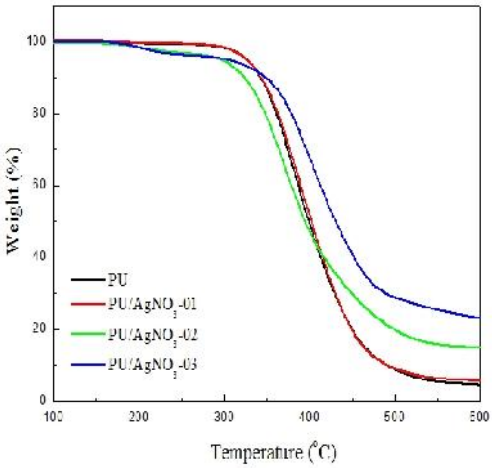


Fig. 2. TGA curves of the PU/$AgNO_3$

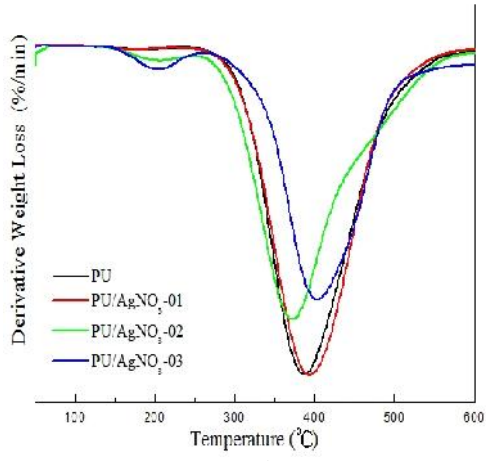


Fig. 3. DTG curves of the PU/$AgNO_3$.

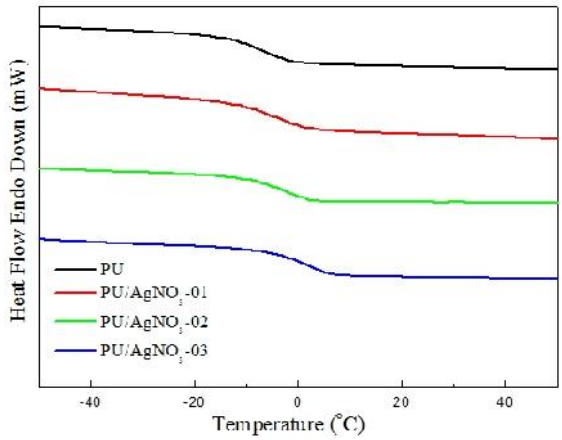


Fig. 4. DSC thermograms of the PU/$AgNO_3$.

Tensile Properties

The stress-strain diagram of PU/$AgNO_3$ is shown in Fig. 5 and the data are shown in Table 3. In the tensile test, the elongation is 890.4% in PU, 835.2% in PU/$AgNO_3$-01, 704.9% in PU/$AgNO_3$-02, and 551.7% in PU/$AgNO_3$-03. The elongation at break of PCL is better in PU, even 90% of silver nitrate is added, the elongation break is still good. The elongation of PU added with metal is reduced significantly, but the tensile strength will be increased. The tensile strength is 10.3MPa in PU and 11.3 MPa in PU/$AgNO_3$-01. When 90% of silver nitrate is added, the tensile strength is reduced by 1.8 MPa in PU/$AgNO_3$-03. There is the best elongation and biggest tensile strength in PU/$AgNO_3$-01, which is 835.2% and 11.3MPa, respectively.

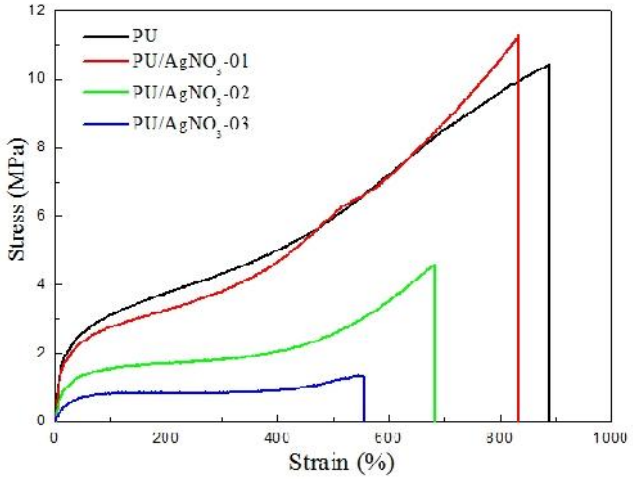


Fig. 5. Tensile properties of the PU/$AgNO_3$..

Table 3. Tensile properties of the PU/$AgNO_3$

Designation	Maximum Stress (MPa)	Strain At Break (%)
PU	10.3	890.4
PU/$AgNO_3$-01	11.3	835.2
PU/$AgNO_3$-02	5.6	704.9
PU/$AgNO_3$-03	1.8	551.7

Hydrolytic Degradation and Morphology Analysis

The hydrolytic degradation of PU/$AgNO_3$ is shown in Fig. 6 at (a) of 37°C, and (b) of 45°C. Two different trends are observed significantly.

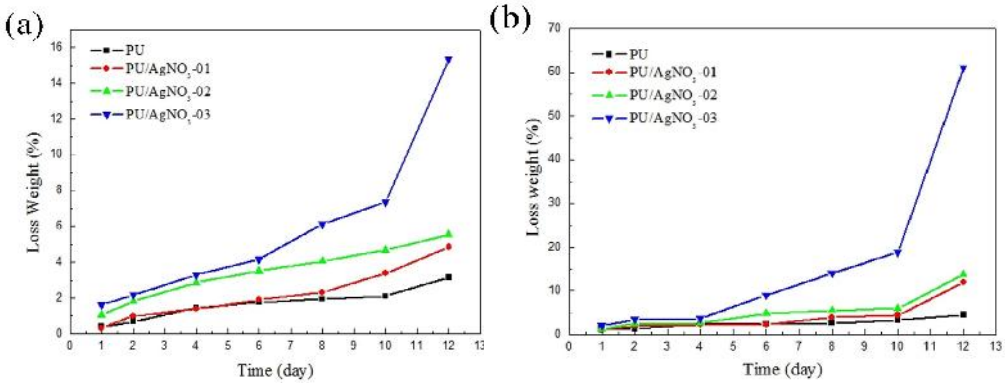


Fig. 6. Hydrolytic degradation results of the PU/$AgNO_3$..

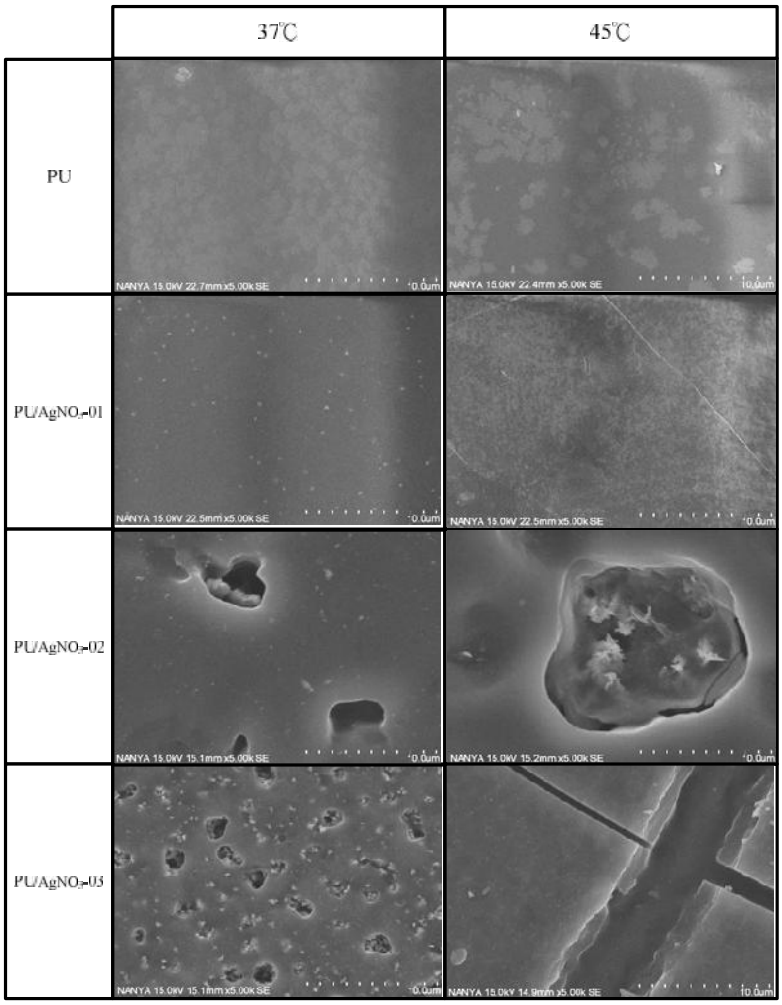


Fig. 7. SEM micrographs of the PU/$AgNO_3$ with hydrolytic degradation for 12 d at 37°C and 45°C.

The first trend is when the temperature is increased, the degradation rate will be increased significantly. The second trend is when the content of silver nitrate is increased, the degradation of PU will be quicker. It is observed the weight loss is 3.1% and 4.4% at 37°C and 45°C at day 12. It is 15.3% in PU/$AgNO_3$-03 at 37°C and 61.0% at 45°C. It is known when PU/$AgNO_3$ is immersed in NaOH solution, the hydrolytic degradation of PU will be accelerated. It is possible that there is no other material to be attacked by NaOH solution, so PU will only be decomposed slowly.

The morphological shape of PU/$AgNO_3$ at 37°C and 45°C at day 12 is shown in Fig. 7. It is observed that the pores are appeared from flat surface to textile surface. The pore size is increased with the content of silver nitrate and the pore is irregular. At 45°C, the irregular pores of PU/$AgNO_3$-03 become the cracks.

Conclusion

The silver nitrate was added into the PU synthesized by the polycaprolactone diol (PCL), 4,4'-diphenylmethane diisocyanate (MDI) and 2,6-Pyridimthanol (2,6-PDM) to form the PU/$AgNO_3$. The successful synthesis of PU/$AgNO_3$ was confirmed in FTIR. In TGA, it was found when silver metal is added, the decomposition temperature will be reduced. In DSC, it was shown that the Tg was increased significantly. The polycaprolactone diol (PCL) is a biodegradable and soft polymer. It is known from this experiment if this material is used as main ingredient, even the metal is added into the synthesized PU, the elongation at break is still very good. When the NaOH solution is used to decompose PU/$AgNO_3$ at higher temperature, the degradation rate of PU/$AgNO_3$ will be increased with the content of silver nitrate. From the SEM observation, the irregular pores will be appeared with the content of silver nitrate in PU, and big cracks will be appeared in PU/$AgNO_3$-03 at 45°C.

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Received: June, 10, 2016
Accepted: September 4, 2016