

*Supporting Information for*

**UV-curable coating crosslinked by a novel hyperbranched polyurethane acrylate  
with excellent mechanical properties and hardness**

Qingyan Zhang,<sup>a</sup> Chi Huang,<sup>b</sup> Hongxia Wang,<sup>a</sup> Mingjie Hu,<sup>b</sup> Houbin Li,<sup>a</sup> Xinghai Liu<sup>\*a</sup>

<sup>a</sup> School of Printing & Packaging, Wuhan University, Wuhan 430072, PR China

<sup>b</sup> College of Chemistry & Molecular Sciences, Wuhan University, Wuhan 430072, PR  
China

\*To whom correspondence should be addressed

E-mail: liuxh@whu.edu.cn; Fax: +86-27-68778433; Tel: +86-27-68778489

### I. Using "di-n-butylamine-acetone" method to monitor the reacting process.

As shown in Fig.1, the reaction of PEG-400 and TDI basically ended 1.5 h later. After adding HEA, this reaction reacted smoothly 6 h until the isocyanate groups ( $-NCO$ ) near 0. As shown in Fig. 2, the reaction of HBPE-OH and TDI basically completed 2 h later. After adding HEA, this reaction kept going 8 h until

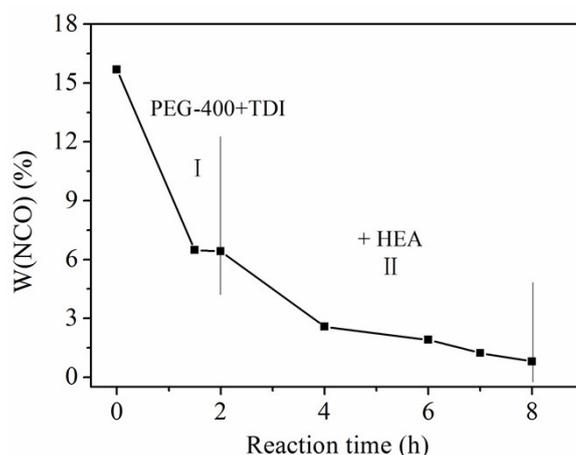


Fig. 1 Change of NCO content in the reacting process to synthesize PUA

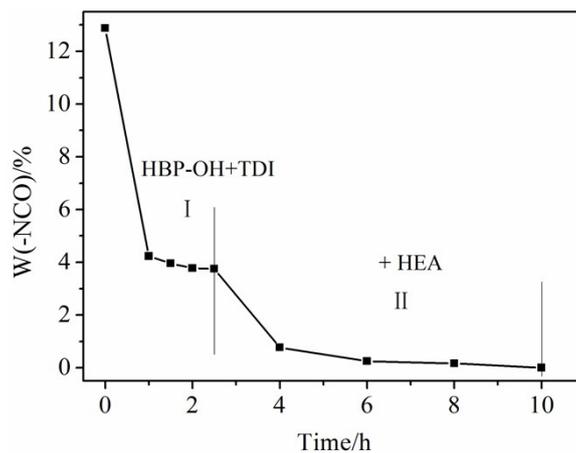


Fig. 2 Change of NCO content in the reacting process to synthesize HBPUA.

the isocyanate groups ( $-NCO$ ) near 0.

### II. FTIR spectra of the UV-curable films after UV-curing

As shown in Fig. 3, the absorption area at  $1635\text{ cm}^{-1}$  completely disappeared after exposing to ultraviolet radiation with 250 s, which indicates completely cured of the UV-curable coatings. (1), (2), (3), (4), (5) represent the curing system containing 0 wt. %, 5 wt. %, 10 wt. %, 15 wt. %, 20 wt. % HBPUA, respectively.

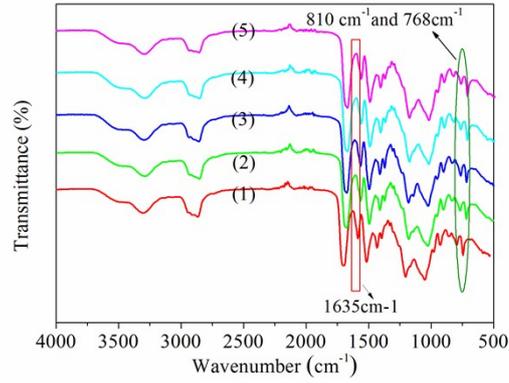


Fig. 3 FTIR spectra of the UV-curable coatings after UV-curing.

### III. The properties of the sample without Nano silica.

Table 1 Properties of the sample without nano silica (a) and the sample with nano silica (b)

	$\sigma_b$ (MPa)	$\varepsilon_b$ (%)	Pencil hardness	Abrasion resistance (mg)
a	7.2	18.9	8H	2.8
b	7.8	19.8	9H	3.4

As can be seen from table 1, the mechanical properties, hardness and abrasion resistance of the sample without nano silica was a little bit lower than the sample that with nano silica. There is no denying that the addition of nano silica has enhanced the mechanical properties, hardness and abrasion resistance of the cured coatings to some extent. But it cannot achieved such a good result as discussed in the manuscript. Besides, as can be seen from Fig.7 of the manuscript, the transmittance of all the UV-curable coatings is beyond 90 %. This is because the content of nano silica is very little, and it was not enough to affect the optical property. Therefore, we set TMPTA-SiO<sub>2</sub> content as constant, and the only parameter was the amount of HBPUA.

### IV. Scanning electron microscopy (SEM)

SEM was employed to further supplement the result obtained by DMA. As demonstrated in Fig. 4a ~ 4c, the fracture surfaces of PUA without HBPUA has a smooth surface, and a rough surface like patch pattern was appeared with 5 % HBPUA. In addition, the patch patterns were disrupted obviously when 10 % HBPUA was added. This can be attributed to that the increased cross-linking points disrupted phase separation. After fracture, a layer of soft phase rearranges to cover the surface of the polyurethane because the soft phase has a lower surface energy and a low  $T_g$ .<sup>1</sup> This soft-phase surface layer creates a smooth surface to minimize the surface area. However, in the samples that phase separation was disrupted by cross-linking points, the soft phase cannot efficiently cover the surface. When the content of HBPUA was

more than 10 %, the reduction of  $T_g$  was observed in Fig. 5a of the manuscript. It can be interpreted that as the content of HBPUA continuously increased, an excess amount of HBPUA was blended in the cured films. Due to the highly branched structure of HBPUA, the excess amount of HBPUA reduced the ratio of rigid volume and increased the flexible polyurethane segment of the cured films. As specified in Fig. 4d and Fig. 4e, the patch pattern liked rough surface was also appeared, but the domain of the patch pattern was larger than that in Fig. 4c. This proves that the disrupted phase separation was repaired partly by the excess HBPUA.

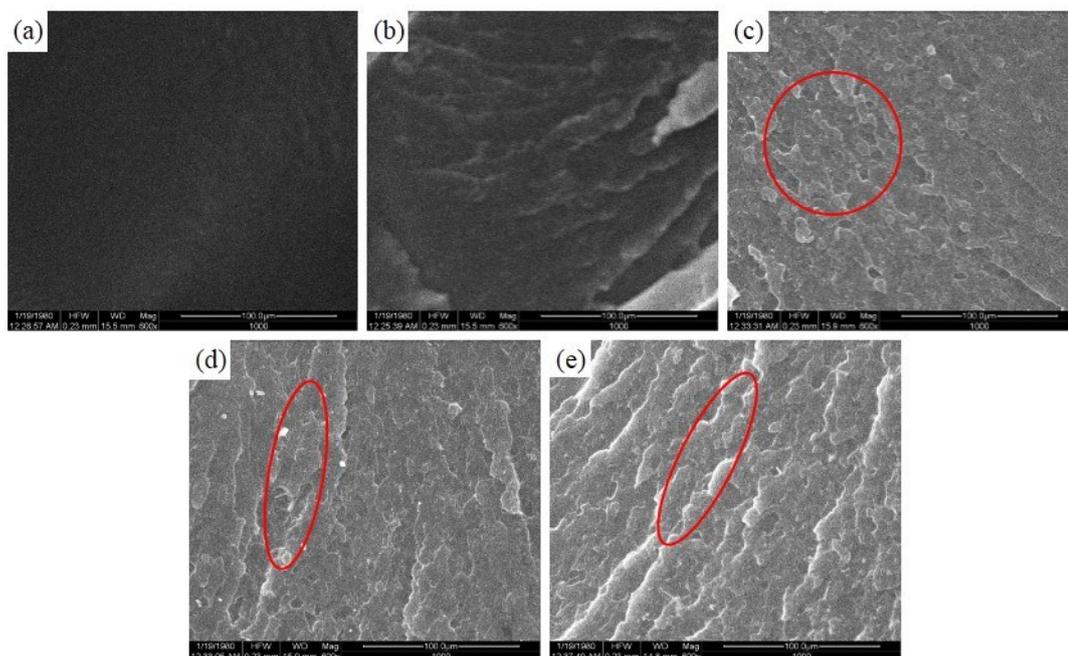


Fig. 4 SEM fractographs of the cured films with different content of HBPUA: (a) 0 %, (b) 5 %, (c) 10 %, (d) 15 %, (e) 20 %.

1. R. S. Mclean and B. B. Sauer, *Macromolecules*, 1997, **30**, 8314.