TMS 2012 supplemental proceedings, Vol. 1: Materials Processing and Interfaces
Hoboken, N.J.; WILEY, ©2012, (DLC) 2012405373, ISBN: 9781118356043; 1118356047

POSITRON LIFETIME ANALYSIS OF POLYUREA-NANOCLAY COMPOSITS

Naidu V. Seetala[1], Gabriel Burks[1], Danny Hubbard[2], Alex Trochez[2] and Valery N. Khabashesku[3]

[1]Department of Physics, Grambling State University, Grambling, LA 71245, naidusv@gram.edu
[2]Department of Chemistry, Grambling State University, Grambling, LA
[3]Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX

Keywords: Aliphatic Polyurea, Nanoclay, Positron Lifetime, Positronium, Pore Structure

Abstract

Positron lifetime spectroscopy (PLS) is used to study 1-5 wt% nanoclay incorporated aliphatic polyurea films prepared by two different methods. Set-1 used aliphatic polyaspartate polyurea system consists of aliphatic diisocyanate resin, while set-2 used pre-made aliphatic-polyurea granules. PLS was used to study pore structure in polyurea samples. The third lifetime component, related to positronium formation in free spaces, provided the information on pore size and concentration of pores. The third lifetime component showed ~ 2 ns for set-1 and ~ 1.8 ns for set-2 with relative intensities of 16% and 19%, respectively; indicating that set-1 polyurea has larger pores with lesser concentration compared to set-2 polyurea. There is good correlation between positronium lifetime parameters (both lifetime and intensity) and % nanoclay in set-1 polyurea, but no correlation is observed for set-2 polyurea. The set-2 films showed bad quality and the polymer curing is not as good as set-1 films.

Introduction

Nanoclay reinforced polymer composites improve multifunctionalities such as structural and thermal properties [1, 2]. Polyurea with nanoclay is important in developing appropriate composite material for the blast and fragmentation resistant applications. Understanding the mechanisms involved in improving the mechanical strength of polyurea with nanoclay is important in developing appropriate composite material for the blast and fragmentation resistant applications. Free volume parameters, such as pore size and pore concentration in polymers, play an important role in determining the physical properties of the polymer. Positron Annihilation Techniques (PAT) are very sensitive to the microporosity of the sample [3, 4]. Positron lifetime spectroscopy (PLS) is very sensitive to free volume in polymers. The third lifetime component, related to positronium formation in free spaces in polymers, provides the information on pore size (proportional to positronium lifetime) and concentration of pores (proportional to the intensity of the positronium component). Here, we use PLS to study the pore structure variations in aliphatic polyurea with 1-5 wt% nanoclay prepared by two different procedures: 1) starting with aliphatic polyaspartate polyurea system consists of aliphatic diisocyanate resin (set-1), and 2) starting with pre-made aliphatic-polyurea granules (set-2).

Experimental

Two sets of aliphatic polyurea (PU) samples were prepared with 1-5 wt% nanoclay. The first set of organoclay-polyurea composites have been prepared [5] from castable aliphatic polyaspartate polyurea system acquired from Bayer Materials Research Company. The system consists of

aliphatic diisocyanate resin (component A). Commercial nanoclay product, Cloisite 15A, functionalized with a quaternary amine containing a C_{14}-C_{18} long-chain alkyl tails, was obtained from Southern Clay Products. The nanoclay powder was exfoliated by placing it into a mixture of secondary polyetheramines (Component B) and then stirred at 80 °C for 3 hrs. This was followed by degassing of the dispersion and of aliphatic resin in vacuum oven at 75 °C. The components were mixed in desired ratio to get 1-5 wt% nanoclay by placing the PU components A and B into a dual cartridge gun equipped with a mixing pipe dispenser purchased from PLUS PAK, then cast into a Teflon mould and left for curing overnight. A second set of aliphatic polyurea-nanoclay composites has been prepared starting with gently warming the pre-made polyurea obtained from Versaflex to 37 ^{o}C, added 1-5 wt% montmorillonite nanoclay, heated the mixture to 75 ^{o}C and stirred for 2 hours, placed the mixture into a ceramic plate containing a 2 cm well to make a mold, and allowed to dwell for 24 hours in a convectional oven at 90 ^{o}C followed by letting it stand for 1 hour in vacuum oven.

Positron lifetime system is used to study porous structure in 1-5 wt% nanoclay incorporated both sets of aliphatic polyurea films. A ^{22}Na source is sandwiched between two identical polyurea films under study and the lifetime spectrum was collected. When a positron is emitted from the source, a high energy (1.28 MeV) nuclear gamma is simultaneously emitted from the source, which serves as birth signal and detected by the first scintillator. The positron (antiparticle of electron), which enters the sample, is trapped in a lattice defect and finally annihilates with an electron around the defect site and gives two low energy (0.511 MeV) annihilation gammas, which serve as the death signal and detected by the second scintillator. The time delay between the birth and death signals gives the positron lifetime at the annihilation site in the sample. The positron lifetime depends on the average electron density around the defect site, which is a function of the defect size and type. As the defect size increases the electron density at the annihilation site decreases, thus the corresponding positron lifetime increases. A 16 ns delay is introduced for the time calibration of the spectrometer and found to be 0.0125 ns/ch. The positron lifetime spectra were analyzed using POSFIT computer program [6] and obtained three lifetime components for all samples. The first and second lifetime components are related to positron annihilation with electrons with in polymer chains and between polymer chains, respectively, without forming a positronium (hydrogen like) atom. As the electron concentration at the annihilation site increases the corresponding positron lifetime increases. The electron concentration within the free volume (pores) of the polymer is so low such that a positron can find an isolated electron to combine to form a positronium atom that eventually decays to gamma rays. The third lifetime component is related to the positronium lifetime in these films, which is related to free volume in polymer. The positronium lifetime is proportional to the pore size. The relative intensities of these three lifetime components are proportional to the number of positrons annihilated in these three states described, which are directly related to the concentrations of these different sites available within the polymer.

Results and Discussion

Figure 1 show the positron lifetime spectra for two sets of blank aliphatic polyurea films prepared by different methods described above using ^{22}Na positron source along with a time resolution peak collected using ^{60}Co source (^{60}Co emits two high energy gammas simultaneously, thus it serves a instrumental resolution function to use in the POSFIT program). The third lifetime component has longer lifetime in set-1 sample compared to set-2 sample. The difference can be clearly seen at the higher time scale (right edge of the lifetime spectrum).

Indicating the set-1 sample has larger pores compared to set-2 sample. More detailed analysis is described below.

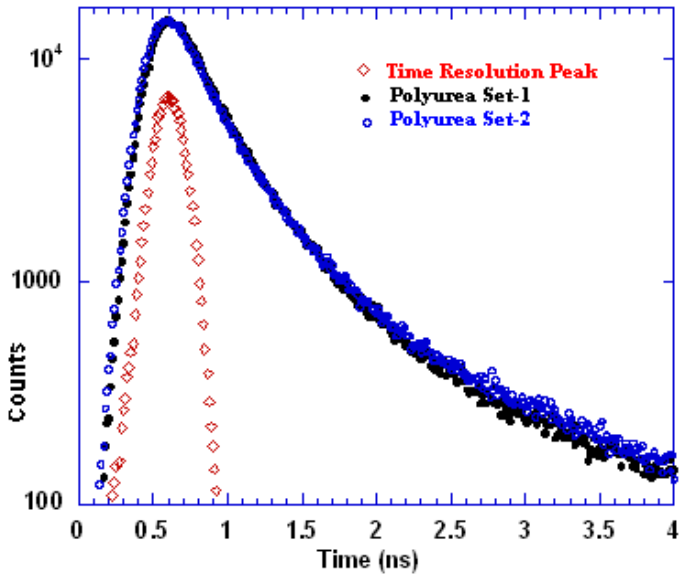

Figure 1: Positron lifetime spectra for two sets of aliphatic-polyurea prepared by different methods along with time resolution function.

The positron lifetime results for Set-1 aliphatic polyurea with 1-5 wt% nanoclay samples are summarized in Figures 2 and 3, where the third lifetime positronium component variations are shown with varying wt% nanoclay in the aliphatic polyurea. The positronium lifetime decreases with the wt% nanoclay in the polyurea, indicating that the pore size in the polymer decreases with the percentage nanoclay in the polymer. The positronium intensity increases with the wt% nanoclay in the polyurea, indicating that the pore concentration in the polymer increases with the percentage nanoclay in the polymer. This may indicate that the larger pores are breaking into smaller pores as the percent of nanoclay increases in the polymer.

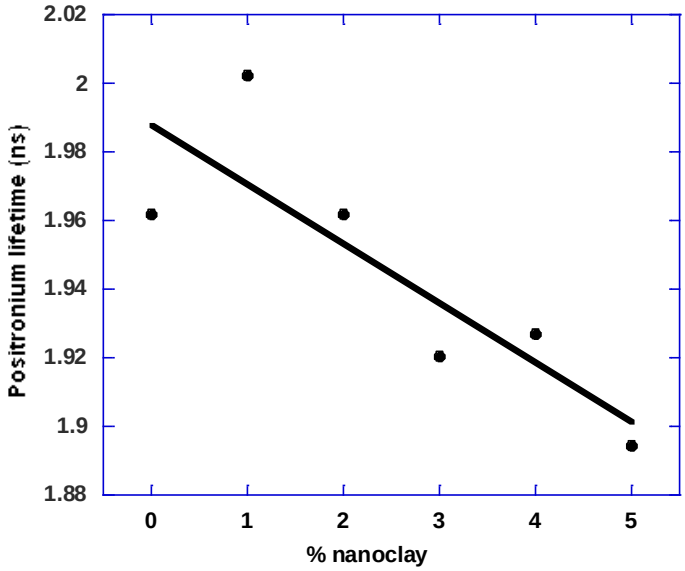

Figure 2: Positron lifetime third (positronium) component with % nanoclay in polyurea (set-1)

Set-1 samples are most consistent and reproducible compared to the set-2. The set-2 films are of bad quality and the curing of the polymer film is not good. Thus the positron lifetime results for

set-2 did not show systematic variations with % nanoclay as in the case of set-1. So, we will only make a qualitative comparison between set-1 and set-2 samples, and the curing process in the process for set-2 samples need to be improved in order to obtain good quality samples.

The third component lifetime (τ_3) and its relative intensity (I_3) for blank polyurea prepared in set-2 have values of 1.8 ns and 19%, respectively. These values for set-1 samples showed ~ 2.0 ns lifetime with 16% intensity. These results indicate that set-1 polyurea has larger pores with lesser concentration compared to set-2 polyurea. There is no good correlation between positron lifetime components (both τ_3 and I_3) and % nanoclay in set-2 polyurea, unlike set-1 polyurea. We are trying to improve the consistency in the polymer film preparation for set-2 procedure and investigating to improve the curing step in set-2 preparation methods. Set-1 polyurea preparation procedure seems to be better compared to the set-2 preparation procedure.

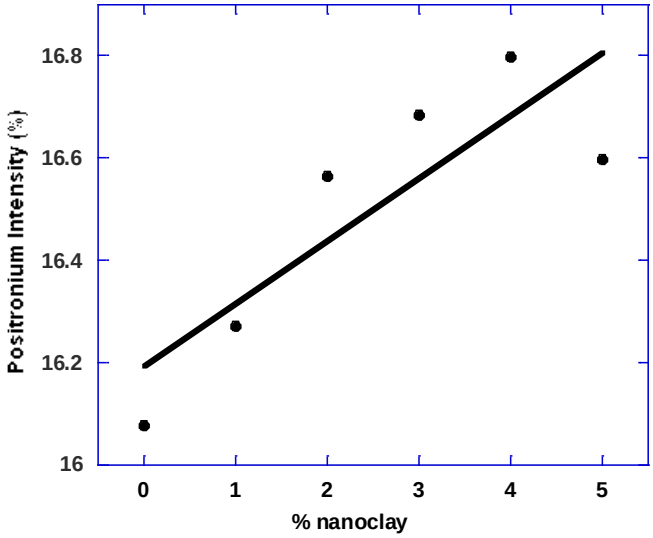

Figure 3: Intensity of the positron third lifetime component with % nanoclay in polyurea (set-1).

Conclusions

Aliphatic polyurea films with 1-5 wt% nanoclay are prepared by two different methods (set-1 and set-2). Set-1 used aliphatic polyaspartate polyurea system consists of aliphatic diisocyanate resin, while set-2 uses pre-made aliphatic-polyurea granules. Positron lifetime spectrometer is used to characterize the pore structure (relative pore size and pore concentration) using the positronium (third) lifetime component. The positronium lifetime decreases with the % nanoclay in the set-1 aliphatic polyurea as the % nanoclay increased, indicating a decrease in pore size with increasing % nanoclay. The positronium intensity increases with the % nanoclay, indicating that the pore concentration increases with % nanoclay in the set-1 polymer. The set-2 films, prepared from pre-made polyurea granules, showed bad quality, less consistency, low reproducibility, and the curing of the polymer film is not as good as set-1 films. The positron lifetime results indicate that set-1 polyurea has larger pores with lesser concentration compared to set-2 polyurea. There is a need to improve the curing process in the set-2 polyurea films preparation methods.

Acknowledgements

The work has been supported by a grant from Clarkson Aerospace, Air Force contract FA8650-05-D-1912 from the Air Force Research Laboratory Materials and Manufacturing Directorate.

Hoboken, N.J.; WILEY, ©2012, (DLC) 2012405373, ISBN: 9781118356043; 1118356047

References

[1] H. H. Wang and K. V. Chen, "A novel synthesis of reactive nano-clay polyurethane and its physical and dyeing properties", J. Appl. Polym. Sci., **2007**, Vol. 105, pp1581-1590.

[2] N. Sheng, M. C. Boyce, D. M. Parks, G. C. Rutledge, J. J. Abes, and R. E. Cohen, "Multiscale Micromechanical Modeling of Polymer/Clay Na-nocomposites and the Effective Clay Particle", Polymer, **2004**, Vol. 45(2), pp.487-506.

[3] Y. Itoha, A. Shimazu, Y. Sadzuka, T. Sonobe and S. Itai, "Novel method for stratum corneum pore size determination using positron annihilation lifetime spectroscopy", International J. Pharmaceutics, **2008**, Vol. 358, p-91-95.

[4] S. V. Naidu, S. V. Sastry, C. S. Maxie and M. A. Khan, "Effect of Plasticizer on Free Volume and Permeability in Cellulose Acetate Pseudolatex Membranes Studied by Positron Annihilation and Tracer Diffusion Methods", Mat. Sci. Forum, **1997**, Vol. 255-257, pp333-335.

[5] N. Seetala, G. Burks, D. Hubbard, A. Trochez, and V. Khabashesku, ACS Division of Polymeric Materials: Science and Engineering Preprint **2011**; V. N. Khabashesku, R. Krishnamoorti, B. Eranezhuth, "Organoclay-Polyurea Nanocomposites with Advanced Mechanical Properties", US Patent application 20110081494. PCT filed on October 1, 2009.

[6] P. Kirkegaard, N. J. Pedersen, and M. Eldrup, a program from Risø National Laboratory (1989).