

Hydrophobic and Oil-Resistant Coatings Based on Advanced Green Polyurethane Dispersions

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ABSTRACT: In recent years, there have been significant interests among scientists around the world to design smart coatings that combine the standard desirable mechanical and chemical resistance properties with additional functionalities such as oil and water repellency, hydrophobicity, self-cleaning and gas barrier properties. In the present research work, advanced aqueous polyurethane dispersion (PUD) systems have been designed and developed using three different types of polyols as soft-segments. These polyols differ in their chemical structure, functionality, polarity, and interfacial properties. The effects of soy-based polyol, hydroxy-terminated perfluoropolyether, and hydroxy-terminated polydimethylsiloxane—on various mechanical properties of their uncross-linked and cross-linked films, and more specifically on their hydrophobicity and oil-resistance (oleophobicity) have been studied. Hydrophobicity of these coatings has been characterized by their Dynamic Contact Angle measurements and their oleophobicity by n-octane absorption method. The investigations showed that presence of fluorine and siloxane structures significantly improve the hydrophobicity and oil resistance of these coatings and it is possible to optimize these properties using suitable composition of PUDs. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3874–3884, 2013

KEYWORDS: coatings; biopolymers & renewable polymers; polyurethanes; ring-opening polymerization; surfaces and interfaces

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INTRODUCTION

Environmental legislations, depleting fossil resources, and economic burdens have motivated industrial and academic researchers to develop renewable feedstock for sustainable development of environmentally friendly coatings, adhesives, sealants and elastomers.^{1,2} For sustainable development and growth of such advanced material technologies, it is increasingly important to develop a platform of polymer building blocks based on renewable resources.^{3,4} Vegetable and plant oils are important agricultural resources that are available at low costs. The unique combination of chemical structure, functionality, reactivity, low toxicity, and biodegradability makes vegetable oils excellent resources for deriving sustainable polymers.^{3,5–7} Using principles of green chemistry and through chemical transformations, it is possible to derive bio-based materials with significantly lower carbon footprint while meeting the high performance demands of application.^{5,8–13}

A variety of soy-polyols, prepared from different synthetic routes, have been reported in the literature.^{10–21} Polyurethanes prepared from these soy-polyols, replacing petro-based polyols, show interesting performance properties, besides their high

bio-renewable contents.^{10,13–22} Soy-polyols for use in polyurethane dispersions (PUD) require unique set of property requirements and hydroxyl functionality. In keeping with this, we developed a soy-polyol with low molecular weight and hydroxyl functionality of ~ 2.0 , from epoxidized soy methyl esters, using a novel process.^{25–27}

The polymeric binders for coating applications require customized bulk properties and surface, to meet the challenging demands during end-use applications. The bulk properties contribute to the coating's chemical resistance and mechanical properties, such as film toughness, hardness, flexibility, and thermal properties such as glass transition temperature and thermal stability. Whereas surface properties control such attributes as water repellency, oil repellency, hydrophilicity, besides many more. Control over surface properties are important, to ensure better performance of materials in many engineering and scientific applications.^{28–31} It has been well established that wettability of solid surface is governed by both surface free energy (surface chemical composition) and topographical microstructure of coating surface. Coatings with high water and oil repellency is very important because of myriads of industrial

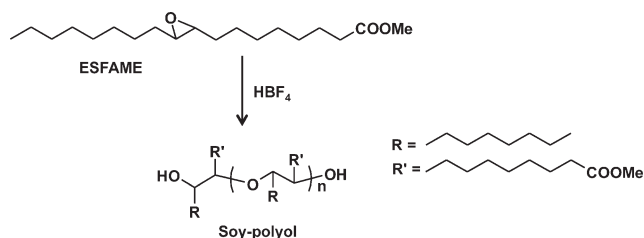


Figure 1. Schematic reaction scheme for synthesis of soy-polyol.

applications such as oil water separations, antireflection, printing, and antibio adhesion.^{32–38}

In this present research work, we have developed novel hydrophobically modified PUDs to study their mechanical properties, water-repellency and oil-resistance. The PUDs have been prepared with bio-based soft-segments (bio-PUD) using a novel hyperbranched soy-polyol derived from epoxidized soy fatty acid methyl ester (ESFAME). Soy-polyol was synthesized by following our earlier research work.^{25–27} The polyurethane architecture has been modified by the incorporation of perfluoropolyether and/or polydimethylsiloxane (PDMS) moieties as hydrophobizing structures in varying proportions. The effect of these modifications on various mechanical properties, water and oil resistance properties of their cross-linked and un-cross-linked films are reported. The study shows that it is possible to optimize mechanical properties (bulk), water and oil-resistance (surface) using suitable polymer compositions.

EXPERIMENTAL

Raw Materials

Soy-polyol was derived from epoxidized soy fatty acid methyl ester (ESFAME) which was procured from Arkema, USA, under trade name of Vikoflex 7010, PDMS-based polyol (PDMS polyol) was obtained from Siltech Corporation, Canada under the trade name of Silmer OH-Di-10 and perfluoropolyether polyol (Fluoro polyol) was purchased from Solvay Solexis, USA as fluorolink D10/H. All three polyols were used to build a soft segment of aqueous PUD. Desmodur I, the trade name of Isophorone diisocyanate (IPDI) was received from Bayer

Material Science, USA, and dimethylolpropionic acid (DMPA) from Geo Specialty Chemicals, USA, were used as procured. All other raw materials such as triethylamine (TEA) as neutralizing agent, ethylene diamine (EDA) as chain extender, N-methylpyrrolidone (NMP), acetone, dibutyltin dilaurate (DBTDL), 1,4 Butane diol, 48% tetrafluoroboric acid in water, were purchased from Sigma Aldrich, USA, and used as received. The carbodiimide-based cross-linker carbodilite SV-02, a product of Nisshinbo was procured from GSI Exim America.

Standard Testing Methods

Intermediates, products and coatings were characterized using ASTM methods where applicable; % oxirane content (ASTM D-165297), Acid number (ASTM D-1639-96), hydroxyl number (ASTM D-4274-05), Pencil hardness (ASTM D-3363), impact resistance (ASTM D-2794-99), Adhesion (cross-cut) test (ASTM D-3359-02), MEK double rub test (ASTM D-4752-98). Functional group characterization of Soy-polyol was done recording Fourier Transform Infrared (FTIR) spectra with Bruker Tensor 27 FTIR analyzer in the range of 400–4000 cm^{-1} at room temperature and Brookhaven 90Plus particle size instrument was used to determine the particle size of PUD at 25°C.

Synthesis of Soy-Polyol

A novel hyper-branched soy-polyol was derived from ESFAME using a cationic ring-opening polymerization mechanism developed by our research group earlier.^{25–27} Figure 1 shows simplified schematic reaction scheme for the synthesis of soy-polyol. Epoxy (oxirane) compounds can undergo acid-catalyzed cationic ring-opening polymerization reactions through oxiranium intermediates with the formation of polyether chains^{13,25–27,39} as shown in Figure 2. Soy-polyol was characterized for viscosity, Acid number (ASTM D –1639-96) and hydroxyl number (ASTM D 4274-05) and stored in airtight glass jar.

Synthesis of Green (bio)-PUD

Calculated amount of Soy-polyol, NMP, DMPA, and 1,4 butane diol were placed in a 3-neck flask connected with mechanical stirrer, water condenser, nitrogen inlet and outlet, and heating mantle connected with temperature controller. Reaction was carried out at 100°C until DMPA was completely dissolved in

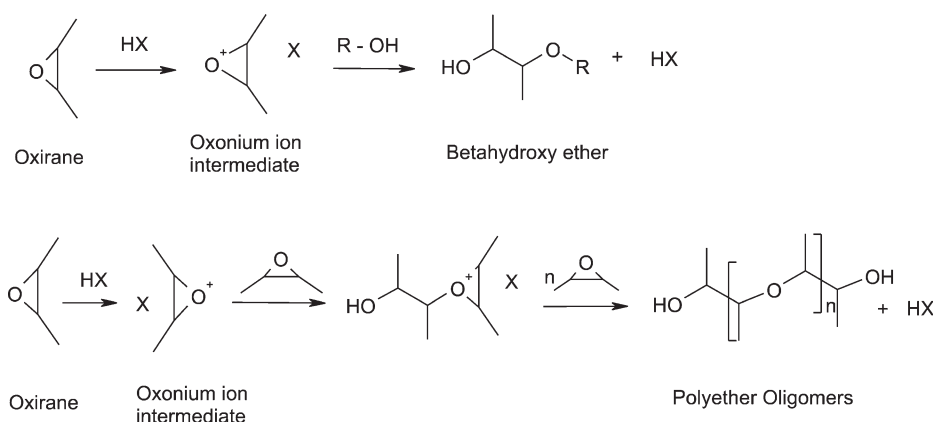


Figure 2. Cationic ring-opening polymerization mechanism of epoxy compound.

Table I. Composition of Green PUDs

PUD Composition & Characteristics	Bio PUD 1	Bio PUD 2	Bio PUD 3
Soy-Polyol (moles)	0.018	0.026	0.050
1,4-Butane diol (moles)	0.026	0.010	0.000
DMPA (moles)	0.030	0.038	0.065
IPDI (moles)	0.108	0.111	0.174
EDA (moles)	0.031	0.032	0.050
NMP (% based on final dispersion)	6.0	6.0	6.0
Pre-polymer NCO/OH(Equivalent weight ratio)	1.40	1.40	1.40
% Neutralization	90	90	90
Acid value (mgKOH/g)	30.0	30.0	30.0
Soft Segment (SS) (% by weight)	45.0	55.0	60.0
Hard Segment (HS) (% by weight)	55.0	45.0	40.0

polyol and NMP mixture. Then reaction temperature was cooled down to 70°C at which point IPDI was slowly added into the reaction mixture in the presence of DBTDL catalyst. Every 30 min a sample of reaction mixture was drawn and tested for % isocyanate content (ASTM D 2572-97). When desired % isocyanate content was reached, reaction mixture was cooled down to 55°C and calculated amount of triethylamine (neutralizer) was added (degree of neutralization ~ 90%) and the mixture was stirred for 30 min. Immediately after neutralization, prepolymer was transferred to high-speed disperser to extend the prepolymer chain with EDA and further dispersed with de-ionized water. Table I shows composition of PUDs used in present study. Figure 3 shows the general reaction scheme for the synthesis of bio-PUD.

Synthesis of Hydrophobically Modified Bio-PUDs

Hydrophobic PUDs were synthesized by incorporating silicone and fluorine groups into the backbone of polyurethane soft segment. For these PUDs, the soft segment content was kept constant at 55% as at this level bio-PUD-2 showed balanced properties. The hydrophobic PUDs were synthesized by using the same procedure that was followed for the bio-PUDs. Table II shows the compositions and some important parameters of hydrophobic PUDs prepared for this study. Following Figure 4 represents the hydrophobic PUD reaction mechanism.

RESULTS AND DISCUSSION

Characterization of Soy-Polyol

The oligomerization reaction was monitored by following % oxirane content as well as by FTIR spectroscopy, which showed a decrease in the absorption peaks of 824 and 843 cm^{-1} corresponding to an oxirane ring, and finally disappeared. An increase in the absorption at 1070 cm^{-1} (C-O-C ether) and in the broad band around 3400–3500 cm^{-1} (O-H hydroxyl group) was also noticed. This indicated that oxirane ring opening took place to form ether linkages and the formation of hydroxyl groups. Figure 5 presents FT-IR spectrum for soy-polyol. The resultant soy-polyol was a clear yellow viscous oil having –OH number 88 (mgs

of KOH per g), viscosity 6200 cPs (at 25°C), hydroxyl equivalent weight of 637.5 g. The number average molecular weight of polyol was 1517 g/mole (GPC) with polydispersity index of 6.04.

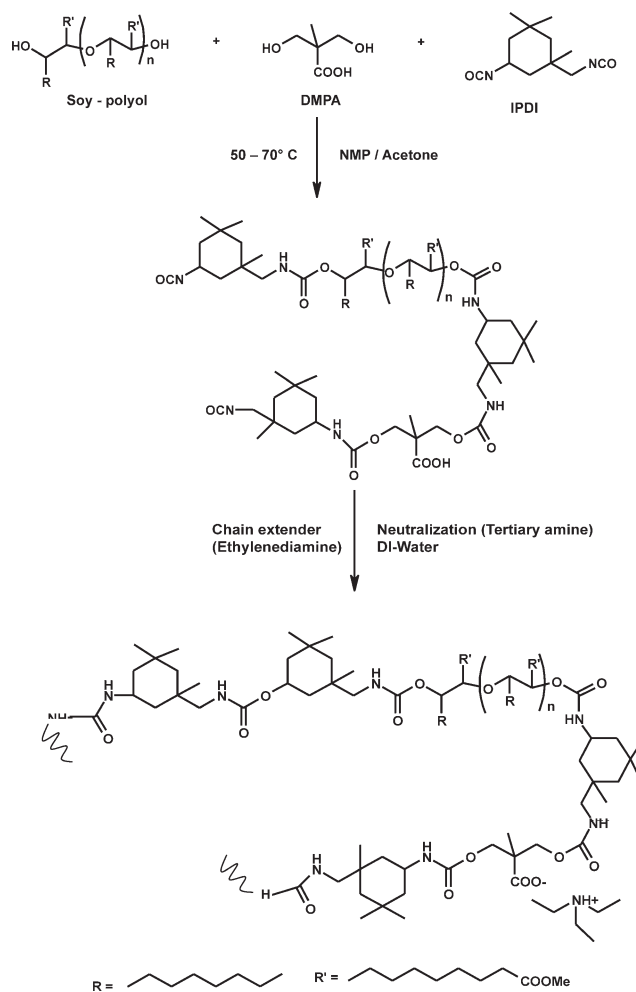
**Figure 3.** Schematic reaction scheme for synthesis of bio-PUD.

Table II. Compositions of Hydrophobic PUDs

PUD Composition & Characteristics	Surface Modified PUD								
	55B	55Si	55F	30B25Si	30B20Si5F	30B15Si10F	30B10Si15F	30B5Si20F	30B25F
Soy-polyol (Mw =1517g/mole)	0.026m	0	0	0.012m	0.012m	0.012m	0.012m	0.012m	0.012m
PDMS polyol (Mw =1000g/mole)	0	0.026m	0	0.016m	0.012m	0.009m	0.006m	0.003m	0
Fluoro polyol (Mw =1539g/mole)	0	0	0.013m	0	0.002m	0.004m	0.012m	0.008m	0.010m
1,4 Butane diol (Mw = 90 g/mole)	0.01m	0.001m	0.009m	0.006m	0.007m	0.008m	0.009m	0.010m	0.011m
DMPA (Mw =134.13g/mole)	0.038m	0.025m	0.019m	0.033m	0.032m	0.031m	0.031m	0.032m	0.031m
IPDI (Mw = 222g/mole)	0.111m	0.076m	0.056m	0.098m	0.095m	0.093m	0.093m	0.094m	0.092m
EDA (Mw =60g/mole)	0.032m	0.020m	0.014m	0.025m	0.024m	0.024m	0.026m	0.024	0.023m
SoftSegment Composition (%)									
Soy - Polyol	55	0	0	30	30	30	30	30	30
PDMS Polyol	0	55	0	25	20	10	15	5	0
Fluoro Polyol	0	0	55	0	5	15	10	20	25
Pre-polymer NCO/OH (eq.wt)	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40
% Neutralization	90	90	90	90	90	90	90	90	90
Acid value (mgKOH/g)	30	30	30	30	30	30	30	30	30
NMP(% based on final dispersion)	6	6	6	6	6	6	6	6	6
Soft Segment SS (% by weight)	55	55	55	55	55	55	55	55	55
Hard Segment HS (% by weight)	45	45	45	45	45	45	45	45	45

m = moles, eq.wt = equivalent weight ratio

Characterization of PUD Film Properties

Table III and Table IV respectively shows the basic mechanical properties of green PUD and uncross-linked hydrophobic PUDs prepared for this study. Coatings with dry film thickness of approximately 35 μm were applied on cold-roll steel panel and cured at room temperature. Films were tested for mechanical properties after one week of room temperature cure. As can be seen from Table III and Table IV, incorporation of PDMS polyol in the soft segment (sample 30B25Si) decreased the pencil hardness from 2H to B. The decrease in pencil hardness, which is related to the modulus of the film, can be attributed to lower modulus of the film because of the incorporation of low T_g PDMS. Interestingly, Koenig hardness, which measures dampening property of coatings, is much higher with samples containing both PDMS polymer chains. We believe that this is because of higher hard-segment content in samples containing PDMS because of its lower molecular weight compared to that of soy-polyol. The resulting higher urethane group content is believed to be the reason for higher Koenig hardness of these films. Introduction of the fluoro-polyol backbone (sample 30B20Si5F) increased both pencil and Koenig hardness. Two factors might be at play here: (a) fluoro-polyols have high modulus (compared to PDMS polyol and soy-polyol), which will tend to increase pencil hardness of the film. (b) Also, in all fluoro-polyol-based PUD formulation, it was necessary to use some amount of 1,4-butanediol (hard segment) in order to maintain soft segment / hard segment ratio to 55:45 for all PUD compositions. This resulted in increased hard segment content (1,4-

butane-diol-based hard segment content) in 30B20Si5F, 30B15Si10F, and 30B10Si15F resulting in higher pencil and Koenig hardness.

The reduced impact resistance for both Si and F containing films (samples 30B25Si and 30B20Si5F) can be attributed to the possibility of microphase separation in the film. It can be seen from Figures 6 and 7 that increasing amount of fluorinated polyol in PUD increases the nano-structured surface roughness (peaks) and changing the phase morphology, respectively. Interestingly such phase contrast morphology was also showed in Ref. 43 with the help of microscopy images. Number of researchers⁴⁰⁻⁴⁶ have shown that PDMS polyol and fluoro polyol contributes to phase separation and can affect impact resistance of their films. It is interesting, however, that the cross-cut adhesion was not affected by this possible phase morphology. This indicated minimal perturbation to the underlying coating layer of modified PUD. The increase in solvent resistance (MEK double-rub) for PUDs containing siloxane and fluorine (compared to bio-PUD) is because of the low swelling nature of siloxane and fluorine containing polymers to MEK.

Self-Cross-Linking of PUD

With a view to improve mechanical properties of PUDs discussed above, we thought of cross-linking these PUDs. This was achieved by self cross-linking the carboxylic acid groups from PUD backbone with poly-carbodiimide, as shown in Figure 8. Compositions were added with poly-carbodiimide (5% by weight based on PUD nonvolatiles) were applied

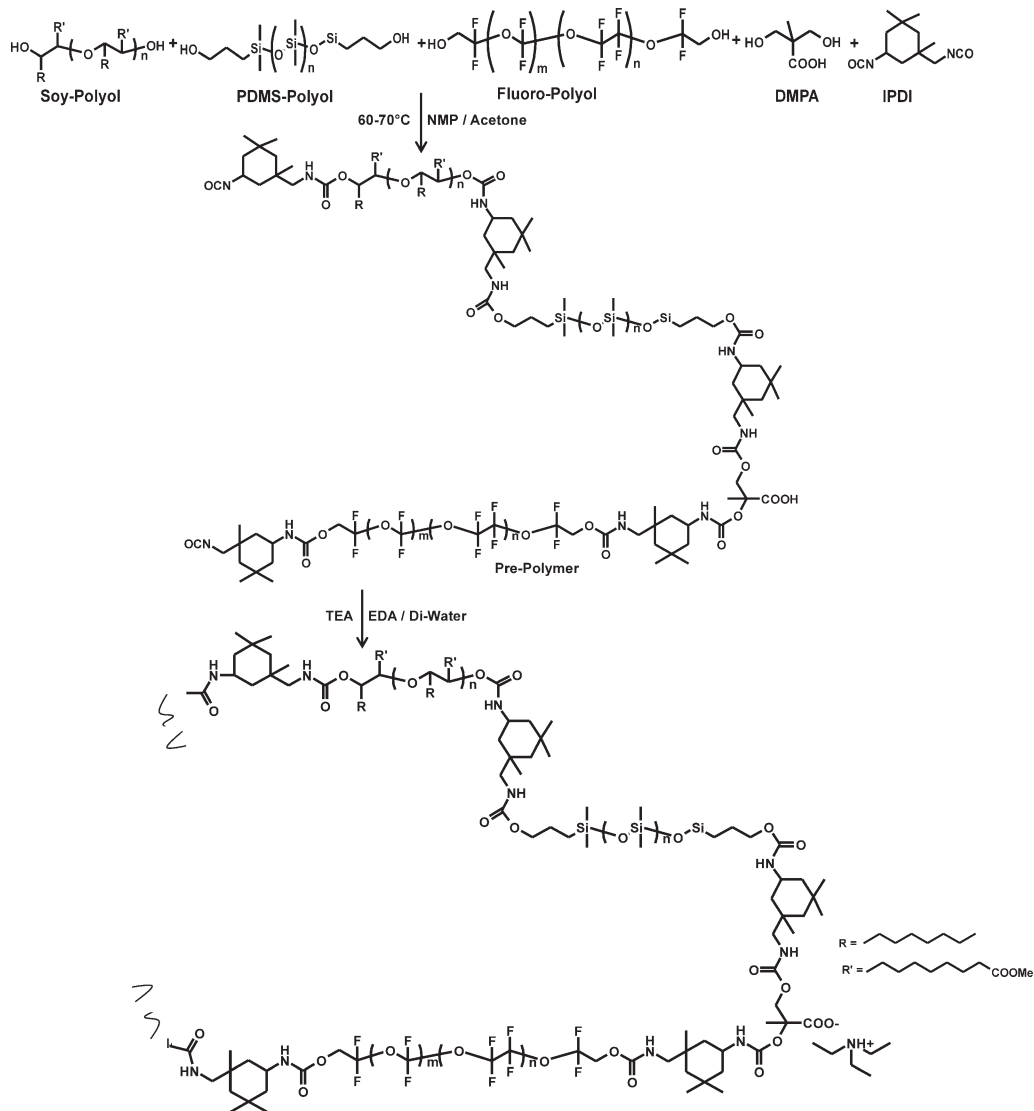


Figure 4. Schematic representation of hydrophobic PUDs with three different polyol polymeric chain backbone.

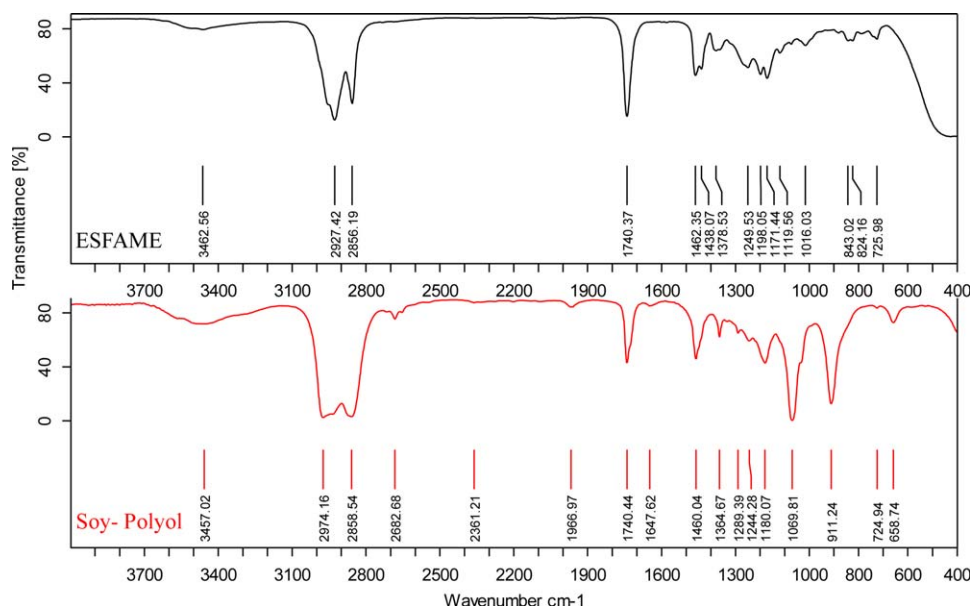


Figure 5. FTIR characterization of ESFAME and Soy-polyol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Characteristics of Green PUDs and Their Film Properties

Bio - PUD Characteristics and Film Properties	Bio PUD 1	Bio PUD 2	Bio PUD 3
Pencil Hardness	4H	2H	3B
Koenig Hardness (seconds)	120	108	60
Cross Cut Adhesion	5B	5B	5B
Impact Resistance(lbs x inch)			
Direct	100	160	160
Reverse	60	160	160
Contact Angle (degree)	69	73	75
Average Particle Size (nm)	203	146	137
Stability (60 days @ 60°C)	Stable	Stable	Stable

(~35 μm dry-film thickness) on cold-rolled steel and cured for seven days at ambient temperature. Upon curing, neutralizing amine will be released from the coating film, leaving the free carboxylic acid groups available for reaction with poly-carbodiimide cross-linker. In order to enhance the rate of cross-linking, pH of PUDs was kept slightly acidic. Therefore, all the PUDs (containing carbodiimide cross-linkers) were prepared with degree of neutralization of ~ 90%.

As can be seen in Table V, cross-linked PUDs showed good overall improvement in mechanical properties. This clearly indicates appreciable degree of cross-linking by poly carbodiimide under the conditions of curing. Remarkable improvement can be observed in MEK double rub and impact resistance of the coating. MEK double rubs values were almost doubled compared to their noncross-linked counterparts. The increase in cross-link density and formation of urea groups were believed to have improved the reverse impact resistant by increasing overall toughness of the coating.

Contact Angle Measurements

As shown in Figure 9, increasing the siloxane content in pre-polymer backbone increased the water contact angle. Since, contact angle measurements characterizes hydrophobicity of coating surface, the increased contact angle could be the result of hydrophobic siloxane groups that are readily available on the surface of the coating. Since, 18.15% siloxane content formulation (55Si-PUD) exhibits lower contact angle, surface enrichment of siloxane appears to have limited values. It is very interesting to note that contact angle of sample 30B25Si, which contains a blend of soy-polyol and PDMS exhibit much higher contact angle compared to the samples containing pure individual components (samples 55B and 55Si). This clearly shows the synergistic effect of two types of polyols. We believe that the hyper-branched soy-polyol may be facilitating siloxane group orientation at the surface. Comparison between cross-linked and uncross-linked films showed no appreciable difference in contact angle values. This indicates, cross-linking with carbodiimide increases mechanical properties of the films but does not have appreciable effect on their surface properties.

Table IV. Characteristics of Hydrophobically modified PUDs and their uncross-linked cured Film Properties

Film Properties	Surface Modified PUD									
	55B	55Si	55F	30B25Si	30B20Si5F	30B15Si10F	30B10Si15F	30B5 Si20F	30B25F	
Pencil Hardness	2H	B	Very Poor Film Appearance	B	F	H	2H	Very Poor Film Appearance	Very Poor Film Appearance	
MEK Double RUB	0	0		75	70	25	30			
Koenig Hardness (seconds)	49	91		133	136	128	148			
Cross Cut Adhesion	5B	5B		5B	5B	5B	5B			
Impact Resistance (lbs.in)										
Direct	160	160		100	160	140	160			
Reverse	160	160		40	40	80	40			
Average Contact Angle (°)	72	95	127	124	121	111				
Average Particle Size (nm)	146	34	143	88	98	102	110	126	135	
Stability (60 days @ 60°C)	Stable	Stable	Settled after 20 days	Stable	Stable	Stable	Stable	Settled after 14 days	Settled after 17 days	

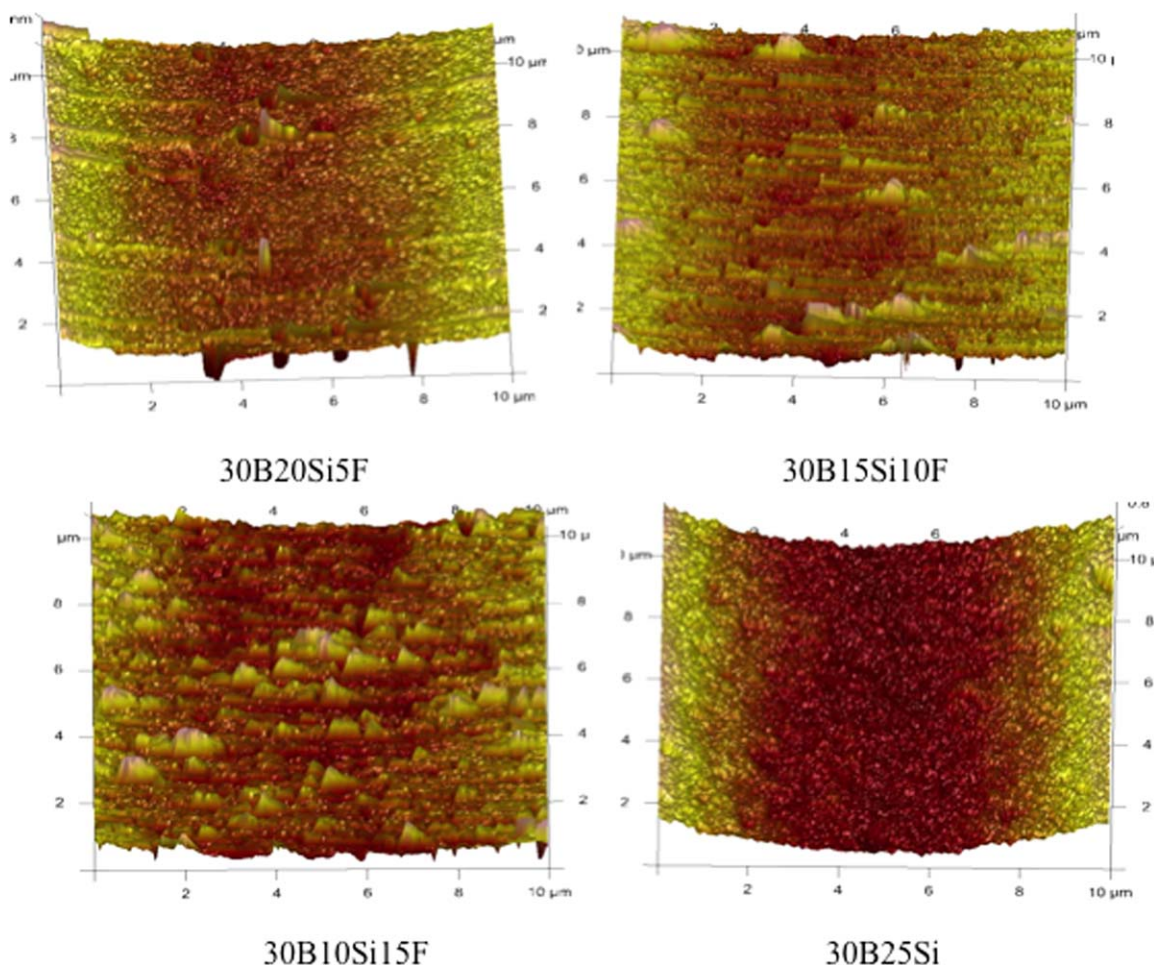


Figure 6. Three-dimensional AFM $10 \times 10 \mu\text{m}$ images for hydrophobic PUDs obtained by tapping method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The PUDs 30B10Si15F, 30B15Si10F, and 30B20Si5F have 8.55%, 5.70%, and 2.85% fluorine content, respectively. Unlike siloxane content, increasing the fluorine content decreased the hydrophobicity of the coating. This behavior contradicts the general notion of fluorine groups migrating to the surface and decreasing the surface free energy and hence increasing the water contact angle. As stated in Ref. 44 to exhibit surface properties, all the fluoroalkyl groups in the coating system should be at the surface rather than at bulk. The fluorinated urethane is amphiphobic in nature in which high energy urethane groups are chemically connected with low energy perfluoropolyether groups. When the fluorocarbon groups segregate at polymer/air interface, the high-energy urethanes could be pulled to the coatings subsurface by low-energy moieties. The concentration of urethane groups near subsurface increased as the percent of fluorine content in PUD formulation was increased. When such surface comes in contact with water the urethane groups from subsurface easily migrate to the polymer/water interface and lead the fluorine groups' re-orientation towards bulk of the coating film. Thus the water contact angle decreased with increased perfluoropolyether polyol content. The aforemen-

tioned claim is in accordance with Refs. 47,48. Also the achieved pencil hardness from Table IV proves fluorine groups' re-orientation towards bulk of the film. As fluorine content increased the pencil hardness also increased because of more re-orientation of fluorine into bulk. Such phenomenon could be expected in PDMS-urethane part of the PUD, but the alkyl chain length (propyl group) that chemically bonds the urethane with PDMS is longer than the alkyl chain (methyl group) bonding urethane with fluorine. This linker length made the urethanes belong to fluorine closer to surface than the urethanes belong to PDMS. Thus the reduction in contact angle was observed with fluorine moieties. When percent content of fluorine was increased from 8.55 along with other two polyols the appearance of films were hazy. In this case the larger quantity might have possibly phase separated the fluorochemical domains from hydrocarbon of the polymer. As fluorine percent increased, the haze increased and rendered the films (30B5Si20F, 30B25F, 55F) unusable for further analysis. For the aforementioned reason, to improve the appearance and surface property of the film, % of fluorine used in the coating formulation should be optimized.

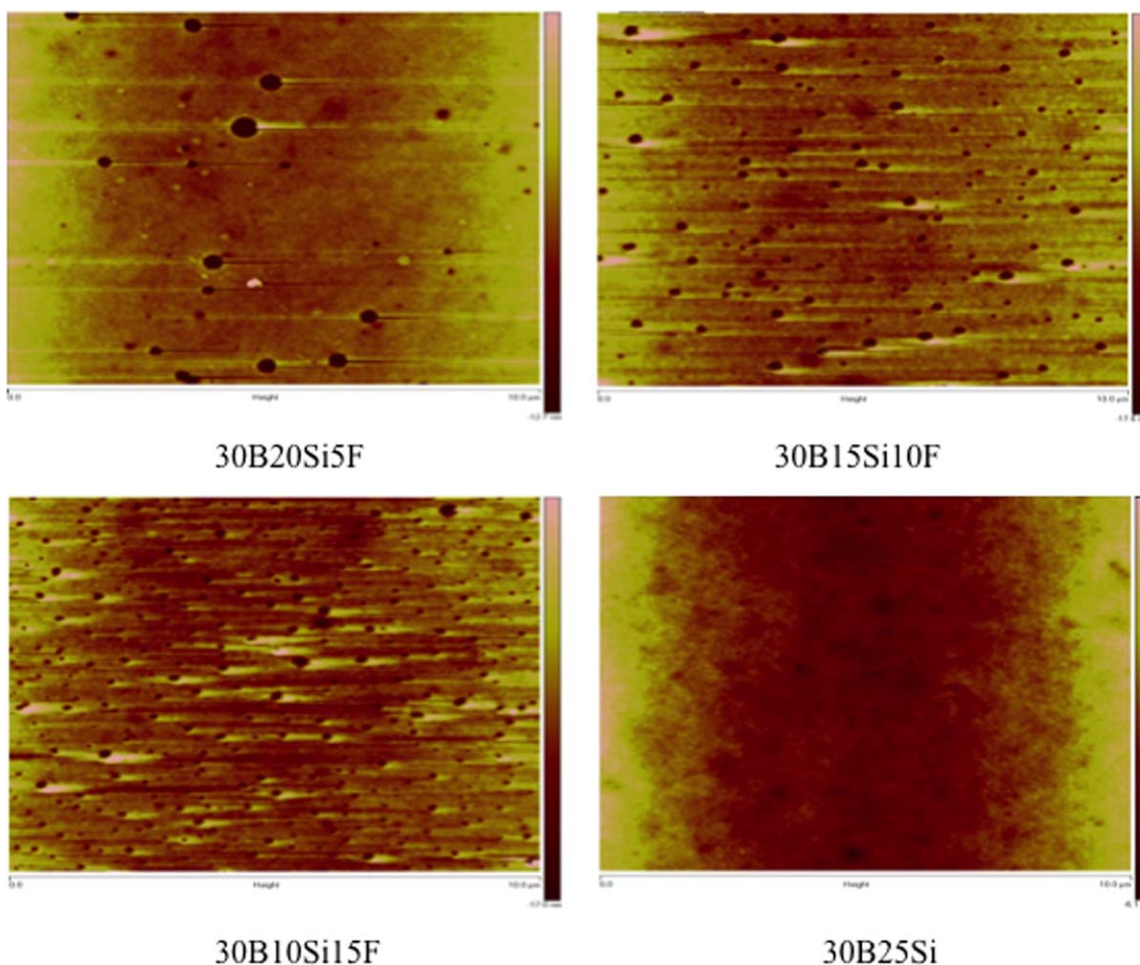


Figure 7. Two-dimensional AFM $10 \times 10 \mu\text{m}$ changing phase morphology images for hydrophobic PUDs obtained by tapping method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Hydrophobic and Oleophobic Properties

General solvent absorption technique was used to characterize hydrophobicity and oleophobicity of coating. About 1 square inch of free PUD film was dipped in Di-water (for hydrophobicity) and in n-octane (for oleophobicity) for 24 hours. After 24 hours both hydrophobicity and oleophobicity of coating films were measured based on % absorption (swelling ratio) of solvent (Figure 10).

$$\% \text{Swelling Ratio} = \frac{\text{Final film weight} - \text{Initial Film Weight}}{\text{Final film weight}} \times 100$$

The water resistance of free PUD films is shown in Figures 10 and 11. Once again, synergistic effect can be observed when more than one polyol type was present in soft segment. PUDs 30B20Si5F, 30B15Si10F, and 30B10Si15F have all of the three types of polyols in their soft segments. Water and oil resistance has been studied as a function of % siloxane and % fluorine content of PUD films. It is evident from Figures 9 and 11 that increasing the siloxane content increased the hydrophobicity of

coating. When siloxane content was increased from 3.36% to 6.72%, the water absorption was decreased from 55.1% to 14.2%. This is 74.23% improvement in water resistance.

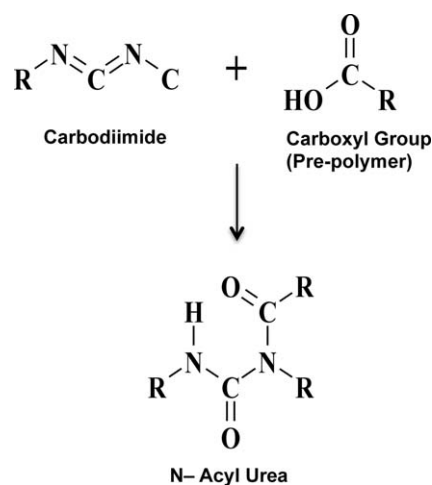


Figure 8. Schematic reaction of formation of N-Acyl Urea.

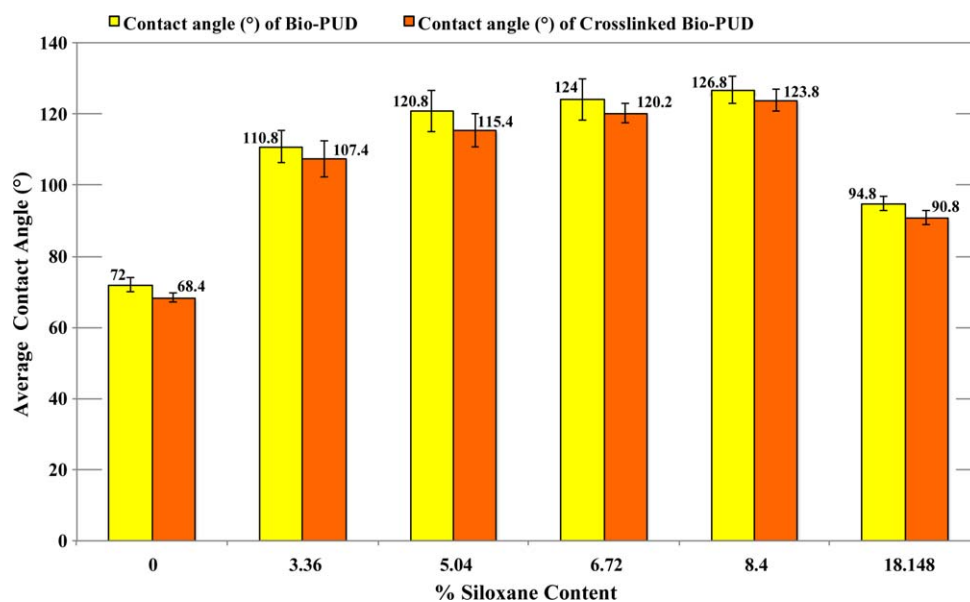
Table V. Mechanical Properties of Self Cross-Linked PUD Film Properties

Film Properties	Surface Modified PUD					
	55B	55Si	30B 25Si	30B20Si5F	30B15Si10F	30B10Si15F
Pencil Hardness	3H	F	F	F	2H	2H
MEK Double RUB	25	25	150	145	50	60
Koenig Hardness (seconds)	67	100	140	140	144	154
Cross Cut Adhesion	5B	5B	5B	5B	5B	5B
Impact Resistance (lbs.in)						
Direct	160	160	160	160	160	160
Reverse	160	160	160	160	160	120
Average Contact Angle (°)	68	91	124	120	115	107

Table VI. Contact angle of uncross-linked PUD and their respective % Content of Siloxane and Fluorine

Types of PUD	Contact Angle (°)	% of Siloxane content	% of Fluorine content
55B	72	0	0
55Si	95	18.15	0
55F	-	0	31.35
30B25Si	127	8.4	0
30b25F	-	0	14.25
30B20Si5F	124	6.72	2.85
30B15Si10F	121	5.04	5.70
30B10Si15F	111	3.36	8.55

Interestingly, unlike hydrophobicity (water contact angle), oil resistance increased with increasing the amount of fluorine content. Even though % improvement in oil resistance that resulted because of increased fluorine content is considerably small, it is still evident that contribution of fluorine groups to oil resistance is greater than that of siloxane content. In fact, increasing the siloxane content compromised the oil resistance of coating. Attempts were made (30B5Si20F, 30B25F, 55F) to increase the fluorine content more than 8.55%, but because of the poor film integrity and appearance of haze, these samples were excluded from the data pool. A comparison of cross-linked and uncross-linked coatings showed that both water and oil resistance can be improved with self-crosslinking of PUDs. Though newly formed hydrophilic groups (N-acyl urea) in cross-linked PUD slightly lowered the contact angle, the increase in cross-link density appeared to improve the water and oil resistance properties.

**Figure 9.** Effect of % siloxane content on water contact angle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

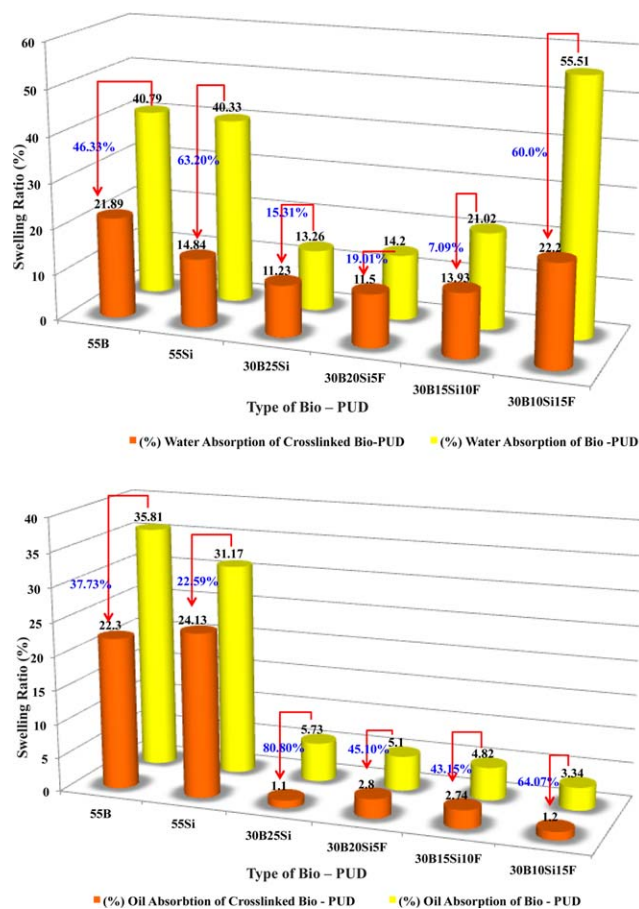


Figure 10. Solvent absorption of bio-PUD and cross-linked bio-PUD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSION

A range of green PUDs have been synthesized using soy-based polyether polyol (soy-polyol) synthesized from epoxidized soy methyl ester. The synergistic effect on water and oil resistance was observed, when the surface of the soy-polyol-based PUD was modified with PDMS and fluoro-polyol. The study of water contact angle, hydrophobicity, and oleophobicity showed that surface enrichment of siloxane increased the hydrophobicity (water resistance), whereas fluorine modification improved oil resistance of coatings. Combining siloxane and fluorine content in bio-PUD and changing their ratio in the formulation it is possible to develop a wide variety of coatings for water and oil resistance application. Self-crosslinking the green PUDs with carbodiimide cross-linkers further improved the solvent resistance, impact resistance, water and oil resistance of surface modified green PUDs.

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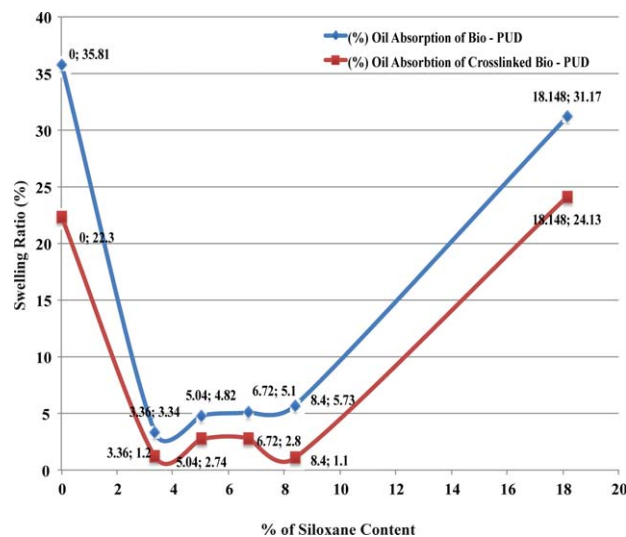


Figure 11. Solvent absorption of bio-PUD and cross-linked bio-PUD based on % siloxane content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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