

Flame Retardant Waterborne Polyurethanes: Synthesis, Characterization, and Evaluation of Different Properties

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Abstract: A series of flame retardant waterborne polyurethanes (WBPU) with varying NCO:OH mole ratio, i.e., isocyanate:hydroxyl groups, was synthesized using phosphorus-based polyester polyol and isophorone diisocyanate (IPDI). The phosphorus moiety was kept in the polymeric chain, which improves flame retardancy of the WBPU films. The prepolymer mixing process was adopted for the synthesis route of WBPU systems. The presence of structural-functional groups was confirmed by Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy. The thermal stability and percentage char yield were observed by TGA analysis. As a consequence of the existence of phosphorous moiety, these WBPU also exhibit flame retardancy, which was examined by limiting oxygen index (LOI) and UL-94 test. All the samples show an increment in thermal stability with an increase in NCO:OH ratio. Maximum flame retardancy was obtained in FWP5 and FWP6 systems with LOI value of 32%.

Keywords: waterborne; flame retardancy; polyurethanes; thermal stability; limiting oxygen index.

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1. Introduction

The waterborne polyurethanes (WBPU) have become a matter of apex research for the steep reduction in the cost of the WBPU and to manage the volatiles during and after the casting. WBPU offers a wide spectrum of advantages like environmental friendliness, appreciable molecular weight, rigidity, tailored properties of the cast, controlled viscosity, and user-friendly applicability [1-5]. Controllable chemical formulation and excellent properties of WBPU have led to a many-fold increment in the application sectors for the usability of WBPU. There are various ways of combining polyols and diisocyanates in order to produce a tailored waterborne polyurethane product [6-10]. Most recently, there is major attention given to impart flame retardancy in polyurethanes, and it has become a principal aim [11]. Hence, the most beneficial way is to add phosphorous moiety to enhance flame retardancy. There are two ways to deal with flame retardancy in polymers, known as the 'additive' type and the "reactive" type [12-15]. From the various literature, conclusions have been made that flame retardancy of the waterborne polyurethanes improved through incorporating additives like phosphorus [16], organo-modified montmorillonite (O-MMT) [17], carbon nanotubes [18], silicone [19], phosphorus, and nitrogen [20], etc. into the WBPU. By means of this, thermal stability and flame retardancy can be easily improved. Presently, various issues like poor compatibility, leaching, and a reduction in mechanical properties come into observation.

Therefore, the utilization of reactive type flame retardants through copolymerization with a flame retardant moiety in the main polymeric chain can resolve these problems, i.e., compatibility, thermal stability, flame retardancy, and poor mechanical property [21]. Patents around the world reveal that halogen-containing flame retardants exhaust corrosive smoke and toxic gases upon combustion. Henceforth, there is exponential demand for flame retardant systems, which ought to be halogen-free for convenient use in WBPU [22]. To attain high-performance polymer materials, the degradation process allows the formulation of the optimal parameters and conditions to design WBPUs. Thermal degradation studies of WBPUs are concluded in many decomposition steps involving the formation of various gaseous products. Therefore, to evaluate the thermal degradation properties, thermogravimetric analysis (TGA) is a suitable method for different types of waterborne polyurethane systems [23-28].

For preparing waterborne polyurethane dispersions, various processes like the prepolymer mixing process, acetone process, melt dispersion process, and ketamine-ketazine processes are existing. In the prepolymer mixing process [29], prepolymer, which is hydrophilically modified, is mixed with isocyanates followed by water. Chain extension then proceeded with amines in the dispersion medium. In the acetone process [30], acetone is to be chosen as a solvent medium in which the hydrophilic isocyanate prepolymer is dissolved, followed by chain extension with diamines and water. As the water starts to add into the prepolymer system, solvent starts to remove from the charge, resulting in pure waterborne dispersion. Melt dispersion process [31], ketamine-ketazine processes, and other processes [32] are also existing, but these two processes, i.e., prepolymer mixing process and acetone process, are extensively used in the production of waterborne dispersions.

In this work, the prepolymer mixing method was adopted [32]. Phosphorous containing polyester polyol was reacted with isophorone diisocyanate, which results in the isocyanate-terminated prepolymer. This prepared prepolymer was neutralized with triethylamine. After constant stirring for 30 minutes, a certain amount of water was added, and a chain-extension process was carried out to form the dispersion. In this way, phosphorus-containing WBPUs have been prepared. Various analytical and instrumental methods have been used for characterization. The effect of phosphorus content and varying NCO:OH mole ratio on the thermal stability and degradation of the waterborne polyurethanes have been investigated.

2. Material and Methods

2.1. Materials.

The reagents resorcinol, phosphorous oxychloride (POCl_3), N,N- dimethyl aniline, adipic acid, xylene, methyl-ethyl ketone (MEK), p-toluene sulphonic acid, polyethylene-glycol (PEG-M.W.400), isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL) were procured from Sigma Aldrich. Triethylamine (TEA), diethylenetriamine (DETA) were obtained from Himedia laboratories, Mumbai. These reagents were used as such without refinement. For the synthesis of dispersions, deionized water was used. Teflon mold was used for casting flame retardant waterborne polyurethane dispersions.

2.2. Synthesis of polyester-polyol based on phosphorous-containing Tris (m-hydroxyphenyl) monophosphate (THPP).

Tris (m-hydroxyphenyl) monophosphate [33] (1.0 mole), adipic acid (3.0 mole), and polyethylene-glycol (PEG 400) (2.0 mole) were charged in a three-necked round bottom flask equipped with dean & stark apparatus and condenser. As a catalyst, p-toluene sulphonic acid was used, and xylene was the reaction medium. Initially, the reactants were heated to 120°C for 4 hours, and the further reaction was carried out between 195 °C to 200°C temperature. The conversion of polyester-polyol was monitored by determining an acid number with respect to time. When the acid value has reached a constant of 20 mg KOH/gm of resin, the reaction was stopped. A pure viscous liquid product was obtained by vacuum distillation. Finally, polyester polyol was taken out into a glass bottle. The reaction scheme for the synthesis of polyester-polyol based on phosphorous-containing Tris (m-hydroxyphenyl) monophosphate (THPP) is shown in Figure 1.

2.3. Synthesis of flame retardant waterborne polyurethane dispersion.

In a four-necked flask, the polyester-polyol (1.0 mole) was taken and dissolved in a methyl ethyl ketone solvent with stirring at room temperature. The flask was equipped with a thermometer, overhead stirrer, reflux condenser and heated up to 75°C temperature in a water bath under continuous stirring. At this stage, over a time of 30 minutes in the presence of dibutyltin dilaurate (DBTDL) catalyst (0.05 mole), isophorone diisocyanate (1.5 mole) was added in the reaction flask drop by drop. The percentage NCO content during the reaction was determined using the dibutyl amine back-titration method [34]. Heating proceeded to the point that the %NCO content came to 2-3 %. Prepolymer was then cooled to room temperature, and a required amount of triethylamine (TEA) was added. To neutralize the carboxylic group, stirring was continued for 30 minutes. A calculated quantity of deionized water was added dropwise under vigorous stirring. After that, diethylenetriamine (DETA) was added for the chain extension process. Final dispersion has a pH between 7.0 to 8.0. Similarly, other dispersions with the NCO:OH mole ratios of 1.6:1, 1.7:1, 1.8:1, 1.9:1, and 2.0:1 were prepared. The reaction scheme for the synthesis of flame retardant waterborne polyurethane dispersion is illustrated in Figure 4. Experimental arrangement for the synthesis of waterborne polyurethane is shown in Figure 2. Pictographic representations of synthesized flame retardant waterborne polyurethane dispersions (FWBPUDs) and films are shown in Figure 3.

3. Characterization

To determine the number average molecular weight, weight average molecular weight, and molecular weight distribution of polymers, the Gel Permeation Chromatographic (GPC) technique was used. GPC instrument, Perkin Elmer USA make with Model Turbo matrix – 40 was used for analysis. FTIR spectra were recorded on ATR- FTIR spectrometer, Bruker, ALPHA model, Germany. The presence of phosphorus was confirmed by ³¹P NMR spectrum with Bruker, Switzerland Model AVANCE 400 at 400MHz using CDCl₃ as a solvent and H₃PO₄ as an internal standard. Microtrac, Particle size Analyzer USA model was used for Particle size measurement. For particle size study, samples were first diluted with deionized water and subsequently exposed through ultrasonic frequency. The viscosity of flame retardant waterborne polyurethane dispersions (FWBPUDs) was measured at 25 °C with the spindle

No.61 at 60 rpm in a Brookfield Digital Viscometer (Model DV-II+PRO). The colloidal stability and appearance determine the safety period for storage of waterborne polyurethane dispersions. This study was examined at room temperature by monitoring any kind of phase separation up to 12 months in sealed, cleaned containers with freshly synthesized FWBPUDs. Thermogravimetric analysis of FWBPU films was performed using Diamond Perkin Elmer Thermogravimetry Analyzer, Pyris-1 TGA model. Samples around 6 to 8 mg were taken and heated from 50°C to 500°C in a platinum crucible under nitrogen atmosphere at a heating rate of 10°C min⁻¹, and the decompositions of samples based on weight loss concerning temperature were recorded. Flame retardant properties of the cured waterborne polyurethane films were determined by limiting oxygen index (LOI) (ASTM D2863) and vertical burning test method Underwriters Laboratories, UL-94 (ASTM D3801). Chemical resistance tests of coated panels were performed according to ASTM D 1647-89.

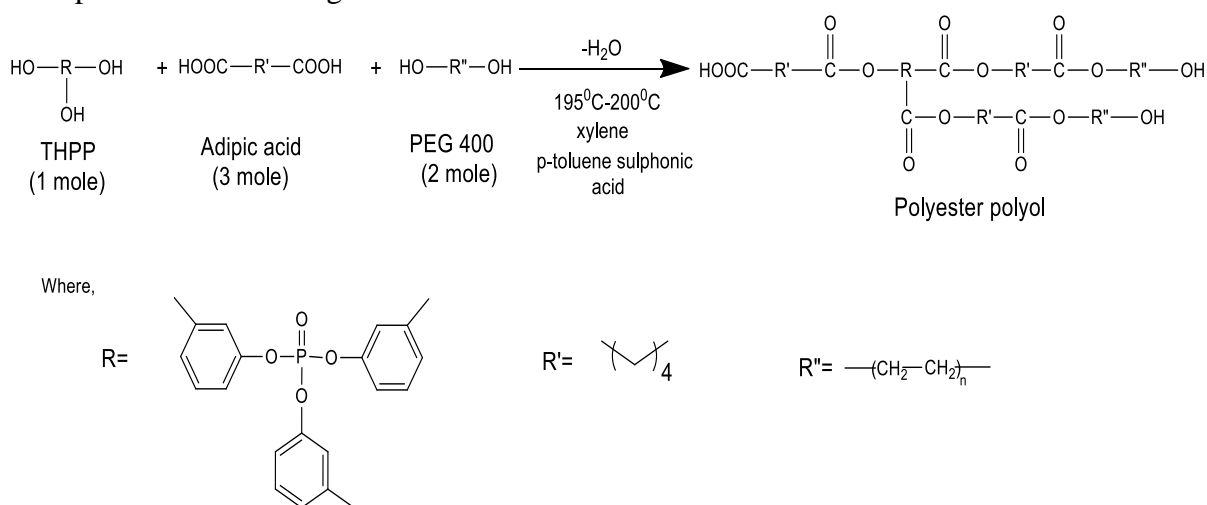


Figure 1. Reaction for the synthesis of polyester-polyol based on phosphorous-containing Tris (m-hydroxyphenyl) monoposphate.

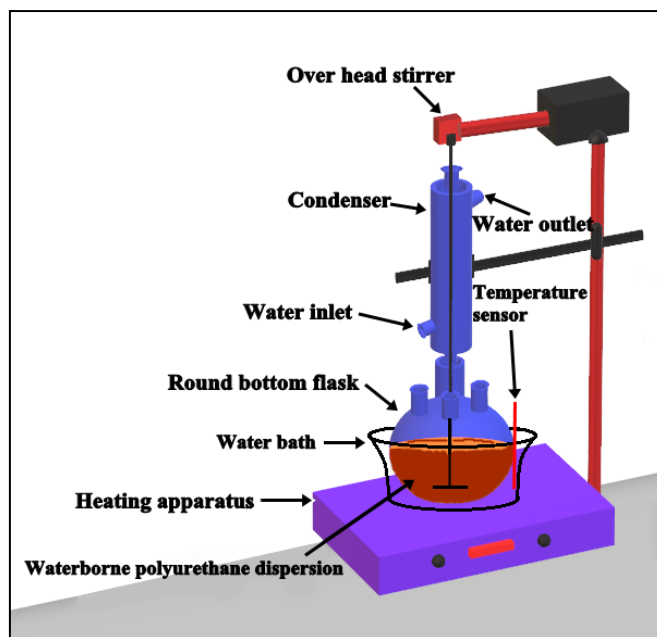


Figure 2. Experimental arrangement for the synthesis of waterborne polyurethane.

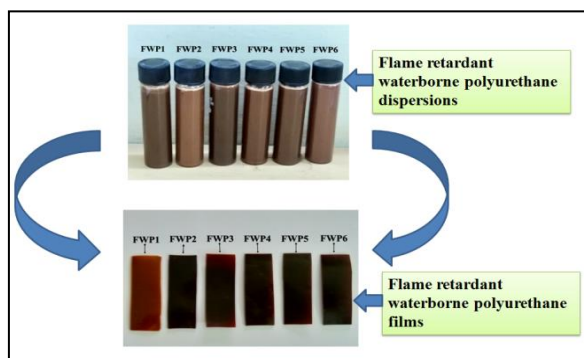


Figure 3. Photographic representation of flame retardant waterborne polyurethane dispersions and films.

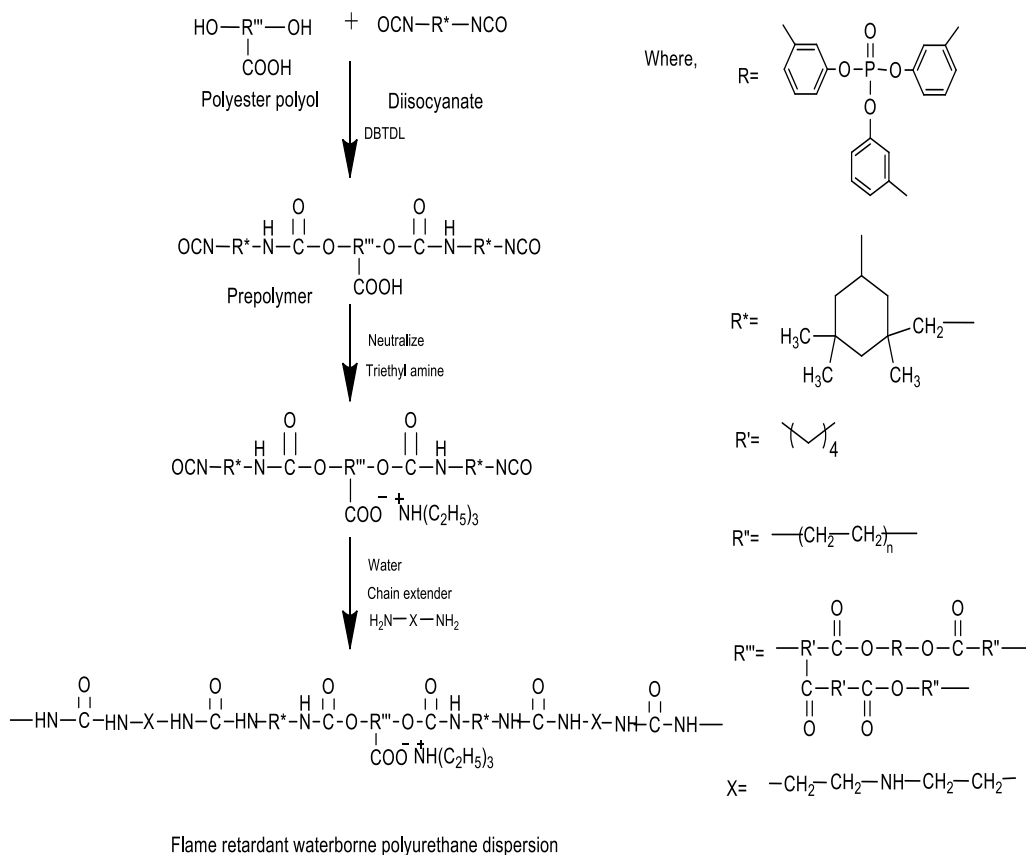


Figure 4. Reaction scheme for the synthesis of flame retardant waterborne polyurethane dispersion.

4. Films and Coatings

4.1. Preparation of films.

Freshly synthesized waterborne polyurethane dispersions were cast onto a Teflon mold and allowed to sit at room temperature over 24 hours. Later, completely tack-free films were kept in the oven at 60°C for 8 hours and at 70°C for 6 hours. Afterward, cured films were stored in a desiccator at room temperature for further studies.

4.2. Preparation of coatings.

Dispersions of waterborne polyurethanes were coated on dirt-free mild steel panels and glass panels with the assistance of a film applicator. Dispersions were allowed to remain on the

panels for 24 hours at room temperature for setting and were dried out by keeping in an oven at 60°C for 8 hours and 70°C for 6 hours.

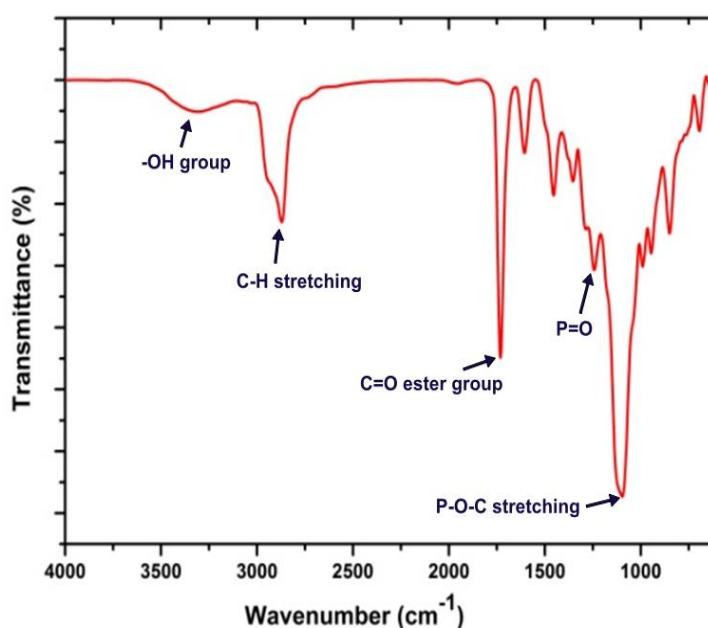
5. Results and discussion

5.1. Characterization of phosphorous-based polyester polyol.

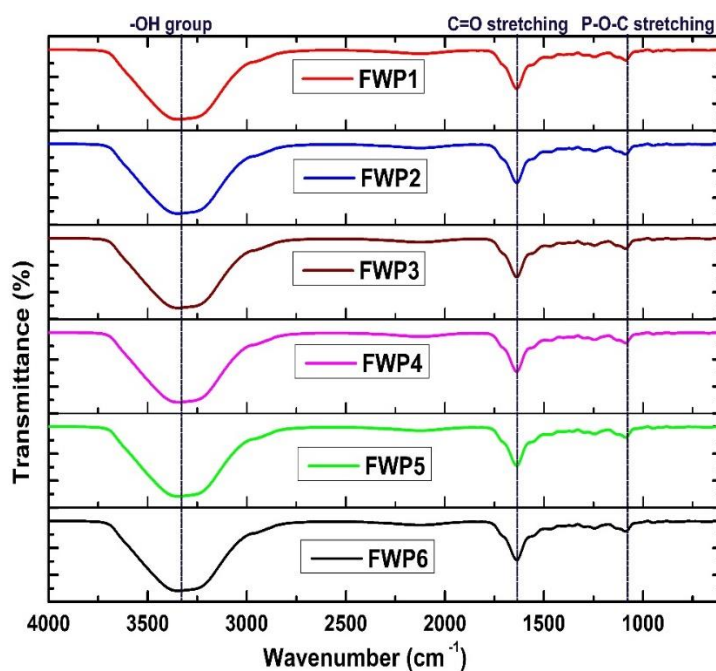
The number average molecular weight \bar{M}_n , weight average molecular weight \bar{M}_w and polydispersity index as determined through GPC technique is $\bar{M}_n = 3069$, $\bar{M}_w = 4565$ and 1.48 respectively. The acetylation method was used to estimate the number of hydroxyl-free groups in the phosphorus-based polyester polyol. From the estimation, 2 numbers of free hydroxyl groups were obtained.

5.2. FTIR spectroscopy.

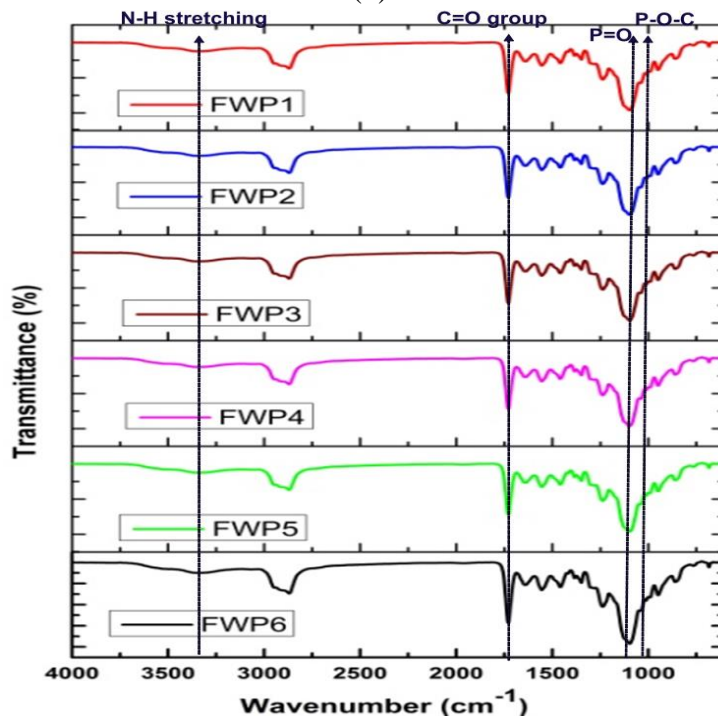
The FTIR spectrum of polyester-polyol based on phosphorous moiety containing Tris (m-hydroxyphenyl) monophosphate (Figure 5 a) shows the band at 2869 cm^{-1} corresponds to C-H stretching vibration, the band at 1245 cm^{-1} is due to the presence of P=O group, and band at 1099 cm^{-1} appears for P-O-C stretching frequency. The band at 1731 cm^{-1} due to C=O ester group gives evidence of the formation of polyester. In Figure 5 b, due to the presence of water in the dispersion systems, the absorption band appears at 3367 cm^{-1} for (-OH) hydroxyl group. The band at 1600 cm^{-1} corresponds to C=O symmetric stretching frequency, and the band at 1098 cm^{-1} is due to the P-O-C stretching frequencies. The analysis of FWBPU films (Figure 5 c) shows the absence of a characteristic NCO band at 2270 cm^{-1} which indicates the formation of urethane linkage [35] as the active hydrogen of a chain extender completely reacted with NCO [5]. N-H stretching band appears at 3392 cm^{-1} . Peaks, respectively, to the absorption of N-H and C=O groups at 3392 cm^{-1} and 1730 cm^{-1} signifies that the FWBPUDs have -NHCOO (urethane group). The band at 1238 cm^{-1} is due to the presence of P=O group, and the band at 1097 cm^{-1} is due to the P-O-C stretching frequency. Absorption bands at 2927 cm^{-1} indicate C-H stretching mode available in the synthesized FWBPUs.



(a)



(b)



(c)

Figure 5. FTIR spectra of (a) phosphorus-based polyester polyol; (b) six flame-retardant waterborne polyurethane dispersions; (c) six flame-retardant waterborne polyurethane films.

5.3. NMR spectroscopic analysis.

Figure 6 clearly indicates the ³¹P NMR spectrum, which shows a peak at $\delta -17.3$ ppm and confirms the presence of phosphorus moiety of Tris (m-hydroxyphenyl) monophosphate in the waterborne polyurethane systems. Thus, phosphorus is present in all the FWBPU systems, although Figure 6 represents the NMR spectrum of one of the system FWBPU systems.

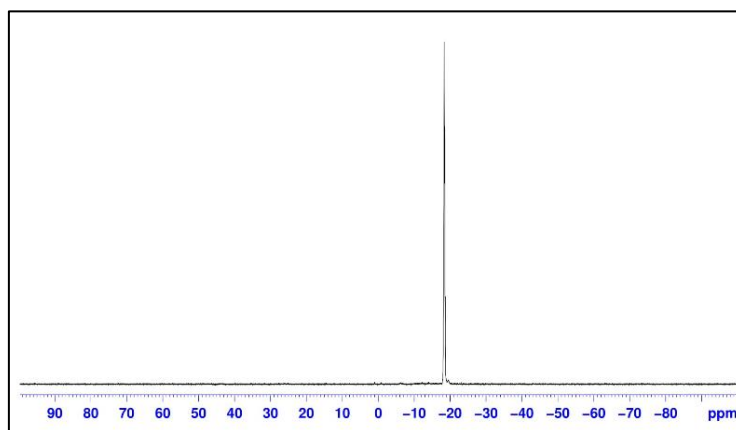


Figure 6. ^{31}P NMR spectrum of flame retardant waterborne polyurethane.

5.4. Particle size analysis and viscosity measurement.

The performance of waterborne polyurethane dispersions is highly dependent on the particle size and viscosity of the dispersion systems. The particle size of the WBPUDs are affected due to the change in prepolymer viscosity, NCO:OH mole ratio, speed of stirrer, and the method of water addition.

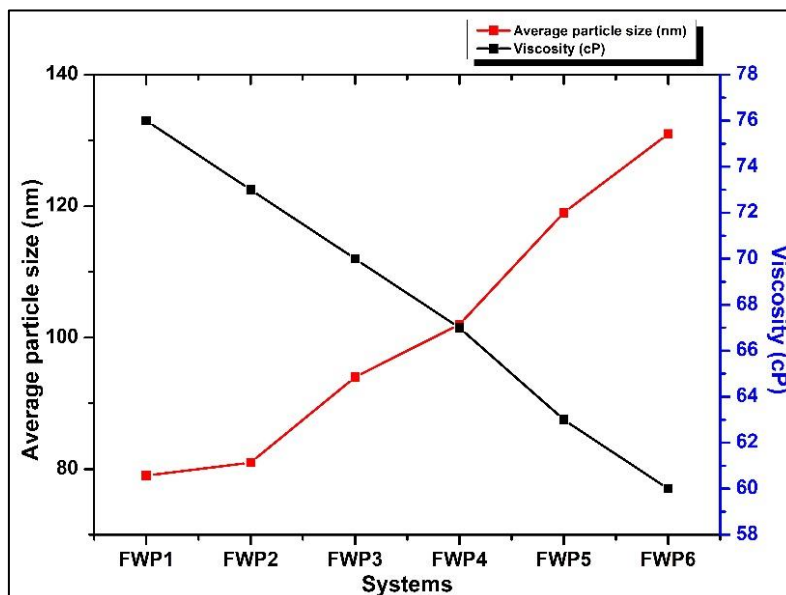


Figure 7. Representation of average particle size and viscosity of FWPUD systems.

The obtained results of particle size, as well as the viscosity of the newly synthesized FWBPUDs, are shown in Figure 7. Data revealed that as the molar ratio of NCO:OH increases, the average particle size of WBPUDs is also increasing. As seen in sample FWP1, the average particle size is obtained as 79 nm, where sample FWP6 has an average particle size of 131 nm. This is due to an increment in molar ratio NCO:OH, whereas the urethane linkage formation increases continuously [36]. As the particle size of dispersions increases, a simultaneous decrement in the viscosity of the WBPUDs is also observed. System FWP1 has 76 cP, whereas the lowest viscosity is obtained in sample FWP6, which is 60 cP (Figure 7).

5.5. Colloidal stability and appearance.

The safety period for storage and appearance are the important characteristics of waterborne polyurethane dispersions. Freshly synthesized WBPUDs were taken into the clean

glass containers, which were sealed from the top opening. This study was performed at room temperature, and any kind of phase separation was monitored up to a period of 12 months. The result of the inspections is shown in Table 1. The appearance showed that the color of dispersions did not vary with the change in a molar ratio of NCO:OH groups. Hence, these systems and their formulations gave least or no discoloration during and after the production of dispersions. The color of the final waterborne polyurethane systems is governed by the color of different reagents used during the synthesis, i.e., the color of the base product (monomer), the color of polyester polyol, and diisocyanate. After 8 months, precipitates were detected in FWP6 system. The reason is as the mole ratio of NCO:OH was increased, the average particle size of the FWP6 became maximum among all the systems due to the agglomeration of the particles. Hence in the FWP6 system, precipitates were appeared earlier as compared to that of the other systems.

Table 1. Colloidal stability and appearance of different waterborne polyurethane systems.

Systems	Mole ratio NCO:OH	Colloidal stability	Appearance
FWP1	1.5:1	> 9 months	Brown
FWP2	1.6:1	> 9 months	Brown
FWP3	1.7:1	> 9 months	Brown
FWP4	1.8:1	> 9 months	Brown
FWP5	1.9:1	> 9 months	Brown
FWP6	2.0:1	> 8 months	Brown

5.6. Properties of casted films.

5.6.1. Flame retardant properties.

Table 2 shows the flame retardant properties like LOI and UL-94 of the films. The LOI is a measurement of the minimal oxygen concentration in a mixture of oxygen and nitrogen that will merely support flaming combustion of material under specified conditions [37,38]. To achieve self-extinguishing property, the material LOI value should be greater than 26 %. This provides a measure of the ease of extinction of the materials. This is an appropriate method for a semi-qualitative indicator of the efficiency of flame retardant polyurethanes. This is because the equipment is low-cost, and the sample size requirement is less [39]. In LOI test, it is evaluated that the sample FWP1 with the minimum content of NCO:OH having the smallest particle size, and the less number of urethane linkages started to burn at 29% LOI value. For sample FWP4, a little hike is observed than for the rest of the systems. For FWP5 and FWP6, the value of LOI is remaining constant, i.e., 32. This result signifies that there is no proportional increase in flame retardancy with an increasing molar ratio of diisocyanate. In UL-94, the test of all the samples, V₀ rating is attained, which denotes that for the vertical samples under observation, the burning stops within 10 seconds [40]. None of the test samples burnt longer than 10 seconds, and no burnt particles were observed during or at the end of the test. These observations show that all the samples have good flame retardancy. Experimental arrangements for the UL-94 V test and LOI flammability test are displayed in Figure 8 and Figure 9, respectively. In addition to this, Figure 10 shows the photographic representation of LOI testing for the FWBPU film.

Table 2. Flame retardant properties of different WBPUDs systems

Systems	Mole ratio NCO:OH	LOI (%)	UL-94
FWP1	1.5:1	29	V ₀
FWP2	1.6:1	29	V ₀
FWP3	1.7:1	30	V ₀
FWP4	1.8:1	31	V ₀
FWP5	1.9:1	32	V ₀
FWP6	2.0:1	32	V ₀

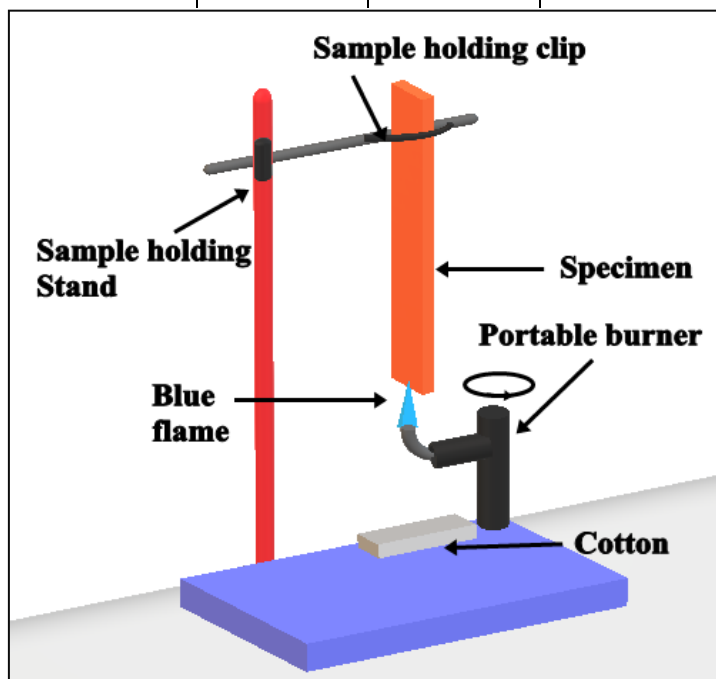


Figure 8. Experimental arrangement for the UL-94 V test.

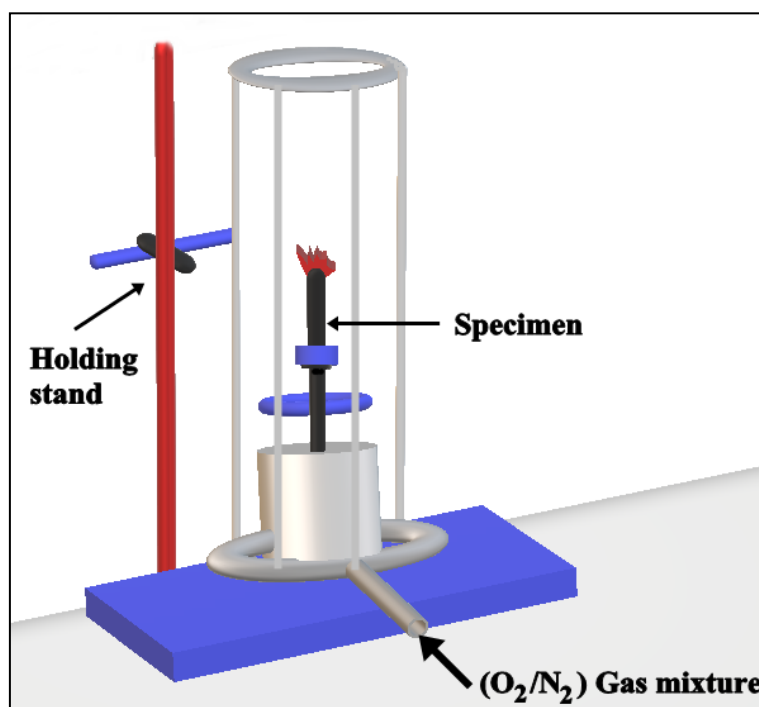


Figure 9. Experimental arrangement for the LOI flammability test.



Figure 10. LOI test performance (a) FWBPU film sample; (b) Sample kept in the LOI testing apparatus before the analysis; (c) After completion of LOI test; (d) sample removed from the LOI testing apparatus.

5.6.2. Thermogravimetric analysis (TGA).

Thermogravimetric analysis was done to determine thermal stability and percentage char yield of the cured waterborne polyurethane films. Figure 11 represents the characteristics thermograms, and in Table 3, the data are reported. The results from the analysis show that the thermal stability of FWP6 is highest, and for the same system, char formation is also maximum among all the systems, which is 14.13%. In the FWP5 system, the char value obtained is less than that of FWP6, but at 70% weight loss, both the systems are stable at 400°C, which is also a significant temperature of both the systems. In the cured films of WBPU, considerable heat energy is required to break bonds inside the bulk polymeric matrix. For that reason, the thermal decomposition of cured WBPU films starts preferentially through side chains. The decomposition process of WBPU is a complex matter involving chemical and physical phenomena which are not quantized to a single process. With the increasing thermal perturbation, the bonds in the polymer molecules undergo thermal agitation, rotation or vibration of polymeric fragments fixed to local space. On further increment in the heat energy, the bonds tend to break and form multiple radical fragments. Formation of smaller molecules is also probable, followed by vaporization or diffuse out. The final decomposition step involves removing all the volatiles, and the process leaves a char at the end of the decomposition. Char being insoluble and containing a major amount of carbon does not further change the phase, and hence a rigid and stable phase is obtained, which cuts down the oxygen supply, and combustion is then least probable [41-43].

During the analysis, the strongest interactions of hydrogen bonds with urethanes, and urea moieties provide high thermal stability and the highest char yield with respect to increasing the NCO:OH ratio of the systems [44]. Hence it concludes that the higher the mole ratio of NCO:OH, the superior is the enrichment in cross-linking density which ensures high thermal stability [45]. For all the samples, 10% weight loss occurs in the temperature range of 300°C -316°C. This may correspond to the breakage of the urethane bonds, which leads to the formation of carbon dioxide, alcohols, amines, carbon monoxide, etc. In the range of 366°C - 371°C, a weight loss of 30% is seen, which is due to the decomposition of ester links followed by the formation of char which starts around 420°C. At 500°C, the final char values are obtained when the stable weight observed in the thermogram corresponding to no further weight changes.

Table 3. Thermal properties of waterborne polyurethane films.

Systems	Mole ratio NCO:OH	% Weight loss from TGA in nitrogen (°C)			Char yield at 500°C (%)
		10%	30%	70%	
FWP1	1.5:1	316	364	398	11.29
FWP2	1.6:1	304	368	399	11.63
FWP3	1.7:1	308	369	399	12.19
FWP4	1.8:1	308	371	400	12.54
FWP5	1.9:1	300	366	400	12.74
FWP6	2.0:1	308	369	400	14.13

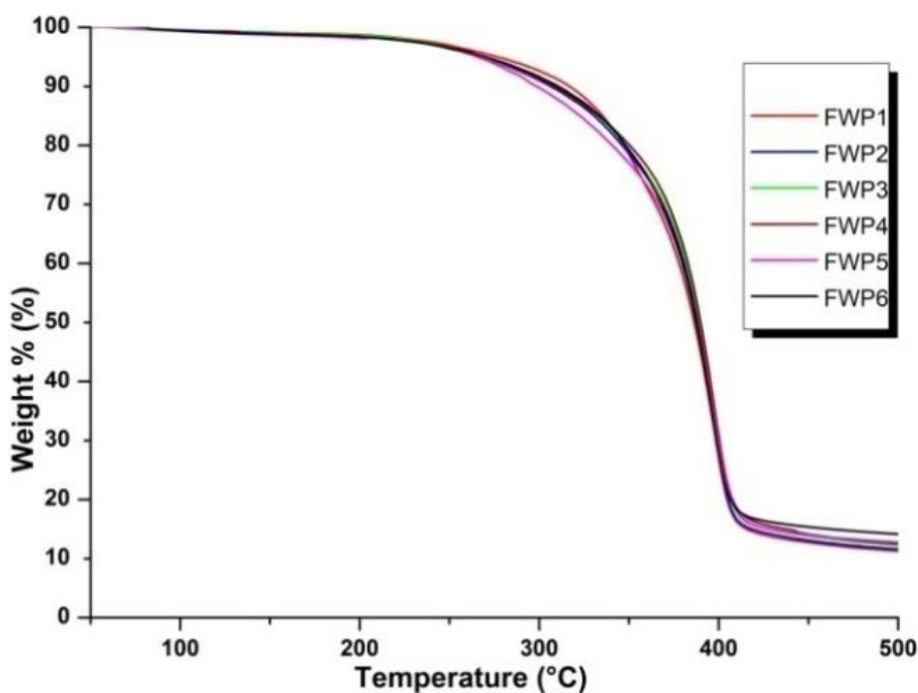


Figure 11. TGA thermograms of flame retardant waterborne polyurethanes at the heating rate of 10°C /min.

5.7. Properties of coatings.

5.7.1. Mechanical properties of the coated panels according to ASTM standards.

Mechanical properties of WBPUDs of coated panels like pencil hardness, scratch resistance, adhesion (cross-hatch), flexibility 1/4" mandrel are determined according to ASTM standard and are shown in Table 4. Pencil hardness data explains that the hardness increases with the increment of NCO:OH molar ratio for the first three systems, i.e., FWP1, FWP2, and FWP3 but its leftovers same for the other three systems, specifically FWP4, FWP5, and FWP6. Scratch hardness is the most significant test mandatory to determine the properties of coatings [46]. A scratch hardness tester was used to determine the hardness (ASTM D 5178) of the coatings, which exhibits the durability of the coatings. For different compositions, i.e., varying NCO:OH mole ratio, the scratch hardness of the coated panels is found to be different. Scratch hardness increases as the NCO:OH ratios increase due to the increment in the hard segments in the polymer due to the increment in the urethane linkages. Adhesion (ASTM D 3359) and flexibility (ASTM D 522) are the principal characteristics of all coatings. The results of flexibility and adhesion are shown in Table 4. These tests reveal that all the systems pass through scrutiny.

Table 4. Mechanical properties of waterborne polyurethane coatings.

Systems	Mole ratio NCO:OH	Pencil hardness*	Scratch resistance Gms	Adhesion (cross-hatch)	Flexibility 1/4" mandrel
FWP1	1.5:1	1H	1780	PASS	PASS
FWP2	1.6:1	2H	2175	PASS	PASS
FWP3	1.7:1	3H	2230	PASS	PASS
FWP4	1.8:1	4H	2400	PASS	PASS
FWP5	1.9:1	4H	2655	PASS	PASS
FWP6	2.0:1	4H	2680	PASS	PASS

*6H >5H >4H >3H >2H >1H >H >1HB >2HB >3HB >4HB >5HB >6HB.

5.7.2. Chemical resistance properties of coated panels.

The outcome of the chemical and solvent resistance properties of coated panels portrayed in Table 5 are optimistic to a certain extent in cured coating performance. Chemical resistance tests of coated panels were carried out in accordance with ASTM D 1647-89 by immersing the panels in various mediums, i.e., water, acid, methanol, and alkali solutions. All the corners of the glass panel were sealed with wax. This was done to prevent any leakage from the glass panel's corners. Water, methanol, 3% (w/w) HCl solution and 3% (w/w) NaOH solution were used to dip the prepared panels. After 10 days, the samples were inspected for visual appearance. Due to lower cross-linking density of lower mole ratio of NCO:OH, FWP1 and FWP2 show discoloration in methanol as well as in alkali, and there appeared a softening of coating in the acid test. While, in FWP3, discoloration was observed in the acid test. Acid and alkali resistance of the panels based on high NCO:OH mole ratio showed better chemical resistance. In a lower molar ratio of 1.5:1.0 and 1.6:1.0, the chemicals can easily penetrate into the polyurethane layer due to the lower number of urethane linkages present compared to a higher amount of NCO:OH mole ratios[47-52]. All the coatings were stable; no cases of removal of the coating were observed in the case of water. Cracking was not observed in any case.

Table 5. Chemical resistance properties of WBPU coated on panels.

System	Mole ratio NCO:OH	Water	Methanol	Alkali resistance 3% NaOH	Acid resistance 3% HCl
FWP1	1.5:1	5	4	4	3
FWP2	1.6:1	5	4	4	3
FWP3	1.7:1	5	5	5	4
FWP4	1.8:1	5	5	5	5
FWP5	1.9:1	5	5	5	5
FWP6	2.0:1	5	5	5	5

1- coating completely removed, 2-Cracking appears, 3-Softening, 4 - Discoloration, 5- No change.

6. Conclusions

In the present study, the synthesized product governs the dependability of various physicochemical properties on the NCO:OH ratio. FTIR spectra disclose the characteristic absorption bands of urethane, confirming the formation of waterborne polyurethane and the

absence of -NCO peak, which confirms all the systems are eco-friendly. TGA analysis shows that the relatively higher thermal stability and % char yield are observed in the higher NCO:OH mole ratio samples. Significant flame retardant property is observed by incorporating phosphorous moiety in the polymeric chain. LOI and UL-94 results show appreciable flame retardancy. The increment of diisocyanate content in the flame retardant waterborne polyurethane systems makes no change in LOI value. In the particular case of the pencil hardness test, the value of 4H is observed, which is appreciable in terms of coating property. Scratch hardness continuously increases with varying NCO:OH mole ratios because of the increment in the hard segments in the polymer, resulting in an increment in the urethane linkages in the respective systems. The chemical resistance properties are exceptionally good. All the systems are extremely good and pass through the flexibility and adhesion tests. Therefore, the coating and casting results shed new light on the utility of these synthesized flame retardant waterborne polyurethanes systems to a vast level.

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Conflicts of Interest

The authors declare no conflict of interest.

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