THERMAL STABILITY OF STARCH–POLYURETHANE NANOCOMPOSITES

[1,2]TAYSER SUMER GAAZ, [3]M.N.M.ANSARI, [4]ROBERT A. SHANKS

[1]Department of Mechanical & Materials Engineering, Faculty of Engineering & Built Environment, University Kebangsaan Malaysia.
[2]Department of Equipment's & Machines Engineering, Technical College Al-Musaib, Al-Furat Al-Awsat Technical University, Iraq.
[3]Centre for Advanced Materials, College of Engineering, Universiti Tenaga Nasional, Kajang, Selangor, 43000 Malaysia
[4]School of Applied Sciences, RMIT University, Box 2476 GPO, Melbourne, VIC 3001, Australia.
E-mail: taysersumer@gmail.com

Abstract- Starch–polyurethane nanocomposites (Starch–PU) were prepared by incorporating starch into a polyurethane matrix by a casting method. Thermal stability and dynamic mechanical properties of the Starch–PU nanocomposites were characterized. Thermal stability and crystallization temperature of the Starch–PU nanocomposites were enhanced compared with that of the pure polyurethane. The storage modulus incremented with starch composition, while the damping factor (tanδ) decreased.

Keywords- Nanocomposite, Starch, Thermal Analysis, Mechanical Property, Morphology, Interface, Dispersion

I. INTRODUCTION

During the past 40 years, there have been numerous studies and excellent publications on the preparation and structural, thermal, mechanical and morphological characterization of TPU systems by various research groups. The potential impact of polyurethanes continues to be very strong and promising in many emerging fields, such as biomaterials and tissue engineering, optoelectronics, shape-memory materials, conducting polymers, molecular recognition, smart surfaces and others.

Hetflejs et al., (2010) found that at room temperature the protection was very slow and requires several days for completion. Our attempts to speed it up by increasing reaction temperature or methanol excess were unsuccessful and always led to distinct formation of byproducts. It was seen that the stabilizers under study act simultaneously as molecular weight regulators. It was found that the DSC or TGA onset temperatures of oxidation to increase with increasing mole concentration of the stabilizers (be it of phenolic or piper-dine type) added to unmodified PU to form a physical mixture.

Polyurethanes are widely used in the production of flexible foams, car paints, insulating materials, adhesives and other commercial goods. The knowledge of the ultimate stability of polyurethanes (i.e., after thermal, oxidative and photochemical exposure) as well as of methods for properly evaluating the material, thus appears to be of great importance. Polyurethanes are generally characterized pyrolysis coupled with capillary gas chromatography, mass spectrometry and a thermal degradation mechanism. Thermo-sensitive polyurethanes are defined as functional materials with the ability to sense and respond to external thermo-stimuli in a predetermined temperature range. Starch is a biodegradable polymeric material that is, renewable and available worldwide at low cost making it attractive as a substitute for petroleum based thermoplastics. Polymer blends of this type are currently receiving increased attention because of the biodegradability of the Starch component. Starch is a natural renewable polysaccharide obtained from a great variety of crops and is a promising raw material for production of biodegradable products [8]. PUs are a broad group of elastomers that contain one common element, a urethane linkage and these segments typically phase separate, while providing biocompatibility and biodegradation due to the biobased feedstock. Biocompatibility is required in the current PUs for preparation of thermoplastic Starch blends. Structure, tensile and impact properties were characterized.

II. MATERIAL AND METHODS

A. Materials

The polyurethane system with polyol (Part A) and isocyanate (Part B) are processed under room temperature (20-25 C). Starch is an organic material, unmodified maize starch (Gelose 80).

B. Sample preparation

A 250 mL beaker equipped with a mechanical stirrer, thermometer was used as a reactor to prepare the polyurethanes polyol (Part A) of 100 parts per hundred added with isocyanate (Part B) of 64 parts per hundred were changed into a 100 mL beaker. Than the polyurethane mix was added with the sequined quantity of filler (Starch) and stirred mechanically to disperse the starch uniformly into the prepolyurethane mix. The soft segment-forming reaction was carried out at 40 C for about 4.0 h, followed by hard-segment-forming reaction at 60 C to 70 C for

2.0 h. The neutralization reaction was carried out at 40 □C for about 20-30 mix.

Table 1 Identification of abbreviations for Starch-PU nanocomposites combined with isocyanate.

Samples	PU (g)	Starch (g)	Isocyanate (g)
PU	21.87	0	13.90
0.1% Starch-PU	21.85	0.037	13.99
0.5% Starch-PU	21.80	0.109	13.95
1.0% Starch-PU	21.74	0.217	13.91
1.5% Starch-PU	21.67	0.325	13.87
2.0% Starch-PU	21.61	0.432	13.83

C. Test Methods

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is a technique used to characterize and measure dynamic moduli of materials. It is most useful for observing the viscoelastic nature of polymers. Dynamic mechanical measurements were determined using a Perkin-Elmer Pyris Diamond DMA that consisted of a temperature programmer, temperature controller, and force control and dimension change sensor. DMA measures dynamic moduli, both storage (E') and loss modulus (E''). DMA spectra were taken in tensile mode at 1 Hz frequency over a broad temperature range (T= -50 °C to 150 °C) with a programmed heating rate of 2 K.min-1 using single cantilever geometry, force applied was 6.35 N, with displacement 20 µm. Composites with dimensions of 11.0 mm x 20.0 mm x 2.9 mm, prepared by compression press were used for analysis.

Thermogravimetry

Thermal stability and composition were assessed using Thermogravimetry (Perkin-ElmerPyris 1 TGA, 30-950 °C at 10 K.min^{-1} under nitrogen with change to air at 700 °C). TGA was used for thermal study of the composites to investigate degradation steps. In this study, each sample weighing about 7-8 mg was heated from 50-950 °C at a rate of 10 K.min^{-1} under nitrogen atmosphere. The composite samples were observed to exhibit change in mass with the change in temperature. Thermal degradation of the components and the amount of moisture absorbed by the composite sample were measured. The mass of the sample was measured as a function of temperature as the sample was heated and a thermo gram was recorded.

III. RESULTS AND DISCUSSION

D. Dynamic Mechanical Analysis

The dynamic mechanical analysis involves measuring the viscoelastic response of a material subjected to a sinusoidal oscillation. This oscillation may be in the form of a strain (strain controlled instrument) or a stress (stress controlled instrument). The sample was tested in the linear viscoelastic region (LVR), where the modulus is independent of the applied stress or strain magnitude. The stress or strain may be applied to the sample in a variety of means such as tension, compression or torsion. This technique was used to characterize the mechanical properties of materials with respect to temperature or stress rate (frequency). Information on glass transition (T_g) temperatures, storage and loss moduli, and heat deflection or softening temperature can be determined with this method Figure 1. Knowing the glass transition or softening temperature for the foam can give a rapid assessment of expected performance at higher temperatures or even expected performance under compression/creep conditions. The DMA provides this data from direct physical testing.

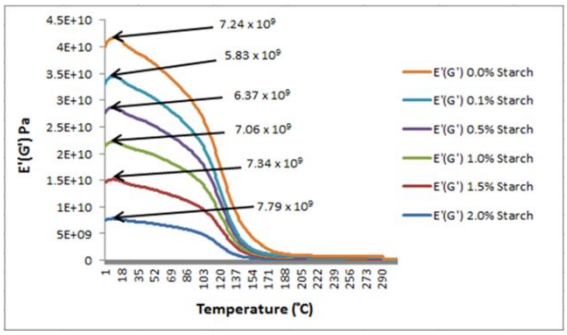

Figure 1 Storage modulus of Starch–PU nanocomposites

The loss modulus curves obtained from DMA of pure PU and Starch–PU nano-composite are shown in Figure 2. The loss modulus curves showed that pure PU crystallized at 126 °C, while PU with addition of 0.1 %.w/w of Starch occurred at 129.12 °C. This verified that even the addition of a small amount of Starch increased the crystallization temperature (T_c) of PU. The addition of Starch into PU matrix enhanced the nucleation process for PU crystallization. High surface area of the Starch–PU provided nucleation sites for the PU to crystallize. It can be observed that the enthalpy of crystallization (H_c) reduced significantly. For the nano-composite, attributed to the reduction of PU crystallinity, the effectiveness of Starch–PU acting as a nucleating agent and uniform heat distribution throughout the matrix were due to the high thermal conductivity of the Starch–PU. A narrower crystallization peak of the nano-composite suggested that the spherulite size distribution was narrower compared with pure PU.

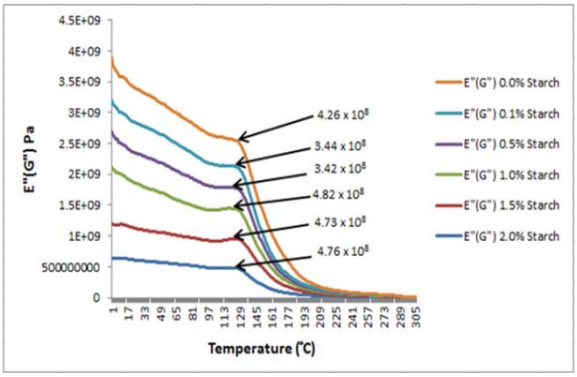

Figure 2 Loss modulus of Starch–PU nanocomposites

The presence of Starch–PU reduced the spherulite size distribution as it acted as a medium for the PU melt to form uniform spherulites. The size of the spherulite in Starch–PU was suggested to be smaller compared with that of pure PU because the PU matrix may be intercalated between the nanotubes, thus reducing the chance of forming large spherulites due to space confinement. Figure 3 indicates that there was little change in melting temperature (T_m). Pure PU melted at 166.23 °C while Starch–PU melted at 166.08 °C. Differences in the magnitude of enthalpy of melting (H_+) between the pure PU and Starch–PU were due to factors discussed above. It can be proposed that there exists a region of trenscrystallinity at the interface based on difference in the peak area. Thus further characterization techniques should be done to validate this.

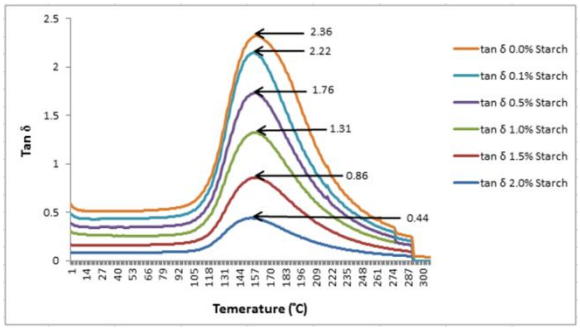

Figure 3 Loss tangent of Starch–PU nanocomposites

E. Thermogravimetry

The TGA curves for pure PU and Starch-PU nano-composites at different loading are shown in Figure 4. For the Starch-PU, the whole degradation step can be observed from 30 □C to 1021 □C. The weight loss of Starch-PU at 284 □C was found to be 15% indicating high thermal stability compared to the Neat PU. The reduction in weight about 75wt.% at 850 □C may be representing the decomposition of the PU and Starch composites, though further heating was done to observe decomposition steps of the Starch-PU composites at higher temperatures. A double degradation step was observed for Starch-PU as seen from the Figure 4. This implies that the thermal stability of Starch-PU is superior to that of Neat PU.

For un-reinforced PU matrix, the molecular chain breaks and chars, while the Starch-PU degradation requires more energy to break depending upon the loading level. It can be seen from the curve that the thermal stability of PU raises as the Starch loading increased from 0.1 to 2.0wt.%. Pure PU starts to degrade at 283 □C and was completely decomposed around 810 □C, while PU with 0.1 and 2.0 wt.% Starch-PU starts to degrade at 284 □C and 292 □C respectively. There was a significant change in the degradation temperature of PU even at 0.1wt.% addition of Starch-PU at 50%wt loss. The presence of Starch in the PU matrix act as thermally conductive pathways that reduced the heat buildup in the matrix. This indicates that Starch-PU is useful for obtaining a nano-composite with high thermal stability but the issues of dispersion, thermal barriers and interfacial adhesion as the dominating parameters will be addressed in the further research.

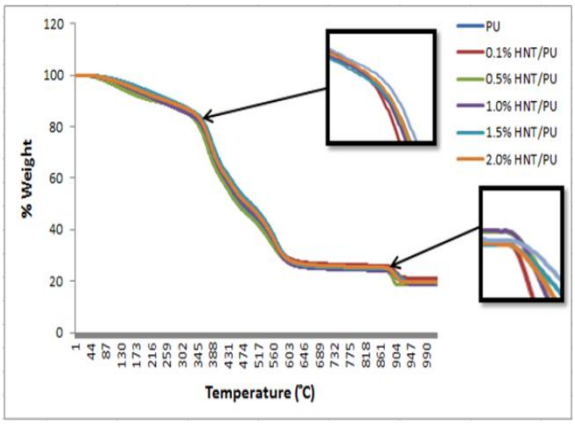

Figure 4 Thermogravimetry of Starch-PU nanocomposites

CONCLUSIONS

The thermal degradation of the Starch-PU composites is more gradual and the temperature increased when compared with the control PU without the presence of Starch. This was due to the presence of the Starch, which has higher thermal stability than the control polyurethane. However, more apparent observations on the degradation of the components within the Starch could have been observed at a slower heating rate.

ACKNOWLEDGEMENTS

This work was financially supported by the Malaysia Department of Energy at Los Alamos National Laboratory, operated under the University of Malaysia under contract W-7405-ENG-36. Funding was provided by the laboratory Directed Research and Development program and the enhanced Surveillance program at Los Alamos. Thank to Bruce Orler and Debra Wrobleski for Specimen preparation and mechanical characterization. DGT wishes to acknowledge LANL Director's Funding postdoctoral Support.

REFERENCES

[1] Yilgor, I., EmelYilgor, I. GucluGuler,"Thomas C. Ward, Garth L. Wilkes. FTIR investigation of the influence of diisocyanate symmetry on the morphology development in model segmented polyurethanes", Polymer 2006; 47: 4105–4114.

[2] Marney, D. C. O., L.J. Russell, D.Y. Wu, T. Nguyen, D. Cramm, N. Rigopoulos, N. Wright, M. Greaves,"The suitability of halloysite nanotubes as a fire retardant for nylon 6", Polymer Degradation and Stability 2008; 93: 1971–1978.

[3] Hetflejs, J., StanislavSabata, JiríPodesva, Jana Kovárová, LubosProkupek, Milos Netopilík, JiríSpevácek, Jan Sýkora,"Novel stabilizers acting simultaneously as molecular-weight regulators in soluble elastomeric

polyurethanes", Polymer Degradation and Stability 2010; 95: 579-586.

[4] Marta Malíková, JozefRychlý, LydaMatisová-Rychlá, KatarínaCsomorová, IvicaJanigová, Heinz-Wilhelm Wilde,"Assessing the progress of degradation in polyurethanes by chemiluminescence. I. Unstabilised polyurethane films", Polymer Degradation and Stability 2010; 95: 2367-2375.

[5] Yi Chen, Yan Liu, Haojun Fan, HuiLi, Bi Shi, Hu Zhou, BiyuPeng,"The polyurethane membranes with temperature sensitivity for water vapor permeation", Journal of Membrane Science 2007; 287: 192–197.

[6] A.L. Chaudhary, M. Miler, P.J. Torley, P.A. Sopade, P.J. Halley,"Amylose content and chemical modification effects on the extrusion of thermoplastic starch from maize", Carbohydrate Polymers 2008; 74: 907–913.

[7] G.F. Fanta, C.L. Swanson & W.M. Doane," Complexing between starch and poly (ethylene-co-acrylic acid)-a comparison of starch varieties and complexing conditions", Carbohydrate Polymers 1992;17: 51-58.

[8] X.F. Ma, J.G. Yu, J.J. Wan,"Urea and ethanolamine as a mixed plasticizer for thermoplastic starch", Carbohydrate Polymers 2006; 64: 267–273.

[9] Nagle, D. J., Mathew Celina, Llewellyn Rintoul, Peter M. Fredericks", Infrared microspectroscopic study of the thermo-oxidative degradation of hydroxyl-terminated polybutadiene/isophorone-diisocyanatepolyurethane rubber", Polymer Degradation and Stability, 2007; 92: 1446-1454.

[10] Xu, Y., ZoranPetrovic, Sudipto Das, Garth L. Wilkes,"Morphologyband properties of thermoplastic polyurethanes with dangling chains in ricinoleate-based soft segments", Polymer 2008; 49: 4248-4258.

★★★