Nanomechanical characterization of UV curable hyperbranched polymers

J. Kim, Z. Chen, B. Chisholm and S. Patel
Center for Nanoscale Science and Engineering, North Dakota State University, 1805 NDSU Research Park Drive, Fargo, ND 58102 USA

ABSTRACT

Hyperbranched polymers were explored to develop UV-curable, protective coatings for aluminum 2024-T3 and their viscoelastic and mechanical properties were characterized using nanoindentation techniques. The coating system consists of a hyperbranched polyester acrylate (CN2300, Sartomer Inc), a modified hyperbranched polyols, and a photoinitiator (Irgacure 2022). Two different hyperbranched polyols (DPP130 and P1000, Perstorp Polyols Inc.) were partially modified with acryloyl chloride to give acrylate functionality for UV curing. The quasi-static indentation results showed that the reduced modulus and hardness of the UV-cured coatings were significantly affected by the type and amount of the modified polyols.

Keywords: hyperbranched polymers, nanoindentation, UV curable

1 INTRODUCTION

Hyperbranched polymers (HBPs) possess unique physical and chemical properties such as low viscosity and high density of terminal reactive groups compared to their linear analogs [1,2]. The rheological characteristics and high functionalities also make HBPs useful in UV-curable coating applications, showing fast cure, low shrinkage, formulation flexibility, and scratch resistance [3,4]. Even though the blends mixed with HBPs were extensively investigated, few studies on mechanical characterization of the UV curable HBPs are found [4,5]. Klang [4] and Schmidt et al [5] measured Young's modulus of HBPs using a tensile tester. However, the UV curable HBPs result in hard, brittle, and thin films, so that instrumented nanoindentation technique provides a good tool to characterize their mechanical properties. The indentation normally is operated in quasi-static mode, controlled by a feedback loop (load or displacement control). Reduced modulus and hardness are calculated using the contact area and the slope (stiffness) of the unloading segment of the resulting force-penetration depth curve [6]. The quasi-static indenting was conducted on the UV-cured thin films (~100 μm) in a displacement feedback control. The films were prepared from a hyperbranched polyester acrylate, a polyol partially modified with acryloyl chloride, and a photoinitiator, which was initially designed to develop UV-curable, corrosion-resistant coatings. The modified polyol was added to the polyester acrylate in an effort to enhance adhesion of the coating to an aluminum surface (2024-T3). In this work, mechanical properties of the UV-cured hyperbranched polymers were characterized by the nanoindentation technique and the effect of the modified polyols on structure-properties of the final coating was investigated.

2 EXPERIMENTS

2.1 Materials

Hyperbranched acrylate polyester (CN2300, MW=1304 g/mole, 8 acrylates groups per molecule, acrylate equivalent weight=163) and photonitiator (Irgacure 2022) were purchased from Sartomer Company Inc. and Ciba Specialty Chemicals Inc., respectively. Two different hyperbranched polyols, DPP130 and P1000, were supplied by Perstorp Polyols Inc. DPP130 is a six hydroxyl functional ethoxylated hyperbranched polyether polyol (MW=830 g/mole, hydroxyl equivalent weight=138) and P1000 is a fifteen hydroxyl functional hyperbranched polyester polyol (MW=1500 g/mole, -OH EW=100). Tertiary amine, HPLC grade acetone, and THF were purchased from Sigma-Aldrich Company. All the chemicals were used as received. The acrylated polyols were synthesized as follows: 0.005 mole of P1000 (7.5g) and 0.05 mole of acryloyl chloride (4.53g) were mixed with 15 g of acetone/THF (50:50 wt%) co-solvent for 10 min in a conical reactor equipped with an ice-water bath. 0.1 mole of tertiary amine (~ 10 g) was then slowly charged into the reaction vessel. White precipitate was formed with the addition of tertiary amine. The reaction mixture was allowed to further mix for 30 minutes before filtration. Solvents were evaporated from the filtered clear solution to obtain the final product. The modification procedure of DPP130 with acryloyl chloride was the same as P-1000, in which 0.01 mole of DPP-130 (8.3g), 0.03 mole of acryloyl chloride (2.71g), 0.05 mole of tertiary amine (5 g) and 10 g of acetone were used. ADPP and AP denote the DPP130 and P1000 partially modified with acryloyl chloride, respectively. The chemicals used in this study were summarized in Table 1.

2.2 Preparation of UV-curable coatings

Ten different coating formulations were prepared by adding ADPP and AP to CN2300, increasing loading amount by 10 wt% up to 50 wt% (Table 2). The control was prepared using CN2300 alone. A constant amount of the photoinitiator (4 wt%) was added to the each solution and mixed thoroughly in a 20 ml vial using a magnetic stir bar. The eleven coating solutions were then deposited onto a 4” × 8” Al 2024 panel with the aid of a 3 × 4 stamped Teflon mask to obtain dry film thickness of ~ 100 μm. The coatings were cured in air by passing two times through Fusion LC6B Benchtop Conveyor system with F300 lamp at belt speed 20 ft/min (Fusion UV systems, Inc). The UV light intensity measured using a NIST Traceable Radiometer (International Light model IL1400A) was approximately 2200 mJ/cm^2.

Table 1: Descriptions on chemicals used in the study.

Abbreviation	Description
CN2300	An eight acrylate functional hyperbranched polyester (MW=1304 g/mole, acrylate equivalent weight=163)
DPP130	A six hydroxyl functional ethoxylated hyperbranched polyester polyol (MW=830 g/mole, hydroxyl equivalent weight=138)
P1000	A fifteen hydroxyl functional hyperbranched polyester polyol (MW=1500 g/mole, hydroxyl equivalent weight =100).
ADPP	DPP partially modified by acryloyl chloride(MW=990 g/mole, three hydroxyl and three acrylate functional groups in a molecule, Acrylate equivalent weight=330)
AP	P partially modified by acryloyl chloride (MW=2040 g/mole, five hydroxyl and ten acrylate functional groups in a molecule, Acrylate equivalent weight=204)

Table 2: Coating formulations.

Chemicals	Control (wt %)	ADPP10 to ADPP50 (wt %)	AP10 to AP50 (wt %)
CN2300	96	From 86 to 4	From 86 to 46
ADPP	0	From 10 to 50	0
AP	0	0	From 10 to 50
Photonitiator	4	4	4

2.3 Indentation methods

Quasistatic indentation was performed using Hysitron Triboindenter (Hysitron Incorporated, Minneapolis, MN) mounted with a 5 µm conospherical diamond tip. The contact area (A) was calculated using the following formula.

$$A = -\pi h_c + 2\pi r h_c^2 \tag{1}$$

Where, r is a radius of the tip and h_c is contact depth.

2.3.1 Quasi-static measurement

Quasistatic nanoindentation was implemented in a displacement control to obtain modulus and hardness of the test sample from a resultant force-penetration depth curve with the following feedback controlled load function - a loading rate of 100 uN/s, a hold time of 30 s at the maximum force to allow viscoelastic and plastic dissipation, and an unloading rate of 100 uN/s. The tip moved towards the surface at a lift height of ~ 500 nm away from the surface and started indenting in the surface until it reached a maximum displacement (~1000nm). The preload at which the indenter will start its indentation on the surface was set to 2 uN. The contact depth and area were calculated using equations 1 and 2.

$$h_c = h_{\max} - 0.75\frac{P_{\max}}{S} \tag{2}$$

Where, h_c is contact depth, h_{max} maximum indenting depth, P_{max} force at the maximum indenting depth, and S stiffness.

The reduced modulus of the specimen (E_r) was then calculated using equation 3 with the known values of contact area (A_c) and the slope (stiffness, S) of the initial portion of the unloading curve. The hardness (H) was calculated using equation 4.

$$E_r = \frac{S\sqrt{\pi}}{2\sqrt{A_c}} \tag{3}$$

$$H = \frac{P_{\max}}{A_c} \tag{4}$$

The reduced modulus, E_r is defined as $\frac{1}{E_r} = \frac{(1-\upsilon_i^2)}{E_i} + \frac{(1-\upsilon_s^2)}{E_s}$. υ is Possion's ratio and the subscript i and s represent the indenter tip and the indented specimen, respectively.

Hardness and modulus reported here are averaged values of six indentations. Multiple indentations on the 11 coatings prepared on the aluminum substrate were conducted automatically.

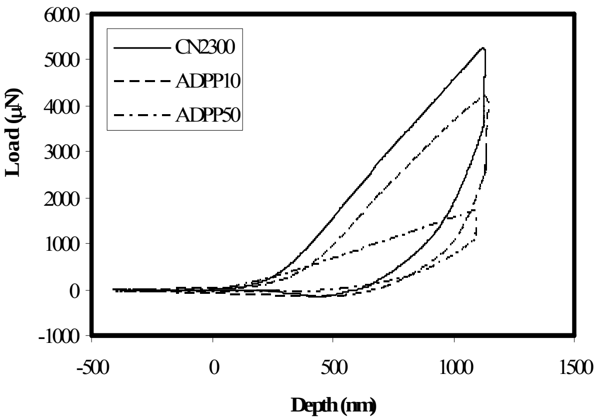
3 RESULTS AND DISCUSSION

3.1 Quasi-static indentation

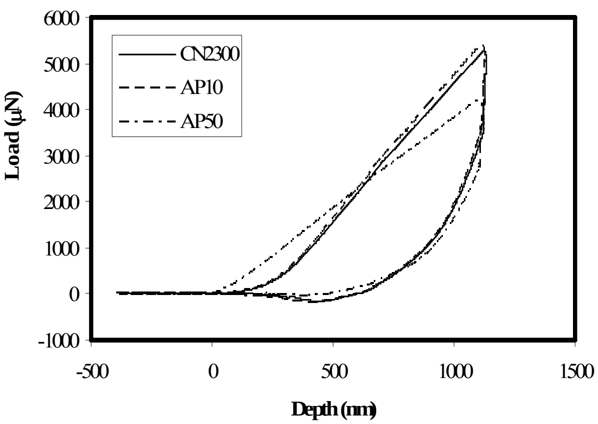
3.1.1 Load-displacement behavior

Figure 1 shows the typical loading-hold-unloading profiles of the UV cured hyperbranched polymers (~100nm). The indentation started at a lifted height of ~ 500 nm away from the surface. The tip was approaching toward the surface and slightly jumped in when the tip sensed the surface. The tip indented into the surface to the predefined maximum displacement (~1000 nm). As the tip was withdrawing from the maximum depth, the coatings recovered elastic portion of the deformation, leaving a residual impression in the surface of the UV-cured coatings. The plasticity index Ψ, defined by the ratio of plastic work to total work during the loading and unloading indentation [7], is ~ 0.74 for all the samples, indicating that the UV-cured films showed considerable plastic deformation. It was also noticed that force (P_{max}) at the maximum penetration depth was relaxed during the hold time. As the amount of ADPP increased to 50 wt%, the P_{max} significantly decreased from 3570 µN to 1010 µN, showing a more significant force relaxation at the maximum depth. On the other hand, the P_{max} was slightly decreased by the incorporation of AP to

CN2300. For AP50 coating, 2740 μN of force is required to penetrate the pre-assigned maximum displacement, which is much higher than the corresponding ADPP50 coating.



(a)



(b)

Figure 1: Load-displacement data for the hyperbranched polymers (CN2300) blended with the modified polyols; (a): ADPP, (b): AP.

3.1.2 Modulus and Hardness

Oliver-Pharr method calculates material stiffness on the assumption that only the elastic deformation is recovered during the unloading. Thus, the reduced modulus and hardness were obtained from the initial unloading segment of the load-displacement response evolved after the force was relaxed at the maximum displacement. As the weight percent of the modified polyols (ADPP) in the coating matrix increased up to 50, the reduced modulus of the UV-cured coatings dramatically decreased from 2.5±0.02 GPa to 0.7±0.02 GPa (Figure 2). This is primarily due to the flexible ether linkages in ADPP backbone and low crosslink density[3]. As the modulus decreases, hardness (H), which represents a material ability to resist indentation, linearly decreases. This linear correlation between hardness and modulus was also observed in other studies [8]. On the other hand, the coatings blended with AP gradually decreased their mechanical properties. The reduced modulus at the loading of 50 wt% of AP decreased to 1.8±0.06 GPa. As shown in Table 1, ADPP has less acrylate functionality than AP and contains flexible ether groups, so the mechanical properties of the UV-cured hyperbranched films were more significantly affected by the incorporation of ADPP to CN2300. A similar trend was observed in the conventional DMTA measurement (TA instrument, Q800), in which glass transition temperature decreased as the amount of ADPP and AP increased. However, the indentation moduli differ from the Young's moduli measured using a tensile tester (MTS systems corporation, Insight 5 EL). The tensile Young's moduli are lower than the indentation Young's moduli calculated with υ=0.3. The tensile moduli of the coatings blended with ADPP more sharply decrease, as also illustrated in the static indentation results.

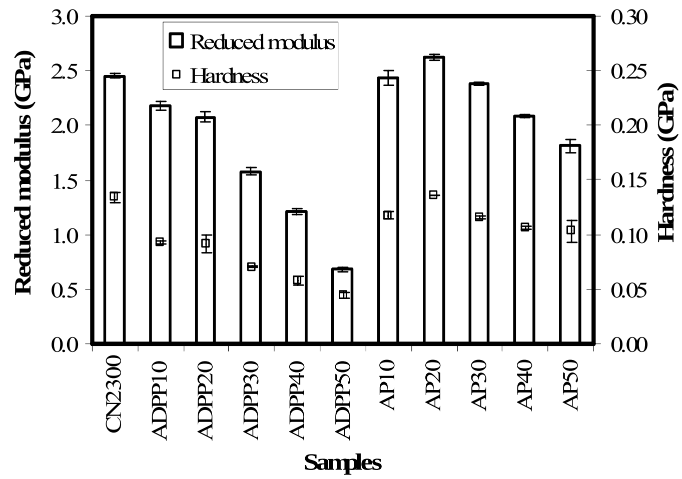


Figure 2: Indentation modulus and hardness of the samples

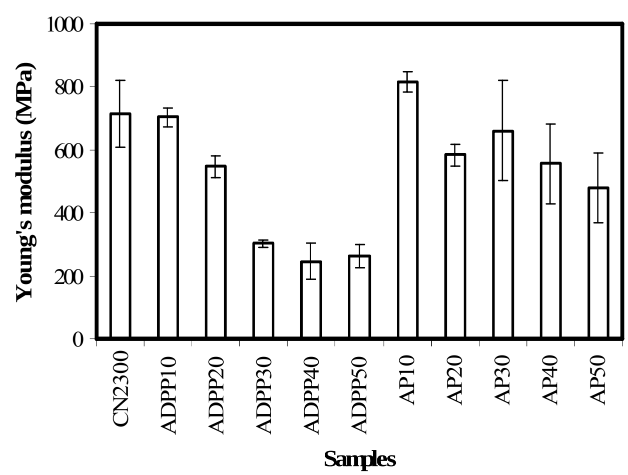


Figure 3: Young's moduli measured by the tensile test. The test speed is 1 mm/min and the modulus was calculated at 0.5% strain.

4 SUMARY

Mechanical and viscoelastic properties of hyperbranched polymers were measured using nanoindentation technique. The UV cured thin films exhibit an elasto-plastic behavior and considerable force relaxation. The moduli of the films calculated using Oliver-Pharr method was higher than those obtained by tensile tests. As the amount of the ADPP increased, the film becomes flexible due to the ether linkage, leading to a low hardness and modulus. On the other hand, incorporation of AP to CN2300 up to 30 wt % did not show any significant impact on mechanical properties. As the amount of AP further increased, the modulus and hardness of the coatings decreased probably due to decrease in crosslink density of the matrix.

REFERENCES

1. A. Hult, M. Johansson and E. Malmstrom, "Hyperbranched polymers", Advances in Polymer Science, 143, 1, 1999.
2. Y.H. Kim and O.W. Webster, "Hyperbranched Polyphenylenes", Macromolecules, 21, 5561, 1992.
3. Z. Chen and D.C. Webster, "Study of the effect of hyperbranched polyols on cationic UV curable coating properties", Polym. Int. 56, 754, 2007.
4. J.A. Klang, "Radiation curable hyperbranched polyester acrylates", Sartomer Inc. technical report.
5. L.E. Schmidt, D. Schmah and Y. Leterrier, J.E. Manson, "Time-intensity transformation and internal stress in UV-curable hyperbranched acrylates", Rheol. Acta. 46, 693, 2007.
6. W.C. Oliver and G.M. Pharr, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, J. Mater. Res. 7, 1564, 1992.
7. B.J. Briscoe, L. Fiori and E. Pelillo, "Nano-indentation of polymeric surfaces", J. Phys. D: Appl. Phys. 31, 2395, 1998.
8. M.L. Oyen, "Nanoindentation hardness of mineralized tissures", Journal of biomechanics, 39, 2699, 2006.