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ORIGINAL PAPER

Hyperbranched waterborne polyurethanes

J. H. Park · S. Y. Bae · B. K. Kim

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Abstract A hyperbranched polyol (HBP), viz. hyperbranched 2,2-bis(hydroxymethyl) propionic acid (MPA) polyester-16-hydroxyl, was incorporated chemically into waterborne polyurethane by a covalent bond as a multifunctional chain extender or chemical crosslink for isocyanate (NCO)-terminated PU prepolymers. In addition, the effects of HBP incorporation on the particle size, tensile properties in the glassy and rubbery states, thermal stability, contact angle, and hardness were examined. After HBP incorporation, the particle size initially decreased during the dispersion step. With time, the particle size increased due to the swelling of HBP, and there was an increase in the contact angle, initial modulus, break strength, and decomposition temperature of the dispersion cast film. In particular, the largest increases in these properties were obtained when the NCO index was unity.

Keywords Waterborne polyurethane · Hyperbranched polyol · Crosslinking · Multifunctional chain extender · Dispersion

Introduction

As a green technology, waterborne polyurethane (WPU) is a versatile eco-friendly material that is being used increasingly in coatings, sealants, and adhesives for wood and automobiles, as well as for a range of flexible substrates, such as textiles, leather, paper, and rubber [1–6].

Generally, WPUs have a slower drying rate and the development of adhesion than conventional solvent borne polyurethane (PU). In addition, their applications have been limited by the type of raw material and manufacturing process. Fortunately, the problems related to their properties and processing can be resolved

J. H. Park · S. Y. Bae · B. K. Kim (✉)
Department of Polymer Science & Engineering, Pusan National University, Pusan 609-735, Korea
e-mail: bkkim@pusan.ac.kr; bkkim@pnu.edu

by proper molecular designs, chemical hybridization with other polymers [7–10], and composite formation with nano-sized materials [11–17].

The modification of WPU by hybridization includes full- and semi-interpenetrating polymer network (IPN) (physical), AB crosslinked polymer (ABCP) (chemical) with other polymers, typically with acrylate and polystyrene, and organic–inorganic chemical hybrids via a sol–gel technique. The fine dispersion of the second component in PU and enhanced properties have generally been obtained with chemical hybridization. For example, 1 % silica particle, which is bonded covalently to PU as a multifunctional crosslink, approximately doubled the Young's modulus, yield strength and break strength of the conventional WPU [18].

A hyperbranched polymer is a hydroxyl functional aliphatic polyester that consists of a polyol core from which branches form a core–shell structure with a large number of hydroxyl groups at the peripheral surface. These reactive groups, in combination with the dense structure, make them less prone to entanglement and hence less viscous and more readily accessible for a reaction [19–21]. Hyperbranched polyester imparts significantly low viscosity and incredibly rapid drying for alkyds, dramatically increasing the toughening for amine cured epoxies, and rapid curing in WPU by hexakis (methoxymethyl) melamine [22].

With regard to the hyperbranched WPU, effects of structural composition [23, 24], end group [20], chain extenders [25], and polymerization kinetics [26] have been reported. In this study, hyperbranched bis-MPA polyester-16-hydroxyl (hereafter called HBP) was incorporated into WPU as multifunctional chain extender for the NCO-terminated PU prepolymers, where the NCO index (NCO/OH) was 1, 1/2 or 1/4, and the effects of the stoichiometric imbalance and chemical hybridization on the dispersion size, surface properties, mechanical, and thermal properties of the hybrid cast film were studied.

Experimental

Raw materials

Polycaprolactone diol (PCL, Mn = 530, Sigma-Aldrich) was dried and degassed at 80 °C under vacuum for 3 h prior to use. Isophorone diisocyanate (IPDI, Aldrich) was dried over 4 Å molecular sieve prior to use. Hyperbranched bis-MPA polyester-16-hydroxyl, Mw = 1749.79 g/mol (HBP, Aldrich), dimethylol butanoic acid (DMBA, Aldrich), ethylenediamine (EDA, Fluka), triethylamine (TEA, Fluka), and dibutyltin dilaurate (DBTDL, Aldrich) were used as received.

Synthesis

Table 1 lists the procedure for the preparation of WPU. PCL diol was placed in a 500-mL four-necked flask with a mechanical stirrer, thermometer, and condenser with a drying tube. A molar excess of IPDI was then added and the reaction was carried out at 70 °C in a constant temperature oil bath to synthesis the isocyanate terminated soft segments. Then, DMBA and additional amount of IPDI were added

Table 1 Recipe for the preparation of WPU/HBP hybrids [unit in g (moles)]

Series	PCL	IPDI	DMBA	EDA	Hyperbranched polyol[a]	[NCO]:[OH][b]
WPU	18.611 (1.05)	10.489 (1.43)	0.900 (0.18)	0.361 (0.18)	–	–
H11				–	1.313 (0.0225)	1:1
H12				–	2.625 (0.0450)	1:2
H14				–	5.250 (0.0900)	1:4

[a] Hyperbranched bis-MPA polyester-16-hydroxyl

[b] Equivalence ratios of prepolymer (NCO) to hyperbranched polyester (OH)

and reacted to build up the ionic segments on the soft segment termini. In this step, an excess amount of IPDI was used to obtain IPDI terminations. The prepolymer molecular weight of ~5,000 g/mol was obtained according to the formulation. Then the reaction mixture was cooled to room temperature, and carboxylic acid groups were neutralized by TEA during the next 2 h to form ionomers. Subsequently, HBP dissolved in water, was added to the mixture, and chain extension by HBP or EDA was carried out at 60 °C until the NCO peak in FT-IR disappeared completely. A stable aqueous dispersion of hyperbranched PU with a solids content of ~30 % was obtained. Detailed procedures to prepare WPU are available elsewhere [27]. The overall reaction scheme to prepare the hyperbranched WPU is shown in Scheme 1.

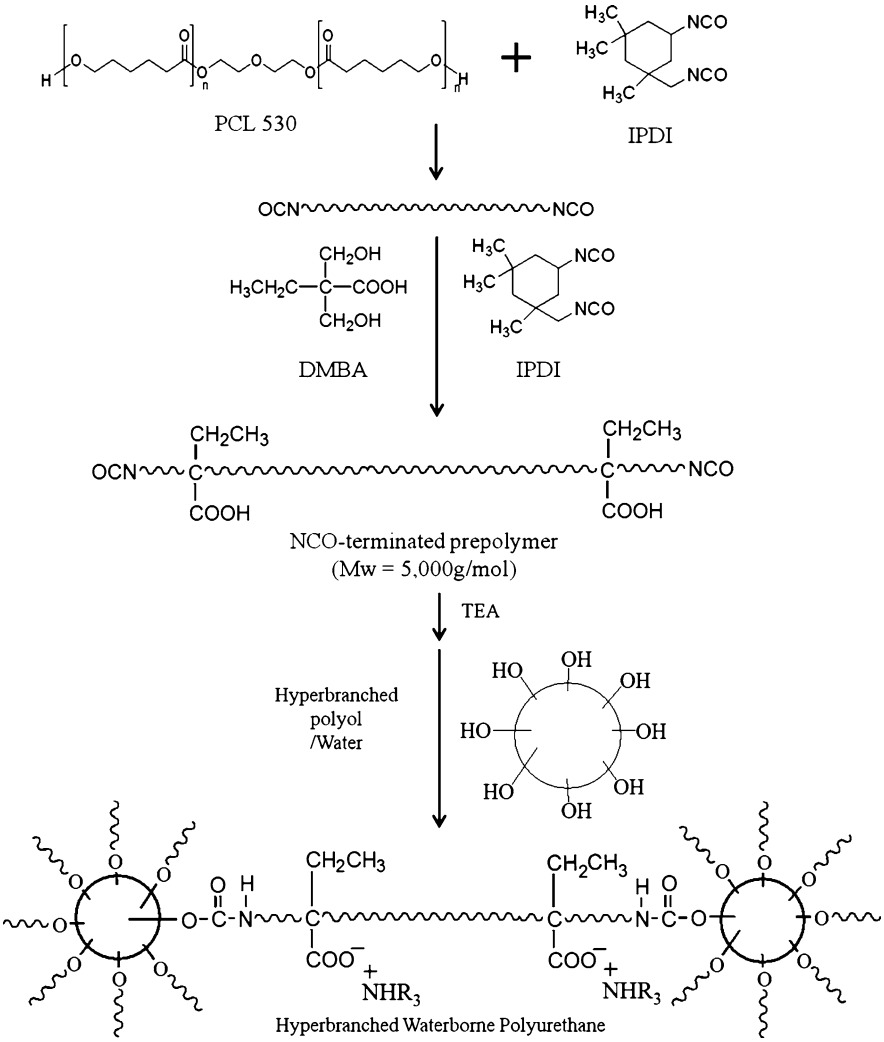
Characterizations

Fourier transform infrared (FT-IR, Mattson Saterllite) spectroscopy was performed to monitor the progress of the reaction and confirm the chain extension reaction of NCO termini of the prepolymer with the OH groups of HBP. The samples were prepared by casting films on a KBr pellet.

The number average diameter of the dispersions was measured using a light scattering method (Submitron Particle Size Analyzer N5, Beckmann Coulter) employing a He–Ne laser with a wavelength of 633 nm. The sample was first diluted in deionized water to 0.5 %, followed by an ultrasonic wave treatment to homogenize the dispersion.

X-ray diffraction (XRD, Rigaku Miniflex) patterns of the cast film were taken at a Cu Kα, wavelength of 1.5418 Å at a speed of 1°/min. The tensile properties were measured using a universal testing machine (Lloyd LRX plus) at a crosshead speed of 500 mm/min with specimens prepared according to ASTM-1822. A mean of five measurements is reported. The thermal stability was determined by thermogravimetric analysis (TA Instruments, TGA Q50). Typically, 8–10 mg of the sample was placed in an alumina crucible and heated from room temperature to 600 °C at 5 °C/min under a nitrogen atmosphere.

The contact angles of the dispersion cast films with deionized water were measured using a conventional contract angle goniometer (G-1, Erma). The tests were conducted at room temperature and at least five runs were made to report the average. The Shore A hardness was measured using an indentation hardness tester



Scheme 1 Overall reaction scheme to prepare the hyperbranched waterborne polyurethane

according to ASTM D 2240–75. Eight sheets with a 1 mm thickness were stacked to about 8 mm thickness. The measurement was carried out by pressing the sample sheet on a type-A durometer at a load of 9.8 N.

Results and discussion

FT-IR measurements

Figure 1 shows the FT-IR spectra of the PU prepolymer, after dispersion (WPU), and after chain extension (WPU/HBP hybrid). The NCO absorption peak at

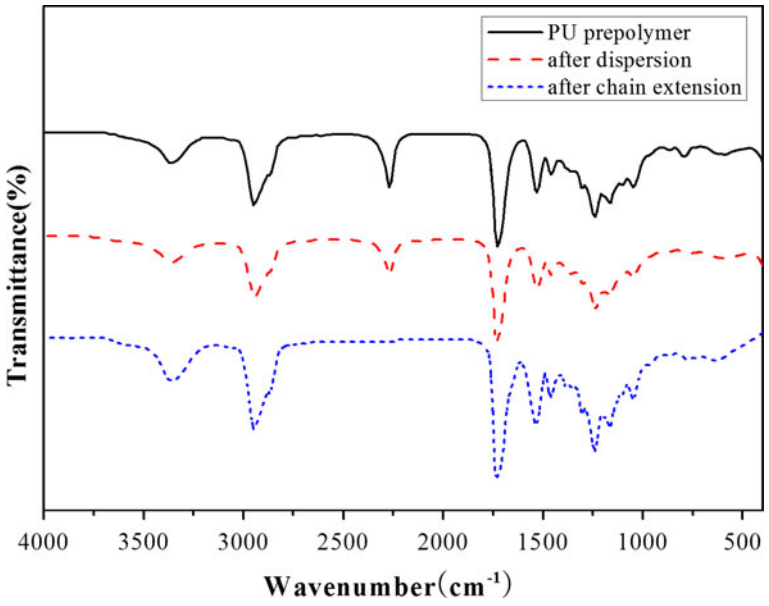


Fig. 1 FT-IR spectra of PU prepolymer, after dispersion (WPU), and after chain extension (WPU/HBP hybrid)

2,270/cm observed before and after dispersion had disappeared completely after a reaction of the NCO groups of WPU with the OH groups of HBP, suggesting that the chain extension of WPU by HBP was complete.

Particle size of dispersion

The particle size was measured at two stages of dispersion, immediately after dispersion and after the chain extension reaction of WPU by HBP was complete. The particle size of WPU extended by EDA remained relatively constant in the two stages, but those of the WPU/HBP hybrids increased significantly upon an extension reaction, and the increase was more pronounced with more HBP (Table 2). This suggests that the HBP molecules diffused preferentially into the WPU particles due to the concentration gradient. The particle size of the hybrids was smaller than that of WPU immediately after dispersion. This is due to the high viscosity of HBP dissolved in water, which was added to the prepolymer to make a dispersion. The finer breakup of a dispersed phase with a higher continuous phase viscosity is obtained by assuming shear stress ($\tau = \eta\dot{\gamma}$) continuity at the interface as follows [28]:

$$\dot{\gamma}_{\mathrm{d}} = \eta_{\mathrm{c}}\dot{\gamma}_{\mathrm{c}}/\eta_{\mathrm{d}},$$

where η and $\dot{\gamma}$ are the viscosity and shear rate, respectively, and subscripts c and d denote continuous and dispersed phases, respectively.

XRD profiles

Figure 2 shows the typical XRD profile of the hybrid materials showing that the major diffraction peak intensity at $2\theta = 20°$ decreases as a result of hybridization, i.e., the regularity of chain packing of WPU decreased by chemical hybridization with HBP. No crystalline peak was observed by differential scanning calorimetry (not shown). The relatively small molecular weight of PCL, along with soft and hard segments phase mixing is one explanation.

Tensile properties

The tensile properties of the hybrids were measured at room temperature (24 °C) and 0 °C (Figs. 3, 4). The stress–strain behavior of the hybrids and WPU were typical of elastomers at room temperature, showing homogeneous deformation and stress upturn at high elongation. Upon hybridization with HBP, the initial modulus and break strength increased and the elongation at break decreased. These effects increased as the NCO/OH index approached unity. On the other hand, the stress–strain behavior at 0 °C is typical of a glassy polymer, showing a positive yield, necking, and stress hardening with an elongation at break >500 %. Such high ductility is essential for coating articles to be vacuum formed, such as automobile crash pads. The initial modulus, yield stress, break strength of WPU was increased significantly by hybridization with HBP, and the effect was more pronounced as the index approached unity.

Thermal stability

Segmented WPU is degraded thermally in two steps, one at ~250 °C for the hard segment and the other at ~350 °C for the soft segment. On the other hand, the present WPU is degraded at a single step, suggesting that the WPU is a well phase mixed (Fig. 5). Phase mixing of the soft and hard segments is expected from the relatively small molecular weight of PCL, which does not allow self-crystallization and provides great miscibility with the hard segment via the hydrogen bonds of rich urethane groups. The incorporation of HBP augments decomposition at low temperatures but expedites the process at high temperatures. This suggests that the globular structure of HBP is more stable than the hard segment but less stable than the soft segment because HBP is located among the hard segments connecting them together. Therefore, hard segments are thermally stabilized by the HBP, whereas the

Table 2 Particle size of WPU/HBP hybrid dispersion (unit in nm)

	After dispersion (d1)	After extension (d2)	Δd ($d2 - d1$)
WPU	224.02	228.58	4.56
H11	189.19	206.00	16.81
H12	186.19	220.40	34.21
H14	191.39	240.15	48.76

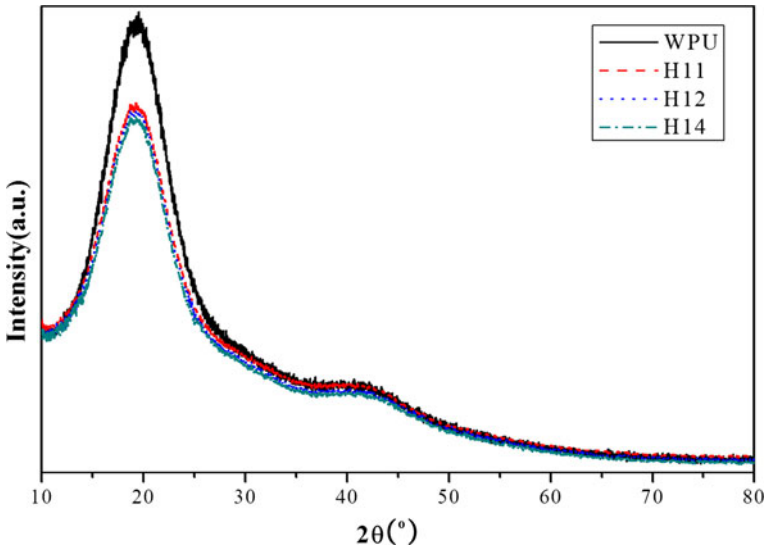


Fig. 2 XRD patterns of the WPU/HBP hybrid films

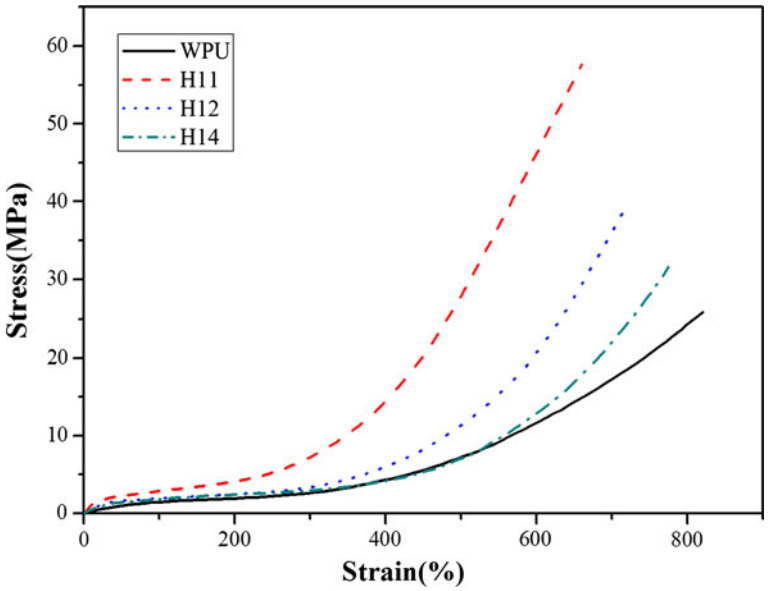


Fig. 3 Stress–strain behavior of the WPU/HBP hybrid films at room temperature (24 °C)

degradation of soft segment is expedited by the less stable HBPs. The increase in decomposition temperature as the index becomes unity suggests that chemical crosslinking augments thermal stability.

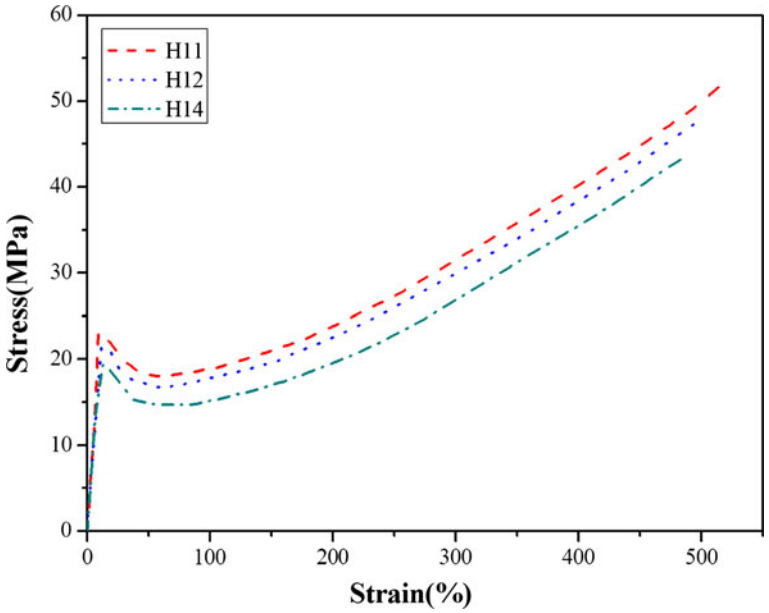


Fig. 4 Stress–strain behavior of the WPU/HBP hybrid films at 0 °C

Contact angle and hardness

The contact angle of the hybrid is expected to increase due to the increased crosslink density but decrease with increasing hydrophilicity of HBP. Figure 6 shows that the contact angle of the hybrid cast film is higher than that of WPU with a maximum when the index is unity. This suggests that the effect of crosslinking is more important. On the other hand, it decreased with decreasing index, indicating that the hydrophilicity of HBP becomes more significant as the HBP content increases, particularly those not crosslinked. The uncrosslinked HBPs migrated preferentially toward the surface due to the lower surface energy of the lower molecular weight substance. Similar results were also noted for hardness (Fig. 7).

Conclusions

The hyperbranched bis-MPA (HBP) polyester that had been chemically incorporated into WPU acted as multifunctional chain extender or crosslink for NCO-terminated PU prepolymers, and the effects along with the NCO index were studied.

The particle size in the hybrids decreased below that of WPU immediately after dispersion due to the viscosity effect, and increased upon extension with HBP due to swelling of the particles with HBPs. The initial modulus and break strength increased and the elongation at break decreased upon hybridization with HBP both in the glassy (0 °C) and rubbery (24 °C) states due to the multiple crosslinking effect of HBP.

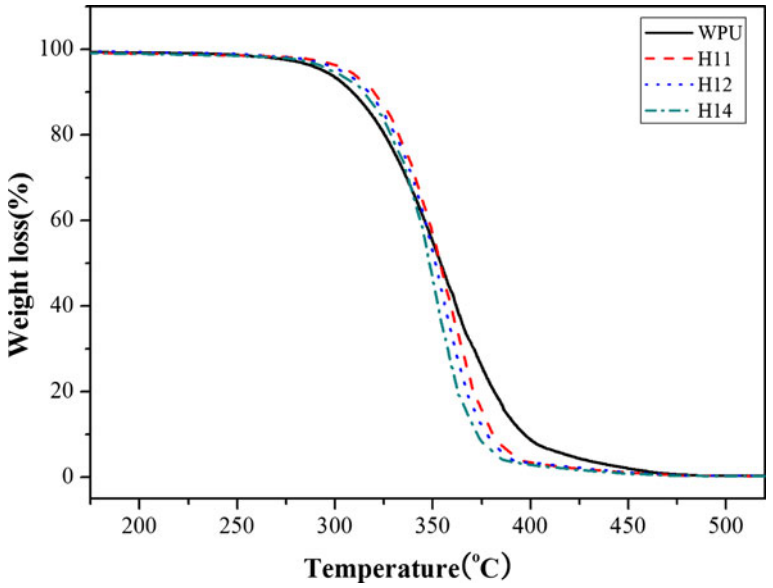


Fig. 5 TGA curves of the WPU/HBP hybrid films

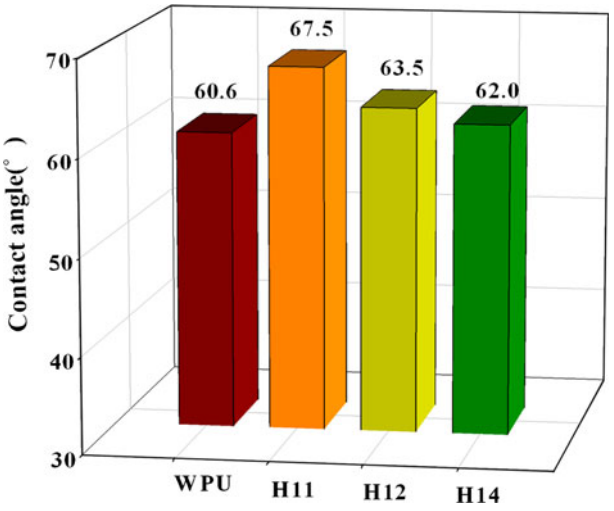


Fig. 6 Contact angle of the WPU/HBP hybrid films

The incorporation of HBP augments the thermal stability of WPU at low temperatures but aggravates it at high temperatures. This suggests that HBP effectively stabilizes the hard segments because most of the HBP is located in the hard segments. On the other hand, those located in the soft segments would expedite soft segment decomposition.

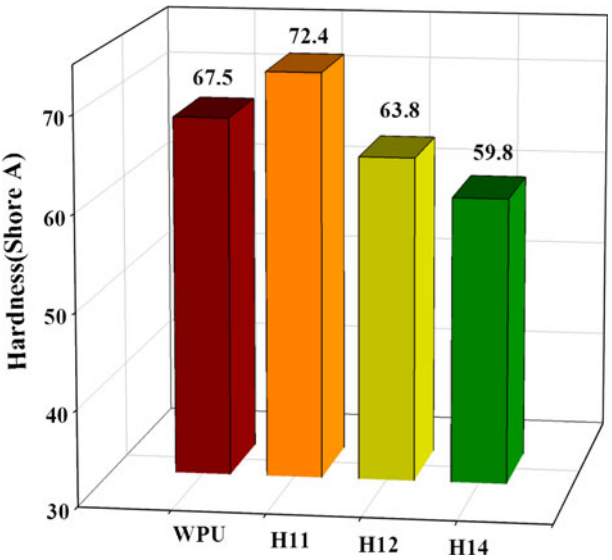


Fig. 7 Shore A hardness of the WPU/HBP hybrid films

The contact angle of the hybrid cast film was greater than the WPU within the experimental range with a maximum when the NCO index was unity. This suggests that the effect of crosslinking resulting in fewer free chain ends is important for controlling the surface energy. Similar results were also obtained for hardness.

Regarding the effects of the NCO index, the one-to-one stoichiometry (NCO/OH = 1) provided materials with the highest modulus, strength, decomposition temperature, contact angle, and hardness, indicating that crosslinking mostly governs the properties, whereas an excess of HBP adversely affects the properties.

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