Fibers and Polymers 2014, Vol.15, No.2, 208-214 DOI: 10.1007/s12221-014-0208-x

Synthesis and Characterization of Hybrid Latexes from Soybean Oil-based Polyurethane and Poly(2,2,2-trifluoroethyl methacrylate)

Dan Yu[1,2]*, Le Wang[1], Bin Sun[3], Jiafu Wang[1], and Wei Wang[1,2]

[1]*College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, P.R. China*
[2]*The Key Laboratory of Science & Technology of Eco-Textile, Ministry of Education, Donghua University, Shanghai 201620, P.R. China*
[3]*College of Materials Science and Engineering, Donghua University, Shanghai 201620, P.R. China*

(Received April 7, 2013; Revised June 27, 2013; Accepted July 13, 2013)

Abstract: A class of novel fluorine containing core-shell hybrid latexes were obtained from soybean oil-based polyurethanes and poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) by two-step synthesis under mild reaction conditions. Structural and morphology properties of the resulting hybrid latexs have been characterized by FT-IR and TEM. In addition, thermal properties (DSC, TGA) and coating performance (contact angle, stress-strain curve, and surface free energy) were investigated and discussed. The hybrid latexes exhibit outstanding thermal stability and coating performance. More importantly, through this method, low-valued foods are successfully transformed into high-valued functional materials which bring new solutions for preparing materials from renewable sources.

Keywords: Soybean oil, Polyurethane, Hybrid latexes, Fluorinated acrylate

Introduction

Polyurethanes (PUs) are one of the most important polymeric materials which are widely used in daily commodity and industrial fields, especially in paints and coating industry [1]. PUs are generally composed of rigid hard segments derived from isocyanates and flexible soft segments derived from polyols. Due to the interactions resulting from micro-phase structure between the hard and soft segments, PUs exhibit excellent bond strength, wear resistance and controllable hardness, which meet the requirements for industrial and construction coatings [2,3].

The conventional PU coatings contain a significant amount of organic solvents, causing environmental pollution regarding the volatile organic chemicals (VOCs) [4]. In order to solve the problem, the waterborne polyurethanes (WPUs), a binary colloidal system where the PU particles are dispersed in a continuous aqueous media, are developed to replace the conventional PU products [5]. Compared with traditional PU products, WPUs present advantages relating to low viscosity at high molecular weight, good applicability [6] and almost free VOCs. Therefore, WPUs products attract more research interests and are widely used as paints and coatings in recent years [7].

In the past decade, significant advances have been made in the development of polymers from renewable sources, because of diminishing fossil fuel reserves along with global warming effects. Vegetable oils, such as soybean oil are considered to be one of the most promising biological sources for the polyurethane industry [8]. Triglyceride structure and multi carbon-carbon double bonds (average 4.6 per molecule) could be open up various strategies to tailor new biosourced target exhibiting the architectural features and chemical functionality of the currently available polyurethane precursors of petrochemical origin, polyether and polyester polyols. Until now, a wide variety of vegetable oil-based polymers have been developed and reported. For example, Gerard's group reviewed the plant oil as platform chemicals for polyurethane, illustrating various approaches to prepare soybean oil-based polyols and the synthesis of polyurethanes with these polyols [9]. To be noted, attention is also paid to improve the hydrophobic properties and weatherability of films for the purpose of better outdoor coating performance [10,11].

Poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) is known as a class of transparent amorphous polymer. Different from styrene, there is no rigid structure in PTFEMA chains which indicates it is relatively soft (half of poly (methyl methacrylate) (PMMA) in hardness). Therefore, introducing PTFEMA to coating materials will not substantially change the mechanical properties. Moreover, PTFEMA has excellent water resistance and fouling resistance due to its high surface free energy, caused by its fluorine-containing lateral chain. Hence, TFEMA is a suitable choice for the modification, to improve hydrophobic properties of PU films.

In this work, soybean oil polyols with hydroxyl value 122 mg KOH/g (c.a. 2.2 hydroxyl per triglyceride molecule) were used to prepare the polyurethane, exhibiting a higher cross-linking capability than petroleum ether such as polyethylene glycol, polypropylene glycol. Then a series of hybrid latexes with different contents of acrylate monomers were prepared by emulsion polymerization. Morphology (FT-IR, TEM), thermal properties (DSC, TGA) analysis of the latex films, as well as contact angle, stress-strain curve and surface

---

*Corresponding author: yudan@dhu.edu.cn

energy have been investigated systematically providing promising results for the development of environmentally friendly paints from the renewable and relatively cheap raw materials.

Experimental

Materials

Isophorone diisocyanate (IPDI >99.0 wt%) and dimethylol propionic acid (DMPA >97.0 wt%) were purchased from Aladdin reagent; Arawana soybean oil was obtained from a local market; 2,2,2-trifluoroethyl methacrylate (>97 wt%) was purchased from Xeogia reagent; Hydrogen peroxide (30 wt%), formic acid (88 wt%), triethylamine (TEA, 99.0 wt%), methyl ethylketone (MEK, 99.0 wt%), methanol (99.5 wt%), isopropyl alcohol (99.7 wt%), fluoroborate (40 wt%), Potassium persulfate (KPS, 99.0 wt%) were purchased from Sinopharm Chemical Reagent. All raw materials mentioned above were used directly without further purification.

Synthesis of Soybean Oil-based Polyols

The soybean oil-based polyols (SOPs) were prepared by an epoxide-ring opening process. Firstly, soybean oil and formic acid were added to flask. Then the hydrogen peroxide was dropped to the flask with the speed of 1 m*l*/min with the epoxidized reagent from formic acid and hydrogen peroxide. The weight ratio of the three is 1:0.35:1.1 in order. Reaction was carried out at 60 °C for 8 h with vigorous mechanical stirring. The epoxy value can be controlled by adjusting the weight ratio of soybean oil, hydrogen peroxide and formic acid. Then 50 m*l* ethyl acetate and 30 m*l* distilled water were added and the oil layer was collected. The processing mentioned above was carried out at least twice using a separatory funnel. After rotary evaporation, the product was dropped to a mixture of methanol, isopropanol with the weight ratio of 1:1:1. Amount of 2 % of total mass of the fluoroboric acid was added to the system as catalyst. The mixture was stirred for another 2 h at 60 °C, and then amount of 1 % NaOH equal to fluoroborate was added to quench the reaction. Except the purification mentioned above, an extra 120 °C evaporation at atmospheric pressure for 1 h was carried out to remove solvent impurities.

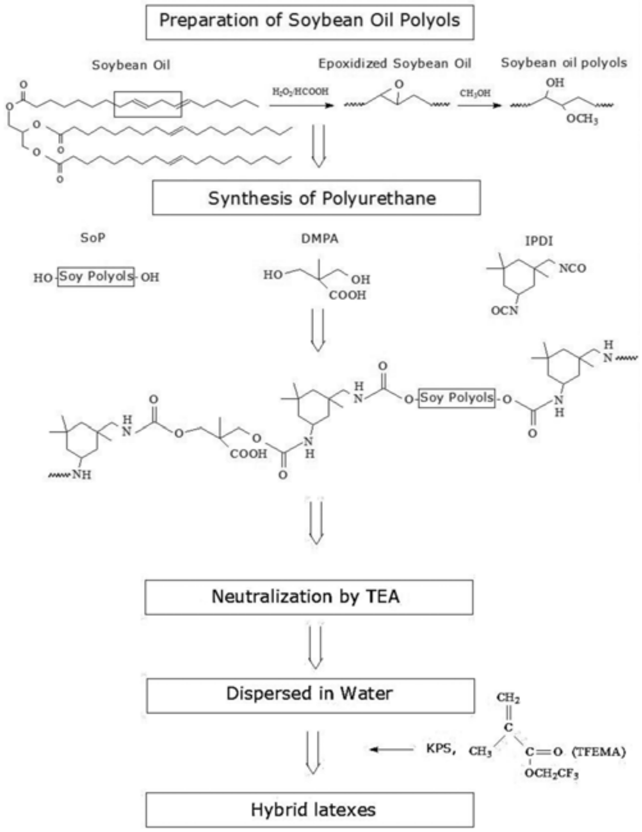
Synthesis of the Segmented SPU Dispersions

The soybean oil-based polyurethane (SPU) was synthesized from SOPs, IPDI, DMPA in a four-neck flask with mechanical stirrer, nitrogen inlet and thermometer. The formula in details was listed in Table 1. The reaction mixture was stirred at 80 °C under dry nitrogen for 2 h and of MEK (around 20 m*l*) was added to control the viscosity of the system. After neutralized by TEA (1.2 equivalents of DMPA) the resulting SPU was dispersed in distilled water with high shear emulsifier. About 20 wt% solid content dispersions were prepared for the next process.

Synthesis of SPU/PTFEMA Latexes

The preparation of the hybrid latexes is illustrated in Scheme 1. 2,2,2-trifluoroethyl methacrylate was selected to prepare the emulsion. Different amount of TFEMA (10, 20, 30 wt% of SPU) was added to the SPU dispersions and potassium persulfate (KPS) was used as an initiator (0.6 wt% of TFEMA). The reaction was performed at 80 °C for 4 h.

The chemical composition of the synthesized hybrid latexes are listed in Table 1. Compared with the regular line structure petroleum ether, the soybean oil molecular exhibits different properties. Considering three unsaturated aliphatic chains in structure, the distribution of hydroxyls varies from molecule to molecule, and it is likely that more than two



Scheme 1. Synthesis process of SPU/PTFEMA hybrid Latexes.

Table 1. Chemical composition of hybrid latexes

Sample name	-NCO/ -OH	Hydroxyl value of Polyols	Functionality	DMPA (wt%)	TFEMA (wt%)
PU20	1.1	108(PEG1000)	1.92	5.0	0
SPU	1.1	122	2.17	5.0	0
SPUFA10	1.1	122	2.17	5.0	10
SPUFA20	1.1	122	2.17	5.0	20
SPUFA30	1.1	122	2.17	5.0	30

hydroxyls appear in one molecule. The molar ratio of -NCO/-OH was kept constant at 1.1:1. An additional 10 % -NCO groups were added into the system to control the viscosity.

Characterization

FT-IR spectra were collected on a NEXUS 670 spectrometer (Nicolet-Thermo) with an attenuated total reflection (ATR) accessory.

Transmission electron microscopy (TEM) studies were performed by a H-800 instrument (Hitachi). After diluted with deionized water to 0.2 wt%, the emulsions were stained with 3 % phosphotungstic acid. The prepared samples were dropped on a 200-mesh copper grid and dried in the air before measuring.

The SPU/PTFEMA films were prepared in a glass mold and the samples were cut from the films for further analysis.

Calorimetric studies were carried out by Q20 Differential Scanning Calorimeter (DSC) with refrigerated cooling system (TA instrument). About 5 mg sample was heated from room temperature to 100 °C to erase the heat history at a heating rate of 10 °C/min, then cooled to −50 °C. The sample was heated to 100 °C again at 10 °C/min. The Discovery Thermal-gravimetric analyzer (TGA) (TA instrument) was used to measure the weight loss under nitrogen atmosphere. Around 5 mg sample was heated to 600 °C at a heating rate of 10 °C/min.

The film was cut to rectangle specimens of 10×100 mm for the test of mechanical properties. After balancing in the constant temperature and humidity chamber for 12 h (25 °C, 65±5 % RH), the specimens were tested on a materials testing machine (Hounsfield H5K-S) to determine the stress-strain curves at the speed of 300 mm/min. An average value from at least three samples was obtained through the experiments.

The contact angle was measured with the sessile drop method at room temperature using a KRUSS DSA30 (Germany) contact angle goniometer. At least three points were performed on each sample from which the mean static contact angle was calculated, and all the angles were read in 10 s after dropped.

Results and Discussion

FT-IR Analysis

The FT-IR was employed to analyze the soybean oil polyurethane and the hybrid latexes with regard to the functional groups, interactions between segments, and hygrogen bonding.

Hydrogen bonding plays a vital role to the properties of PUs materials, which was reported by numbers of studies [12,13]. The PUs prepared from soybean oil were quite different from those from petroleum raw materials, which may contain more ester oxygens and carbonyl groups as hydrogen bond accepters. Figure 1 shows the FT-IR spectra of SOP, SPU and SPUFA with 30 % fluorinated acrylate. Typical bands at around 3350 cm^{-1} were observed in SPU and SPUFA, which correspond to the hydrogen-bonded N-H stretching [14]. The free N-H stretching vibration at around 3450 cm^{-1} is not obvious in the spectra indicting that most of N-H of amide groups involved in hydrogen bonding. The peak at around 1716-1738 cm^{-1} were assigned to hydrogen-bonded C=O stretching. The bands at 1536 cm^{-1} (amide *II*, δN-H and νC-N), 1239 cm^{-1} (amide *III*, νC-N and δN-H) confirm the formation of urethane group [10].

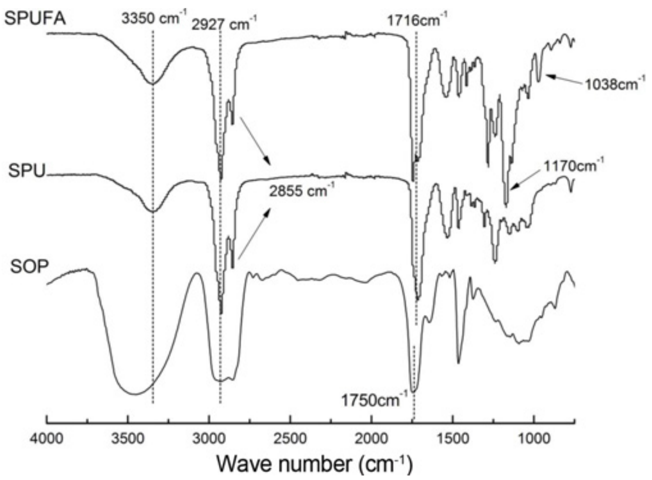


Figure 1. FT-IR spectra of SOP, SPU and SPUFA.

Compared with the SPU without introducing fluorinated acrylate (FA), a progressive change was observed in the spectrum of SPUFA. It is worth nothing that the C=O stretching vibration of acrylic ester groups in SPUFA shift to higher wave number at 1735 cm^{-1} along with a shoulder peak at 1716 cm^{-1}, which indicates that part of non-hydrogen-bonded C=O groups exists [15]. The appearance of peak at 1170 cm^{-1} corresponds to C-O stretching vibration with a shoulder peak at 1158 cm^{-1} relating to C-F stretching vibration. Evidenced by the FT-IR spectra, TFEMA monomers have been successfully introduced into the SPU system.

Conversion and Morphology

Figure 2 shows the conversion of FA monomers. Predetermined amount of TFEMA (10, 20, 30 wt%) were added to the SPU dispersion for the emulsion polymerization at 80 °C. During polymerization, an aliquot of emulsion was taken out by syringe and injected into a petri dish with 0.5 % hydroquinone solution in an ice bath. The conversion was calculated gravimetrically using Lu's method [16]. The results showed that the rate of polymerization increases when increasing the content of FA monomers. This result can be explained that the resin itself reduces the polymerization rate by diluting the monomer concentration and promoting resin chain transfer [17]. The conversion reaches a plateau value after 3 h polymerization in all three cases.

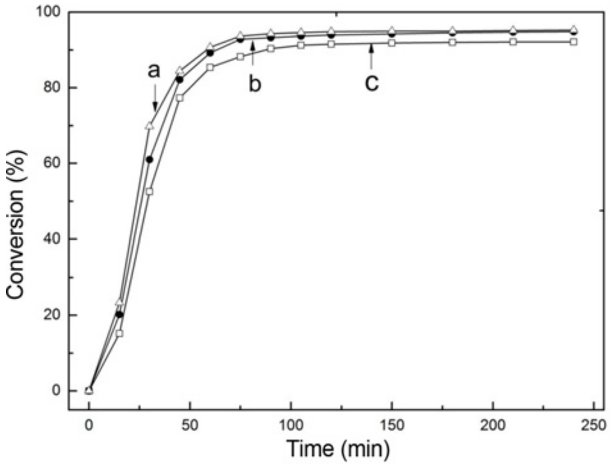
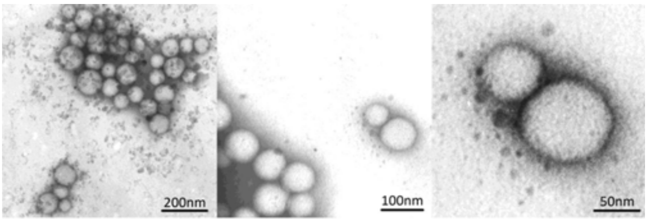


Figure 2. Conversion of TFEMA monomers with different content in wt% (a) 30 %, (b) 20 %, and (c) 10 %.



SPUFA30(×100000) SPUFA(×200000) SPUFA(×400000)

Figure 3. TEM images of SPU/PTFEMA hybrid latexes (SPUFA30) with different magnification. The vinyl polymer forms the lighter core region and the SPU forms the darker shell region.

The morphology of SPU/PTFEMA particles was investigated by transmission electron microscopy (TEM). TEM images of SPUFA30 with different magnification are shown in Figure 3. The particle size from 80 to 90 nm in diameter is observed in 30 wt% TFEMA sample. As shown in Figure 3, a clear core-shell structure was observed due to the different electron penetrability of the SPU and PTFEMA [18], where the vinyl polymer forms the lighter core region, while the SPU forms the darker shell region [19,20]. Due to the amphiphilic feature of SPU/PTFEMA composite system, the more hydrophilic chains tend to locate in the shell region, while the hydrophobic chains are concentrated in the core region in the phase-inversion process [21].

Thermal Properties

The thermal stabilities of SPU and SPUFA were evaluated as shown in Figure 4 (TGA) and Figure 5 (DTG). Two parameters were defined to describe the thermal stability and degradation behavior of the FA-SPU system, namely, temperature at which 25 % weight loss occurs (T_{25}) and temperature of top degradation rate in limited ranges (T_{max}). The better thermal stability of FA-SPU was observed from room temperature to 200 °C and also show an interesting dependence on the content of FA, this is due to more grafting between SPU and FA, the TGA results show that the introduction of FA monomers had little influence on thermal stability above 200 °C. In general, PU materials exhibit relatively poor thermal stability as the dissociation of the urethane bond is around 200 °C [22]. Further, the degradation can be divided to two ranges according to DTG studies (Figure 5). The first range is from 100 °C to 325 °C, and the second is from 325 °C to 500 °C corresponding to two thermal degradation peaks respectively.

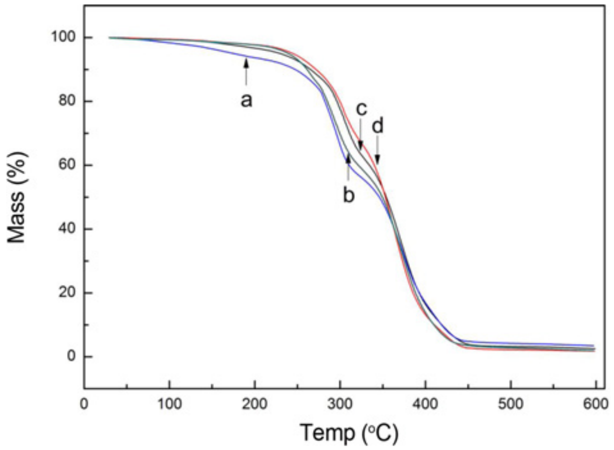


Figure 4. TGA curves for (a) SPUFA30, (b) SPUFA20, (c) SPUFA10, and (d) SPU.

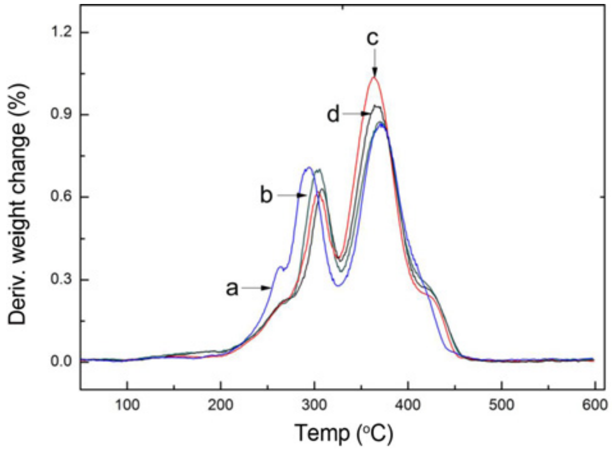


Figure 5. DTG curves for (a) SPU, (b) SPUFA10, (c) SPUFA20, and (d) SPUFA30.

The first thermal degradation peak can be attributed to the decomposition of the urethane bonds, which starts at around 200 °C. The second stage of degradation is attributed to soybean oil scission and the thermo-oxidative degradation of the films [23]. Introducing FA monomers can certainly affect the thermal degradation behavior according to Figure 5. With the content of FA monomers rising from 0 to 30 wt%, T_{25} value increases from 289 °C to 307 °C and a

Table 2. Thermal characterization of SPU, SPUFA from TGA and DSC

Sample	TGA			DSC	
	T_{25} (°C)	T^1_{max} (°C)	T^2_{max}	T_{g1} (°C)	T_{g2} (°C)
SPU	289	292	372	-19.1	20.0
SPUFA10	292	303	370	-17.7	25.8
SPUFA20	303	307	368	-10.4	36.0
SPUFA30	307	308	365	-9.85	40.7

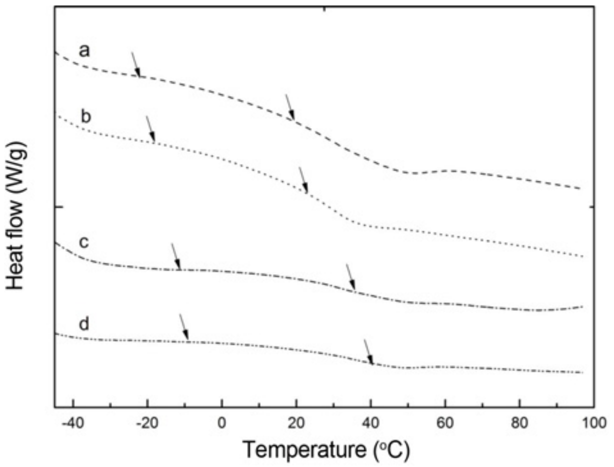


Figure 6. DSC curves of (a) SPU, (b) SPUFA10, (c) SPUFA20, and (d) SPUFA30.

higher T^1_{max} value (308 °C) is observed in the SPU-FA system in the first range (Table 2). However, in the second range, the introducing of FA monomers has little impact on thermal stability (T^2_{max} decreases slightly from 372 °C to 365 °C). These results indicate that the FA-SPU system displays a better thermal stability, especially below 350 °C. The enhancement of thermal stability can be attributed to the extensive interpenetration, tangles and grafting between SPU and PTFEMA [16].

The thermal behavior of the SPU-FA hybrid system was also investigated with DSC (Figure 6). It exhibits a typical amorphous nature of PU materials with no melting or crystallization peaks which is consistent with the reported PU/ST-BA hybrid system [16]. It is known that in a homogeneous phase system, only one glass transition temperature can be found in the DSC curve. But in a segmented polyurethane system, two glass transition temperature can be found, corresponding to the soft segments (T_{g1}) and hard segments (T_{g2}). In the hybrid system, two glass transition temperature are also observed, which demonstrates a phase-separated morphology in the system [24]. With the increase of vinyl monomers content, the T_{g1} shifts from −19.1 to −9.85 °C, and the T_{g2} shifts from 20.0 to 40.7 °C. The T_g values are influenced by interactions among segments, compatibility and interdiffusion of different phases. Introducing vinyl monomers change the affinity of one segment toward the other, as well as the ratio of the segments, resulting in the shifts of glass transition temperatures [25]. Moreover, FA monomers can be copolymerized with the residue double bonds in SPU chain in the process of emulsion polymerization, which reinforces interactions between PU and polyacrylate chains [26].

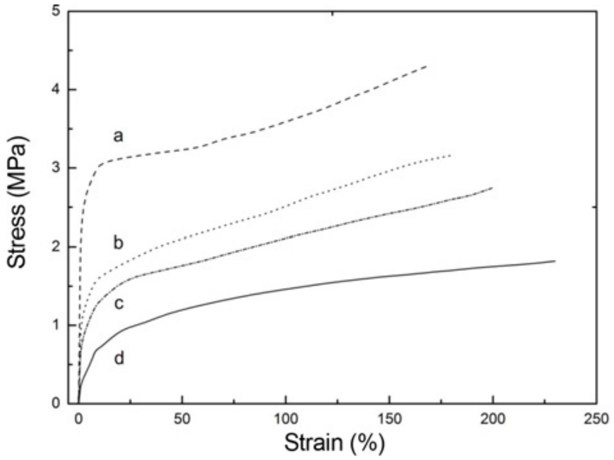


Figure 7. Stress-strain curves of (a) SPUFA30, (b) SPUFA20, (c) SPUFA10, and (d) SPU.

Mechanical Properties

The stress-strain curves of SPU and SPU-FA films are given in Figure 7. The pure SPU films exhibit a typical stress-strain behavior of rubber membrane with no yield point, presenting a stress at break and an elongation at break of around 1.82 MPa and 230 %. For SPUFA10, the stress at break increases, but its elongation at break slight decreases to about 200 %. By increasing the content of FA monomers, a yield point is observed in curves (a) and the stress and strain shifted to about 4.32 MPa, 170 %. According to Peruzzo's research [27], the presence of a yield point is characteristic feature of a two-phase structure, and it is probably related to the formation of polymers with different compositions. Thus, introducing acrylic monomers modifies the segments interactions and changes hydrogen bonding between polymer chains, which are in good agreement with above mentioned FT-IR and DSC analysis. However, the absolute value of mechanical property is rather low. But the hard segment and polyol functionality in SPU-FA have some space to optimize, high content of FA monomers could also increase the absolute value of mechanical property when considering its practical application.

Contact Angle and Surface Free Energy

Generally, PUs exhibit hydrophilic properties because of the urethane groups in its chains, which limit the application in outdoor coatings and materials. In our research, PTFEMA was introduced to improve the hydrophilic properties. In

Table 3. Contact angle (CA), surface free energy (γ) and solvent resistance (SR) of films

	PU20	SPU	SPUFA10	SPUFA20	SPUFA30
θH_2O	42.0	61.7	74.6	80.4	88.5
θCH_2I_2	34.5	49.2	55.3	60.5	69.2
SR (%)	18.7	22.2	27.5	32.2	35.3
γ_{Sd} (mJ/m^2)	34.3	29.1	27.3	24.5	20.9
γ_{Sp} (mJ/m^2)	25.6	15.9	9.23	7.15	5.04
γ_S (mJ/m^2)	59.9	45.0	36.5	31.7	25.9

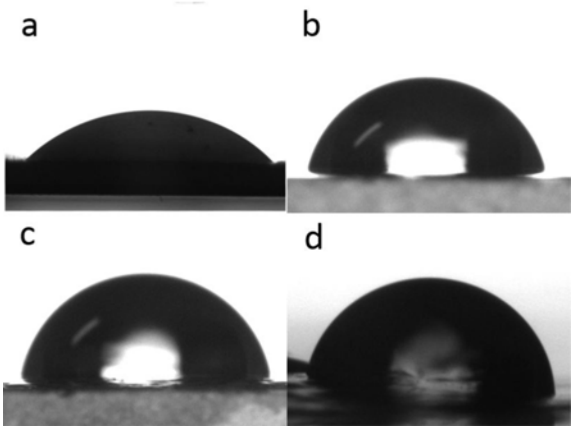


Figure 8. Contact angles for water of (a) PU20, (b) SPU, (c) SPUFA10, and (d) SPUFA30.

order to investigate the changes, contact angles (CA) were determined for two kinds of liquid (water and diiodomethane). According to the Fowkes' equation (2), the surface free energy (γ) of SPU-FA films, their polar (γ_p) and dispersion (γ_d) components were calculated (γ_{Ld}, γ_{Lp}, γ_L for water are 21.8, 51.0 and 72.8 mJ/m^2, and are 49.5, 1.3 and 50.8 mJ/m^2 for diiodomethane). For the purpose of comparisons, a parallel group (PU20) was prepared with PEG-1000 and IPDI and measured. The contact angles and values for calculating surface free energy were listed in Table 3.

$$\gamma_L(1+\cos\theta) = 2(\gamma_{Ld}\gamma_{Sd})^{1/2} + 2(\gamma_{Sp}\gamma_{Lp})^{1/2} \qquad (2)$$

The PU20 and SPU groups exhibit relatively low CA and high surface free energy at 42.0 °, 59.9 mJ/m^2 and 61.7 °, 45.0 mJ/m^2 respectively (Figure 8). Compared with the PU20, the SPU group shows a better performance with the CA increased by 46.9 % and the surface free energy decreased by 24.8 %, which can be attributed to soybean oil chain structure. After introducing PTFEMA, a better performance was observed in CA and surface free energy. The SPUFA30 with 30 % of TFEMA exhibited 88.5 ° in CA and 25.9 mJ/m^2 in surface free energy. Therefore, introducing TFEMA into SPU system will largely decrease the surface free energy and therefore, the resulting films cannot be easily wetted. In addition, solvent resistance (SR) of the films was improved after modification by TFEMA thanks to cross-linking increase and low surface free energy.

Conclusion

In conclusion, a series of hybrid latexes from soybean oil-based polyurethane and poly (2,2,2-trifluoroethyl methacrylate) were successfully prepared from soybean oil-based polyurethane dispersion and Poly(2,2,2-trifluoroethyl methacrylate), and this is believed to be a relatively facile and cheap approach. Physical properties, such as morphology, thermal stabilities and coating performance have been thoroughly characterized and discussed. FT-IR confirmed the FA monomers have been introduced into the system. With the increasing content of FA monomers (0 to 30 wt%), the monomer conversion rate also increases and the particles are bigger in size and broader in particle size distribution. TEM images clearly show the core-shell structure within the hybrid latexes. Evidenced by TGA and DSC, better thermal stability is apparently obtained. Introducing the FA monomers will help delay the thermal decomposition peak and lower the rate of decomposition. Compared with the pure SPU films, the hybrid films exhibit a relative high stress and low strain due to the grafting and tangle between SPU and FA chains.

Overall, SPU-FA hybrid films exhibit a significant increase in weatherability in terms of thermal stability, water resistance and mechanical properties. Furthermore, it is prepared from environmentally friendly soybean oil instead of traditional petroleum raw materials, and being a material from renewable source, it will avoid many problems associated with petroleum based materials. Given these mild reaction conditions and simple chemical reactions, our approach is amenable to other starting materials with similar structures which open up tremendous opportunities for further improvements. Clearly, our SPU-FA is a promising inexpensive material for novel decorative, protective and outdoor coatings. Validations for these potential applications are current undergoing in our lab.

Acknowledgement

The authors gratefully acknowledge the Key Laboratory of Science & Technology of Eco-Textile (Donghua University) for financial support for this work.

References

1. N. Karl-Ludwig, *J. Prog. Org. Coat.*, **32**, 131 (1997).
2. D. K. Chattopadhyay and K. V. S. N. Raju, *J. Prog. Polym. Sci.*, **32**, 352 (2007).
3. D. E. Fiori, *J. Prog. Org. Coat.*, **32**, 65 (1997).
4. Y. Lu and R. C. Larock, *J. Prog. Org. Coat.*, **69**, 31 (2010).
5. B. U. Ahn, S. K. Lee, and S. K. Lee, *J. Prog. Polym. Sci.*,

60, 17 (2007).

6. S. Y. Lee, J. S. Lee, and B. K. Kim, *J. Polym. Int.,* **42**, 67 (1997).
7. A. C. Aznar, O. R. Pardini, and J. I. Amalvy, *J. Prog. Polym. Sci.,* **55**, 43 (2006).
8. G. Lligadas, J. C. Ronda, and M. Galia, *J. Biomacromolecules*, **8**, 686 (2007).
9. G. Lligadas, J. C. Ronda, and M. Galia, *J. Biomacromolecules*, **11**, 2825 (2010).
10. H. Xin, Y. Shen, and X. Li, *J. Colloid. Surface. A,* **384**, 205 (2011).
11. C. Decker, F. Masson, and R. Schwalm, *J. Polym. Degrad. Stabil.*, **83**, 309 (2004).
12. X. Jiang, J. Li, Ming, M. Ding, H. Tan, Q. Ling, Y. Zhong, and Q. Fu, *Eur. Polym. J.*, **43**, 1838 (2007).
13. Y. Lu and R. C. Larock, *J. Biomacromolecules,* **9**, 3332 (2008).
14. P. J. Peruzzo, P. S. Anbinder, and O. R. Pardini, *J. Prog. Org. Coat.*, **72**, 429 (2011).
15. P. J. Peruzzo, P. S. Anbinder, and O. R. Pardini, *J. Prog. Org. Coat.*, **72**, 429 (2011).
16. Y. Lu, Y. Xia, and R. C. Larock, *J. Prog. Org. Coat.,* **71**, 336 (2011).
17. S. T. Wang, F. J. Schork, G. W. Poehlein, and J. W. Gooch, *J. Prog. Polym. Sci.,* **60**, 2069 (1996).
18. H. Xin, Y. Shen, and X. Li, *J. Colloid. Surface. A,* **384**, 205 (2011).
19. A. J. Dong, Y. L. An, and S. Y. Feng, *J. Colloid. Interf. Sci.,* **214**, 118 (1999).
20. A. Guyut, K. Landfester, and F. J. Schork, *J. Prog. Polym. Sci.,* **32**, 1439 (2007).
21. S. L. Chai and M. M. Jin, *J. Appl. Polym. Sci.*, **114**, 2030 (2009).
22. A. Guo, Y. J. Cho, and Z. S. Petrovic, *J. Polym. Sci. Pol. Chem.*, **38**, 3900 (2000).
23. G. Lligadas, J. C. Ronda, and M. Galia, *J. Biomacromolecules,* **7**, 3521 (2006).
24. P. Krol, *J. Prog. Mater. Sci.,* **52**, 915 (2007).
25. G. Lligadas, J. C. Ronda, and M. Galia, *J. Biomacromolecules,* **8**, 686 (2007).
26. Y. Lu and R. C. Larock, *J. Biomacromolecules,* **8**, 3108 (2007).
27. P. J. Peruzzo, P. S. Anbinder, and O. R. Pardini, *J. Prog. Org. Coat.,* **72**, 429 (2011).