Novel Waterborne UV-Curable Hyperbranched Polyurethane Acrylate/Silica with Good Printability and Rheological Properties Applicable to Flexographic Ink

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ABSTRACT: Novel waterborne UV-curable hyperbranched polyurethane acrylate/silica (HBWPUA/SiO2) nanocomposites were prepared by a three-step procedure and sol–gel method. 1H NMR and 13C NMR results indicate that HBWPUA is successfully synthesized. Surface tension and contact angle tests both demonstrate the good wettability of the nanocomposites. Besides, the kinetics of photopolymerization of HBWPUA/SiO2 films were analyzed by attenuated total reflection-Fourier transform infrared spectroscopy, which reveals that the modified SiO2 could accelerate the curing speed of HBWPUA coatings. Thermal gravity analysis indicates that the HBWPUA/SiO2 hybrid films have a better thermal stability than the pure HBWPUA cured films. Furthermore, the hybrid films show enhanced pencil hardness, abrasion resistance, and adhesion. On the basis of the above, HBWPUA/SiO2 nanocomposites were finally applied to waterborne UV-curing flexographic printing ink, which is printed on poly(ethylene terephthalate) and glass. The nanocomposite presents good rheological behavior because the ink has a lower Z∞, a higher Z∞, and the viscosity rebuild time is 375 s. Three colors (red, yellow, and blue) of ink were used to test its printing quality, the curing time was below 30 s, and the adhesion was excellent without being stripped. All of the inks show good water resistance and abrasion resistance. Moreover, the red and blue inks possess better solid densities than the value of 1.07 of yellow ink, and are 1.83 and 1.84, respectively. The current study suggests that the process has promise in applications of food packages.

1. INTRODUCTION

Flexographic printing, which is environmental friendly, has become the second largest printing method in European and American countries, and it is the fastest growing printing method in the world.1 Currently, flexographic printing has been widely applied in various fields, such as packaging materials, magazines, miscellaneous pieces of printing sectors, etc. The flexographic printing ink can be divided into three categories: solvent ink (most are linear polymer), water-based ink, and UV-curing ink,2 which are all widely used. However, solvent-based flexographic printing ink has a particularly stimulating odor, causing environmental pollution and threatening human health, and water-based flexographic printing ink has some problems like weak mechanical properties, slow drying rate, and paper shrinkage defects. Besides, the traditional UV-curable ink also has some disadvantages: the UV ink needs a reactive diluent to decrease its viscosity, which increases its toxicity. The waterborne UV flexographic ink with waterborne UV-curable resin as binder, which combines advantages of both the UV ink and water-based ink, has great rheological properties and can be cured at ambient temperature by short exposure to UV light, earning it more and more attention.

At present, linear polymer solvent-based ink is mainly used in flexographic ink, it has a high viscosity, slow dry rate, and moreover, the use of active diluent is also harmful to the environment and human health. Therefore, the development of a green, low viscosity, fast drying, and high quality flexographic ink is particularly important. Hyperbranched polymer has aroused attention in recent years; it was firstly reported by Flory.3 In recent years, it has gained increasing attention as a novel type of binder material for waterborne UV-curable ink. Compared to its linear counterpart, hyperbranched polymer displays low viscosity, high activity, good oxygen resistance ability, and excellent compatibility because of its highly branched structure, low degree of intermolecular entanglement, and a great number of end functional groups, which can be produced for large-scale application with improved properties.4–9 Geiser et al.6 prepared the thermoplastic hyperbranched polyurethanes with Boltorn H30, which acts as a precursor. Mishra et al.10 illustrated the synthesis of UV-curable

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hyperbranched polyurethane acrylate/ZnO hybrid coatings and studied their thermal, viscoelastic, and surface morphology properties. In 2014, Ren and Liu11 introduced the research and development process of linear waterborne polyurethane UV flexographic ink applied to label printing (patent no. 201310178593.6, China) with fast curing rate, good intermiscibility, and improved adhesion, pencil hardness, and abrasive resistance. Overall, the research of waterborne UV flexographic printing ink is still in the knowledge accumulation stage, the in-depth and comprehensive research on its application has yet to start.

Organic/inorganic nanocomposites can be compounded through physical action between the inorganic and organic surfaces (van der Waals force and hydrogen bond) or chemistry (covalent bonds, coordination bond, etc.) at the nanometer level.12 Organic—inorganic hybrid materials have undergone rapid development in recent years because of their good mechanical properties, wear resistance, and thermal stability,13 where the hyperbranched polymer gives flexibility and toughness and the inorganic part acts as filler in different polymer matrices giving hardness, durability, high thermal stability, and other superior mechanical properties.14,15 At present, they are widely used in light-emitting materials, biodegradable, smart packaging materials, and other fields. Geiser16 prepared UV-curable HBPUA/SiO2 by a physical blending method using acrylic acid, Blotorn H30, and nano-SiO2 as raw materials, which can be used in coatings. Tests showed that the nano-SiO2 system has a small influence on the curing process, and can reduce the curing shrinkage rate of the system.

Figure 1. 1H NMR spectra of different generations of HBWPU.

Figure 2. 13C NMR spectra of HBWPUA.
To sum up, the waterborne UV flexographic ink prepared in this article can be applied in food packaging as it is environmentally friendly and has excellent properties including low viscosity, high activity, good compatibility, and energy saving.

2. RESULTS AND DISCUSSION

2.1. Characterization and Properties of HBWPUA/SiO2 Nanocomposites. Usually, waterborne UV ink consists of binder, pigment, solvent, additives, and so on, of which the binder occupies the most proportion and is the most critical component, thus it has a great impact on the many properties of ink. Therefore, the preparation of binder is particularly important. In this section, many tests were carried out to confirm the successful synthesis and properties of the HBWPUA/SiO2 nanocomposites, which acts as the binder in waterborne UV flexographic ink.

2.1.1. NMR Analysis. The NMR spectra of the first to fourth generations of HBWPU are shown in Figures 1 and 2, and these are based on tetramethylsilane (TMS) as internal standard and heavy water as the solvent. They were measured at room temperature. The peaks of the first to fourth generations of HBWPU are at δ = 1.21 ppm (−NCOO−), δ = 2.16 ppm (−CH2CH2−), and δ = 2.83 ppm (−OH). As they have similar H atoms in their chemical environment, different generations of HBWPU have the same peaks in similar locations, which is in accordance with the Fourier transform infrared (FTIR) spectra. Furthermore, the heights of the peaks present regular change: with the increase of generations, the overall changes are that the heights of the peaks at δ = 2.16 ppm (−CH2CH2−) and δ = 2.83 ppm (−OH) decrease and then increase; the peak at δ = 1.21 ppm (−NCOO−) exhibiting sustained growth, meanwhile, moves left after the first reaction. The decrease in height of the peak at δ = 1.21 ppm (−NCOO−) may result from the remaining hydroxyl of the PEG-400 continuing to react in the next stage, and the increased number of terminated hydroxyls may cause the following increase of height of the peak at δ = 1.21 ppm (−NCOO−), indirectly showing the existence of the hyperbranched structure. Besides, its left chemical shift may be explained by the hydrogen atoms in the carbonate generating a hydrogen bond with the carboxyl group because of a hydrogen bonding effect, which results in an increase of chemical shift; the carbonate groups of poly(ethylene glycol) (PEG)-400 and 2,2-dimethylol propionic acid (DMPA) participating in the reaction may lead to the decrease in height of the peak at δ = 2.16 ppm, which then shows significant growth because of the polycondensation reaction of the product mentioned above. The peak at δ = 1.21 ppm comes from the carbonate, which proves the existence of the branched structure in the hyperbranched waterborne polyurethane (HBWPU), and the growth of their peak heights in turn proves that the higher the generation is, the more macromolecular the chain will be.

The degree of branching (DB) of the hyperbranched polyester was calculated from 13C NMR spectroscopy (shown in Figure 2) with reference to three compound models possessing branched units, a linear unit, and a terminal unit, respectively.14 The peaks at 154.61, 155.68, and 156.63 ppm are the branched units, the linear unit, and the terminal unit, respectively. According to its integral area and the formula: DB = (D + T)/(L + D + T), the DB of the final product can be calculated.15

Therefore, the above results obtained by 1H NMR spectroscopy confirm the formation of HBWPU as a branched structure. Further, from 13C NMR spectroscopy, the degree of branching was calculated, which is 0.402. Next, we used infrared analysis to confirm whether the SiO2 is successfully introduced.

2.1.2. Infrared Analysis. FTIR spectra of the 2,4-diisocyanatotoluene−2-hydroxyethyl acrylate (TDI−HEA), HBWPU, HBWPUA, and HBWPUA/SiO2 nanocomposites are shown in Figure 3, traces (a)−(f). From spectrum (a) of TDI−HEA, the characteristic peaks of N−H stretching vibration, −NCO, C==O, N−H bending vibration, and C−O could be found at 3342, 2274, 1727, and 1540 cm−1, respectively. The peaks at 1632, 1409, and 810 cm−1 associated
with the double bond indicate the existence of an acrylate group. The two peaks of 2920 and 2860 cm\(^{-1}\) are attributed to the C–H stretching vibration of alkane. The FTIR spectra of HBWPU and HBWPUA are shown in traces (b) and (c), respectively. Spectrum (b) with no absorption peak at 2274 cm\(^{-1}\) showed a broad terminal hydroxyl group at 3448 cm\(^{-1}\) and –NHCON– at 1655 cm\(^{-1}\), suggesting that all –NCO groups were consumed and HBWPU had been synthesized. Compared with spectrum (b), peaks at 1641, 1409, and 806 cm\(^{-1}\) were characteristic of the acrylate group in spectrum (c). Furthermore, the peak at 2274 cm\(^{-1}\) disappeared due to –NCO in trace (c), revealing that the reaction between TDI–HEA and HBWPU had completed.\(^{18}\)

The HBWPUA and HBWPUA/SiO\(_2\) nanocomposites are shown in traces (d)–(f). The characteristic absorption of C=O at 1639 cm\(^{-1}\) is prominent in spectrum (d), but disappeared in spectrum (e) of the HBWPUA cured film, which indicated that after being exposed to UV irradiation, C=O completely participated in radical polymerization. From spectrum (f) of the cured hybrid film with 4 wt % SiO\(_2\), the peaks at 1092 and 804 cm\(^{-1}\), which are the characteristic absorptions of the asymmetric and symmetric stretching vibrations of Si–O–Si, respectively, became stronger. Moreover, a new peak appeared at 471 cm\(^{-1}\), which was attributed to the bending vibration absorption of Si–O–Si, indicating that SiO\(_2\) could be successfully introduced into HBWPUA and then form a network structure with the help of methacryloxypropyltrimethoxysilane (MPTS), as desired through this method.

![Figure 4. ATR-FTIR spectra (a) of the HBWPUA film and gel content (b) of the hybrid films at different curing times.](image-url)
The successfully introduced SiO₂ can enhance the hardness and abrasion resistance of binder, thus enhancing the performance of waterborne UV ink.

2.1.3. Kinetics of Photopolymerization Analysis. For UV-curing products, FTIR spectroscopy is a method to measure the change of the absorption peak of C=C bonds and further characterize the UV-curing process, which is one of the most important parameters of curing kinetics. The kinetics of photopolymerization reactions of HBWPUA were studied by attenuated total reflection (ATR)-FTIR (Figure 4a); the spectrum was recorded every 3 s and the gel content (Figure 4b) of the HBWPUA/SiO₂ hybrid films at different curing times was 300 μm thick. Figure 6a shows that the C=C bond peaks of the ATR-FTIR spectrum in the 1635 cm⁻¹ region disappeared gradually with the extension of curing time under UV exposure. When the curing time is 6 s, the C=C bond peak nearly disappears. Also, the gel content of all the hybrid films rises rapidly at first, and then slowly approaches a constant value with the extension of curing time (Figure 4b). These results both imply that C=C bonds participate in radical polymerization by UV radiation constantly until they are almost used up. In addition, the curing speed and gel content of the hybrid films increase with increasing SiO₂ content. When the SiO₂ content is increased to 6 wt %, the curing speed declines slightly and its final gel content is close to that of the hybrid film with 4 wt % SiO₂. This phenomenon can be explained as follows: nanoparticles usually absorb UV light. The increasing SiO₂ content will add more free radicals to the system. The greater amount of C=C bonds leads to a faster curing speed and greater cross-linking density, resulting in the increase in gel content. When the SiO₂ content reaches 6 wt %, excessive free silica will be spread around the polymer, creating a shielding effect for UV light, and this SiO₂ will also compete with 2959 for UV light, which might slow down the curing speed to some degree.¹⁹

2.1.4. Wettability and Hydrophobicity of HBWPUA/SiO₂ Film. The polymeric binder of waterborne ink should have a good wettability for substrates during the printing process, and a favorable hydrophobicity to resist adverse conditions after printing. Typically, the wettability and hydrophobicity of the polymer is usually measured by surface tension (σ) and contact angle (θ), respectively. Figure 5 shows that σ decreased first and then increased with the increase of SiO₂ mass content. The nanocomposites with 2 and 4 wt % SiO₂ content had better wettability than pure HBWPUA according to the smaller σ and the polymer had better wettability.²⁰ This might result from the addition of SiO₂ modified by MPTS, leading to more polar groups going into the hyperbranched chains, which increased the volume and quantity of polar groups, thus making σ smaller.²¹ But, when the wt(SiO₂)% was 6%, σ increased due to SiO₂ coagulation.²¹ Figure 5 also shows that θ rose with the increase of SiO₂ mass content, and when the wt(SiO₂)% = 6%, θ reached 94.12°. The reason for this phenomenon might be that the more modified SiO₂ was introduced, the more cross-linking density and siloxane hydrophobic groups will be induced, which made θ bigger, improving the hydrophobicity of the hybrid films.

2.1.5. Thermal Stability. Figure 6a,b demonstrates the thermogravimetric and first derivative TG thermograms of HBWPUA/SiO₂-0% and HBWPUA/SiO₂-4% cured films, respectively. The TG and DTG curves of HBWPUA/SiO₂-0% and HBWPUA/SiO₂-4% cured films suggest the cured films had a similar process of thermal decomposition, which appears as three obvious weight loss regions. The initial region occurred below 250 °C due to evaporation of solvent in the cured films. The second weight loss region occurring around 250–350 °C may be assigned to the decomposition of urethane linkages. And the third region occurring around 350–500 °C may be related to the decomposition of the organic portion of the polymer attached to the inorganic moiety. The degradation process is illustrated by maximum peak temperatures of the three regions of the HBWPUA/SiO₂-0% and HBWPUA/SiO₂-4% hybrid films at 195, 301, and 433 °C, and 203, 310, and 438 °C, respectively. The characteristic decomposition data implies that the HBWPUA/SiO₂-4% hybrid films have a better thermal stability than the pure HBWPUA/SiO₂-0% cured film, which...
may be because the addition of SiO$_2$ can increase the cross-linking density, and SiO$_2$ also causes a "barrier effect" that delays the volatilization of degraded product, all of which are responsible for giving an improved thermal stability.\textsuperscript{22,23}

2.1.6. Mechanical Properties. The results of Table 1 display the effect of SiO$_2$ mass content on the surface properties of the HBWPUA/SiO$_2$ hybrid films, such as pencil hardness, abrasion resistance, and adhesion. With the increase of SiO$_2$ mass content, the pencil hardness distinctly improved, the abrasion resistance became better first and then decreased slightly, and the adhesion was slightly reduced from grade 0 to 1. The reason for this may be due to both the increase of Si$\equiv$O$\equiv$Si inorganic network and cross-linking density by the addition of SiO$_2$, which improves the hardness and abrasion resistance. However, excessive SiO$_2$ aggregating on the HBWPUA surface causes reduced cross-linking density and volume shrinkage of the cured films, which lead to the abrasion resistance and adhesion decreasing slightly.\textsuperscript{21} The pencil hardness, abrasion loss rate, and adhesion of the HBWPUA/SiO$_2$-4% hybrid film are 4 H, 0.92%, and grade 0, respectively.

From the tests above, we can conclude that the hyperbranched structure is confirmed and the SiO$_2$ is successfully introduced into HBWPUA. Moreover, the HBWPUA/SiO$_2$ nanocomposites have good curing kinetics properties, excellent wettability, and thermal stability, which also lays the groundwork for the good performance of UV flexographic printing ink.

### Table 1. Surface Property Data of HBWPUA/SiO$_2$ Hybrid Films

| sample code     | pencil hardness (H) | abrasion resistance (abrasion loss rate, %) | adhesion (grade) |
|-----------------|---------------------|--------------------------------------------|-----------------|
| HBWPUA/SiO$_2$-0% | 2                   | 1.34                                       | 0               |
| HBWPUA/SiO$_2$-2% | 3                   | 1.03                                       | 0               |
| HBWPUA/SiO$_2$-4% | 4                   | 0.92                                       | 0               |
| HBWPUA/SiO$_2$-6% | 5                   | 1.19                                       | 1               |
2.2. Properties of the Waterborne UV Flexographic Printing Inks. 2.2.1. Rheological Behavior of Inks. A good ink should have a lower zero shear viscosity ($Z_0$) and a higher infinite shear viscosity ($Z_\infty$), so that the ink can have good fluidity in the printing process and a good ability to avoid ink dot expansion after printing. Typically, waterborne UV flexographic ink behaves like Newtonian fluid with viscosity in the range of 100–1000 mPa s. Figure 7a shows that the viscosity of ink will decrease with increasing content of HBWPUA/SiO$_2$ binder, which can be explained by the fact that viscosity is affected by intermolecular forces. The higher the HBWPUA/SiO$_2$ content, the lower the number of particles in the multiunit system, causing less twine and physical interaction between particles, which decreases the viscosity. With the increase of shear rate, at first, the ink remains stable like Newtonian fluid, and then the viscosity decreases and the ink behaves like pseudo-plastic fluid, finally approaching a constant value. This is because the viscosity of ink is also related to the molecular arrangement. At low shear rates, network structures of HBWPUA molecular chains and modified SiO$_2$ chains with HBWPUA can be rebuilt rapidly after being slightly damaged to achieve a balance, thus leading to stable viscosity. As the shear rate increases, damaged network structures cannot be fully rebuilt, and the molecular chains are forced to reorient and arrange, thus thinning the viscosity, which is beneficial to ink transfer during printing. But, when the shear rate is large enough to damage all network structures, making it impossible
to rebuild the structures, the viscosity reaches the lowest and constant value.28

As also shown in Figure 7, viscosity increases with the addition of dye, and all inks show three stages of viscosity, like the binder, with the increase of shear rate. This is mainly related to the dispersion state of dyes in ink. Dyes can be uniformly dispersed in HBWPUA/SiO2 to form condensate at high-speed stirring, and the higher the dye content, the greater the condensate. Therefore, the viscosity almost remains unchanged due to the stable condensate at lower shear rates, and with the increase of shear rate, it gradually becomes thinner owing to the smaller damaged condensate. Finally, the viscosity will slowly become closer to a stable value because of balance occurring between the damaged and rebuilt condensate.28

In addition, viscosity decreases when ink is transferred from printing plate to substrate, and rebuilds after being transferred to the substrate to ensure good printing quality, without ink overspilling, namely, ink thixotropy. Generally, the viscosity of ink decreases rapidly and rebuilds slowly. Therefore, the rebuild time of viscosity can be used to characterize the ink thixotropy (as shown in Figure 8). The longer the rebuild time, the stronger the thixotropy, and strengthened thixotropy may cause incomplete ink delivery.28 Figure 9 shows that the rebuild time of all ink viscosities is in the range of 200–500 s. As shown in Figure 9a, with the addition of HBWPUA/SiO2, the rebuild time extends, which means that the thixotropy becomes stronger. The higher the HBWPUA/SiO2 content, the weaker the force of the network structure in the multiunit system. So, the damaged network structure at high shear rate (1000 s⁻¹) was restored more slowly in a sudden return to the low shear rate (0.1 s⁻¹), leading to a longer rebuild time with stronger thixotropy. Also, Figure 9b displays the rebuild time shortens with the increase of dye, causing weak thixotropy. This is because the condensate of ink was larger with the increase of the dye, and the force of the condensate was stronger. Thus, the damaged condensate at 1000 s⁻¹ shear rate can be easily restored to a new condensate when returned to 0.1 s⁻¹ shear rate with a greater chance of particle collision, resulting in a shorter rebuild time with weaker thixotropy. Figures 7 and 8 show that waterborne UV flexographic red ink including 70% binder and 14% dye displayed a lower Z₀ and a higher Z∞ with 375 s viscosity rebuild time.

2.2.2. Influence of Dye on Solid Density and Curing Time of Inks. Dye, as a coloring material, can absorb UV light, determines the printing solid density of ink, and also influences the curing process of ink. Figure 10a displays the UV–vis spectrum of red, yellow, and blue dye with the same content (0.0003 wt %). All of them use deionized water as solvent. In comparison with the red and blue dye, yellow dye has a stronger capacity for UV absorption with minimum UV transmittance and maximum UV absorbance, causing a big influence on UV-curing rate.29 In addition, the UV absorbance increased with the increase of dye. Therefore, it is better to have less dye to ensure a solid density. Generally, the solid densities of red, yellow, and blue ink are required to be 1.8, 1.0, and 1.8, respectively.29 Figure 10 also shows the dependence of solid density and curing time of flexographic printing red (b), yellow (c), and blue (d) inks on dye content. With the addition of dye, the solid densities of the three inks increased, but when the dye content increased to a certain value, the solid density increased slowly. The reason for that is because the dye oil absorption value is constant, and binder with predetermined absorption value is constant, and binder with predetermined content accommodates a limited number of dyes.30 Furthermore, the curing time of inks become longer with the increase of dye. Therefore, it can be concluded that the higher the dye content, the harder it is for UV light to penetrate the ink film, leading to a reduced curing rate.

2.2.3. Printing Quality of Inks. In this work, the properties were tested after being printed on poly(ethylene terephthalate) (PET) and glass. The print quality of three kinds of ink (Table 2) was measured by curing time, solid density, gloss, water resistance, and mechanical properties of printing. On the basis of the enhanced properties of binder, the prepared ink shows a shorter UV-curing time, better abrasion resistance, excellent water resistance, and stronger adhesion. Moreover, the printing solid density and gloss effect become more ideal.

We can learn from Table 2 that the waterborne UV flexographic ink using HBWPUA/SiO2 nanocomposites as binder can show enhanced rheological behavior and printing quality, which is an important property of ink, and forms a
good foundation for research of its potential application in food packaging.

3. CONCLUSIONS

In this work, the waterborne UV-curable HBWPUA/SiO₂ nanocomposites were successfully prepared and applied to flexographic ink as binder. Through ¹H NMR and ¹³C NMR analysis, the degree of branching of hyperbranched polyester was calculated, which is 0.402; TG and DTG curves of HBWPUA/SiO₂ cured films where silica content was 2 and 4 wt % demonstrated that the hybrid films show a better thermal stability than pure HBWPUA cured films, and better wettability was observed after analyzing the σ data. Furthermore, the effect of SiO₂ content on surface properties of HBWPUA/SiO₂ hybrid films was measured, such as pencil hardness, abrasion resistance, and adhesion, and therefore, we can give the conclusion that the films have better adhesion, especially when the silica content is 4%, the abrasion loss rate is the lowest at the same time. Furthermore, the waterborne UV-curable flexographic ink possesses excellent rheological behavior, such as the rebuild time of viscosity.

In the meantime, the printing quality using the optimized formulation shows better performance. The rheological properties of red waterborne UV flexographic ink were studied using a rotational rheometer. Results show that the shear viscosity of red ink shows three different “zones” of change when the shear rate ranges from 0.1 to 1000 s⁻¹, which is beneficial to transfer ink. Moreover, the best red, yellow, and blue pigment contents

| Table 2. Print Performance and Mechanical Properties of Red, Yellow, and Blue Waterborne UV Flexographic Inks |
|---------------------------------------------------------------|
| tested performance | red ink | yellow ink | blue ink |
| curing time (s)     | 27      | 30         | 30       |
| solid density       | 1.83    | 1.07       | 1.84     |
| gloss (%)           | 79.6    | 70.7       | 72.4     |
| water resistance (loss rate, wt %) | 0.1870 | 0.1930 | 0.1850 |
| adhesion (grade)    | 0       | 0          | 0        |
| abrasion resistance (loss rate, wt %) | 0.0181 | 0.0183 | 0.0180 |

Figure 10. UV-vis spectrum of dyes with the same content (a), and influence of dye content on solid density and curing time of flexographic printing ink: red (b), yellow (c), and blue (d).
were determined to be 14, 12, and 14%, respectively. Besides, the three different curing rates of ink in the optimized formulation all have a shorter curing rate, higher printing solid density, and water resistance, pencil hardness, adhesion, and abrasion resistance.

Waterborne UV-curable HBWPUA/SiO2 nanocomposites in this article are nontoxic, and on the basis of the performances above, we can further explore their potential application in food packaging. Because this is the first time that HBWPUA/SiO2 nanocomposites have been successfully applied to printing inks, there is also more work on printability to be done in the future.

4. EXPERIMENTAL SECTION

4.1. Materials. 2,4-Diisocyanatotoluene (TDI) was distilled under vacuum. Poly(ethylene glycol) (PEG, Mn = 400) was distilled at 110 °C under −0.1 MPa for 3 h. 2,2-Dimethylol propionic acid (DMPA; Aladdin Reagents Co., Ltd., Shanghai) was dried in a vacuum oven at 80 °C for 3 h prior to use. Hydroxyethyl acrylate (HEA) was dried over 4 Å molecular sieves for 48 h before use. Acetone was distilled at 78 °C and stored in 4 Å molecular sieves for further use. Dibutyltinilaurate (DBTDL, as catalyst), N-methyl-2-pyrrolidone (NMP, as the solvent), diethanolamine (DEOA), triethylamine (TEA), hydroquinone (as catalyst), absolute ethyl alcohol, and 2-hydroxy-4′-(2-hydroxyethoxy)-2-methyl-propiophenone (photoinitiator 2959; Aladdin Reagents Co., Ltd., Shanghai) were used as received without further purification. Aqueous colloidal silica (solid content: 30 wt %, particle size: 15 nm) and methacryloxypropyltrimethoxysilane (MPTS) were provided by WD Silicone Co., Ltd. Deionized water was lab-made. All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., unless otherwise noted.

4.2. Preparation of HBWPUA/SiO2 Nanocomposites.

4.2.1. Preparation of HBWPUA Emulsion. The emulsion was synthesized via a three-step procedure in a 1000 mL four-necked, round-bottomed flask fitted with a motor stirrer, an inlet of dry nitrogen, a constant pressure dropping funnel, and a reflux condenser with a drying tube. The process of synthesis (shown in Figure 11) is described in the following paragraphs.

In the first step, hyperbranched waterborne polyurethane (HBWPU) was obtained with acetone and the coupling monomer method by reacting PEG (39.36 g) with TDI (37.68 g) under a nitrogen atmosphere at 60 °C for 2 h with continuous motor stirring in the presence of DBTDL (four drops). Specifically, TDI was added dropwise at a constant flow rate to avoid imploding and agglomeration. Next, DMPA (6.60 g) dissolved in NMP (20.00 g) was added into the flask and reacted at 70 °C for 2 h. At that moment, the isocyanate (−NCO) content was tested by the standard dibutylamine back-titration method and found to be 3.15%. After being cooled down to −4 °C in a low temperature constant temperature bath, DEOA (5.32 g) dissolved in NMP (20.00 g) was added into the flask and reacted at 70 °C for 2 h. At that moment, the isocyanate (−NCO) content was tested by the standard dibutylamine back-titration method and found to be 3.15%. After being cooled down to −4 °C in a low temperature constant temperature bath, DEOA (5.32 g) dissolved in NMP (20.00 g) was dropped slowly into the reaction vessel with continuous...
motor stirring at −4 °C and kept for 40 min. Afterwards, the mixture was heated to 65 °C for 3.5 h, and then HBWPU was acquired. At that moment, the −NCO content that was determined by the infrared spectroscopy method was close to zero.

In the second step, semiterminated TDI−HEA with a light curing group was prepared with a one-step method by reacting TDI (7.00 g) and HEA (5.56 g) at 45 °C for 4 h under continuous magnetic stirring until the −NCO content reached half that of the original, which was determined by the di-n-butylamine titration method. The solvent and the catalyst are acetone and hydroquinone, respectively.

In the third step, a HBWPUA emulsion was formed with the anionic self-emulsifying method. The hyperbranched waterborne polyurethane acrylate (HBWPU) resin was synthesized by adding dropwise TDI−HEA (24.00 g) into HBWPU at 65 °C for 4.5 h with continuous motor stirring until the peak at 2274 cm\(^{-1}\) for −NCO groups completely disappeared. After cooling the HBWPUA resin to 35 °C, a mixture containing TEA (5.60 g), absolute ethyl alcohol (32.00 g), and deionized water (128.00 g) was dropwise added with high-speed motor stirring (300−800 rpm) to make the HBWPUA resin fully neutralized and emulsified. One hour later, a stable HBWPUA emulsion was obtained.

**4.2.2. Preparation of HBWPUA/SiO\(_2\) Nanocomposites.** HBWPUA/SiO\(_2\) nanocomposites were formulated by the sol−gel method with the addition of aqueous colloidal silica and MPTS successively to the HBWPUA emulsion at room temperature for 1 h under vigorous stirring (800−1300 rpm).

**4.2.3. Preparation of HBWPUA/SiO\(_2\) Film.** By varying the contents of aqueous colloidal silica and MPTS in the HBWPUA/SiO\(_2\) nanocomposites over the range of 0, 2, 4, and 6 wt %, a series of nanocomposite films were prepared by the following method and coded as HBWPUA/SiO\(_2\)-0%, HBWPUA/SiO\(_2\)-2%, HBWPUA/SiO\(_2\)-4%, and HBWPUA/SiO\(_2\)-6%, respectively. Photoinitiator 2959 (3 wt %) was added to different amounts of HBWPUA/SiO\(_2\) nanocomposites, the mixtures were blended at room temperature for 15 min with ultrasonic cleaner and then spread on clean slides and PET films, then they were left for 10 min at room temperature, and after that they were dried at 105 °C for 30 min to ensure the complete removal of water. After cooling to room temperature, the films were irradiated using a full automatic UV-curing machine at room temperature, and then demoulded for properties measurement (shown in Figure 12).

**4.3. Preparation of Waterborne UV Ink for Flexographic Printing on Food Packaging.** The waterborne UV ink for flexographic printing on food packaging was prepared by mixing HBWPUA/SiO\(_2\) nanocomposites as binder, dye (red, yellow, and blue) (Shenzhen Yonghui pigment Technology Co. Ltd., China), photoinitiator 2959, cosolvent (ethanol and water), monomer (pentaterythritol triacrylate (PETA)), and assistant (defoamer) for 1 h with continuous motor stirring, grinding for 2 h with a planetary ball mill, and homogenizing with ultrasonic cleaner for 15 min at room temperature. The dye was obtained by high-speed dispersion of the HBWPUA/SiO\(_2\) nanocomposites and dyes for 1 h at room temperature with a 1:3 dye to binder mass ratio. Furthermore, red, yellow, and blue, three kinds of waterborne UV flexographic ink formulations were screened (shown in Table 3).

**4.4. Characterization.** 1H NMR and 13C NMR spectra of HBWPU and HBWPUA samples were recorded on a Mercury VX-300 MHz (Varian) and a AV 400 MHz (Bruker, Switzerland) spectrometer in chloroform-\(d\) and deuterium oxide, respectively. Me\(_4\)Si (TMS) is the internal standard at room temperature. For FTIR analysis, HBWPU, HBWPUA, and HBWPUA/SiO\(_2\) samples were prepared by drying the emulsion on a KBr wafer and FTIR spectra were obtained with a iS10 spectrophotometer (Thermo Fisher Scientific) by scanning 16 times within a spectral range of 400−4000 cm\(^{-1}\).

![Figure 12. UV-curing process of the main components of binder.](image-url)
Table 3. Formulation of Red, Yellow, and Blue Waterborne UV Flexographic Inks

| materials                  | red ink | yellow ink | blue ink |
|----------------------------|---------|------------|----------|
| HBWPUPA/SiO2-2%            | 70      | 70         | 70       |
| dye                       | 14      | 12         | 14       |
| photoinitiator 2959       | 3       | 3          | 3        |
| alcohol and water (mass ratio) | 7 (3/2) | 7 (1/1)    | 7 (3/2)  |
| PETA                      | 5       | 5          | 5        |
| 2-propanol                | 0.6     | 0.6        | 0.6      |
| defoamers                 | 0.4     | 0.4        | 0.4      |

For cured films, an affix of attenuated total reflectance (ATR) was necessary. Mean particle sizes of the HBWPUPA/SiO2 nanocomposites were measured at 25 °C by a BT-90 laser particle size instrument (Dandong Bettersize, China).

Kinetics of the curing process were studied by ATR-FTIR spectroscopy and a gel content test. The gel content was calculated by eq 1.

\[
gel\% = \frac{m_0 - m_1}{m_0} \times 100\% \tag{1}
\]

where “\(m_0\)” is the mass of the cured film and “\(m_1\)” is the mass of the cured film after extracting for 48 h in a soxhlet extractor with acetone.

The contact angle and surface tension were obtained by using an A10 dynamic/static surface/interface tension instrument (Kenuo Industries Ltd.); surface tension was obtained by the Wilhelmy Plate method.

The thermal decomposition profiles of the HBWPUPA/SiO2 nanocomposite films were studied by a TG and DTG Setsys16 (Aetaram, France). Approximately 5 mg of the sample was heated at a constant rate of 10 °C min⁻¹ in an inert nitrogen atmosphere from 20 to 600 °C. Optical properties were characterized by a UV–vis spectrophotometer (Shimadzu, Japan) in the 300–800 nm region. Pencil hardness of the cured films was measured using a QH hardness tester (Jingke, China) according to GB/T 6739-2006 standards of China. Adhesion was tested by a QFH paint film scriber (Aice, China) in accordance with GB/T 9286-1998 standards.

Abrasion resistance was studied through the rotating abrasive rubber wheel method according to GB/T 1768-2006 standards and calculated with eq 2:

\[
S = \frac{S_0 - S_1}{S_0} \times 100\% \tag{2}
\]

where “\(S\)” is abrasion loss rate, “\(S_0\)” and “\(S_1\)” are the mass of films before and after 500 abrasion cycles at 500 g load, respectively.

After setting the appropriate printing pressure, the printing process was conducted by a printability tester C1-5 (IGT, Holland). A soda glass substrate was sonicated with deionized water for cleaning, and PET was purchased from Hubei Yunhe Salt Packing Co., Ltd. without further cleaning.

Solid densities of waterborne UV flexographic inks were measured by a Spectra Eye spectrophotometer (Gretag Macbeth, America) at the following settings: D50 illuminant using a 2° observer, 45°/0° (DIN5033) measuring geometry. Gloss was measured by a WGG-60 microgloss meter (Shanghai INESA Physical Optical Instrument Co., Ltd., China) according to GB/T 132.17.2-2009. Rheological behavior (viscosity and thixotropy) of the waterborne UV flexographic inks was investigated using a Kinexus Pro’ rotational rheometer (Malvern, England) equipped with a CP1/60:PL60 (a 60 mm diameter 1° angle cone over a 60 mm plate) at 25 °C. The shear viscosity testing was performed with a controlled applied shear rate increasing from 0.1 to 1000 s⁻¹, and the thixotropy was measured by a peak hold step test and characterized with time of the three step shear viscosity rebuild to the first step shear viscosity, where the three-step shear rate and test time were 0.1, 1000, 0.1 s⁻¹, and 30, 30, and 600 s, respectively.

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