

Improving hydrophobicity of polyurethane by PTFE incorporation

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ABSTRACT: A simple and facile method was established of incorporating polytetrafluoroethylene (PTFE) on to polyurethane (PU) to improve hydrophobicity of PU by incorporating low levels of fluorine at a molecular level. Nanocomposites were made by preparing PU in the presence of PTFE using seeded miniemulsion polymerization method. The resulting PTFE/PU nanocomposites were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectrometry, differential scanning calorimetric, and thermo gravimetric analysis (TGA). FTIR and TEM indicated changes observed in their structure, size and morphology. The water contact angle of PTFE/PU nanocomposite films increased with increasing amount of PTFE and more on blending with silica nanoparticles but a slight decrease in thermal stabilities of SiO₂/PTFE/PU nanocomposites were noticed. The hydrophobicity imparted by PTFE to PU surface was found to be at its best for 1 : 2 PTFE/PU latex film. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42779.

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INTRODUCTION

Polyurethanes (PUs) as single binders or in combination with acrylates or styrene acrylates are extensively used in anti-corrosion coatings, coatings for wood, plastic and textiles, printing ink and adhesives applications.^{1–3} They are known to offer advantages of high gloss, color retention and weather ability to the products in addition to improved scratch and corrosion resistance.⁴ However, barrier properties of PUs such as water resistance and decreased permeability to chemicals need improvement. A convenient approach to address this issue is by incorporating fluorinated compounds (low surface energies) into PUs which can improve surface hydrophobicity of the films. Efforts were placed by many researchers to make glossy and attractive water based PU coatings having desirable properties of fluoropolymer that can be applied under mild conditions. Most of the fluorinated polymers used for modification of PU surface properties in literature are fluorinated acrylates. Surface properties of cationic fluorinated PU-acrylate hybrid dispersions were reported to give a remarkable enhancement in surface hydrophobicity recording a water contact angle of 100° for PU films with 20 wt % fluoroacrylate.⁵ Investigation on two sets of fluorinated PUs, namely, poly(ether urethane)s and poly(carbonate urethane)s containing various amounts of chain extender of fluorinated side chains had shown self-stratification of fluorinated PUs with increasing amounts of fluorinated side chain.⁶ Similarly, studies on cationic PU-fluorinated acrylic hybrid latexes having quaternary ammonium groups with per-

fluoroalkyl acrylate have shown remarkable enrichment of fluorine on the film–air interface on annealed films.⁷ However, literature pertaining to using other fluoropolymers such as polytetrafluoroethylene (PTFE), PVdf, and fluorinated ethers into PUs is limited in comparison with fluoroacrylates which is mainly due to the difficulty in processing them. An emulsion of fluoroethylene vinyl ether polyol, Lumiflon FE-4400, was incorporated into clear coats of PU for use in military topcoats. An increase in hydrophobicity of the film surface with increasing amounts of fluoropolymer was observed because of significant fluorine enrichment at the film air interface.⁸ Studies on films of PU and nano-PTFE aqueous dispersions reported higher water contact angles for the blends than pure PU.⁹

Incorporation of silica in fluorinated polymers is known to add value to the coatings performance with exceptional hydrophobicity by providing roughness to the low surface energy material.¹⁰ It is known from literature that synergic effect of fluorine and silicon components resulted in a rough surface that enhances hydrophobicity of the film.¹¹

The objective of present work is to improve hydrophobicity of PU, by preparing PTFE PU nanocomposites in-situ by using a simple and novel miniemulsion method in anticipation of achieving better homogeneous blends of the two polymers compared with physical blending.

Combinations of both the polymers, PU and PTFE in the nanocomposites were varied to target films that offer maximum

Table I. Recipe for Synthesis of PU and PTFE/PU Nanocomposites

Sample code	PTFE (g)	IPDI (g)	Dodecanediol (g)	SDS (g)	HD (g)	DBTL (g)	DH ₂ O (g)
PU	-	2.617	2.383	0.2	0.2	0.02	25
PTFE/PU	3	1.57	1.43	0.2	0.2	0.02	25
PTFE/2PU	2	2.094	1.906	0.2	0.2	0.02	25
PTFE/3PU	1.5	2.356	2.144	0.2	0.2	0.02	25
PTFE/4PU	1.2	2.513	2.287	0.2	0.2	0.02	25
PTFE/5PU	1	2.617	2.383	0.2	0.2	0.02	25

hydrophobicity. Improvement in water contact angle of PU was monitored with respect to PTFE content and presence of silica nanoparticles in SiO₂/PTFE/PU nanocomposites. A comparison of their bulk properties with unmodified PU was done in terms of their morphology and thermal behavior to monitor changes if any on their performance.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI), dodecanediol, dibutyltin dilaurate (DBTDL), hexadecane (HD), Ammonium persulfate (APS), sodium dodecyl sulfate (SDS) Tetraethyl orthosilicate (TEOS), and Hexadecyltrimethoxysilane (HDTMS) purchased from Fluka were used without further purification. PTFE emulsion was a gift from Hindustan Fluorocarbon, Hyderabad.

Preparation of PU and PTFE/PU Nanocomposite Latex

A monomer mixture containing diisocyanate and diol in a 1 : 1 molar ratio and fixed weights of HD, SDS, and water were stirred together for 1 h at room temperature. DBTDL catalyst is added to the mixture and ultrasonicated for 5 min at 90% amplitude at 10°C to form a preemulsion. Then the temperature is raised to

60–62°C for polyaddition reaction to take place forming the mini-emulsion until completion of the reaction for 4 h. PTFE/PU nanocomposites are prepared following the same procedure by adding PTFE emulsion to the reaction mixture before subjecting it to sonication. Nanocomposites of different ratios ranging from 1 : 1 to 1 : 5 of PTFE and urethane monomers were prepared and the details of recipe for reactions are given in Table I.

Preparation of Silica@ PTFE/PU Nanocomposites

These organic inorganic nanocomposites were prepared by drop wise addition of 1.57–3.15 wt % TEOS and 0.01–0.02 wt % HDTMS to the as prepared PU/PTFE miniemulsion for hydrolysis of TEOS in the presence of alkali (NH₄OH) as a catalyst. The reaction was maintained at 75°C for 3 h then a SiO₂/PTFE/PU nanocomposite was formed.

Characterization

FT-IR spectra of composite particles were obtained by making a pellet with KBr powder using a Thermo Nicolet Nexus 670 spectrometer at room temperature. Each sample was scanned 128 times with a resolution of 4 cm⁻¹ within a spectral range of 400–4000 cm⁻¹. Transmission electron microscopy (TEM)

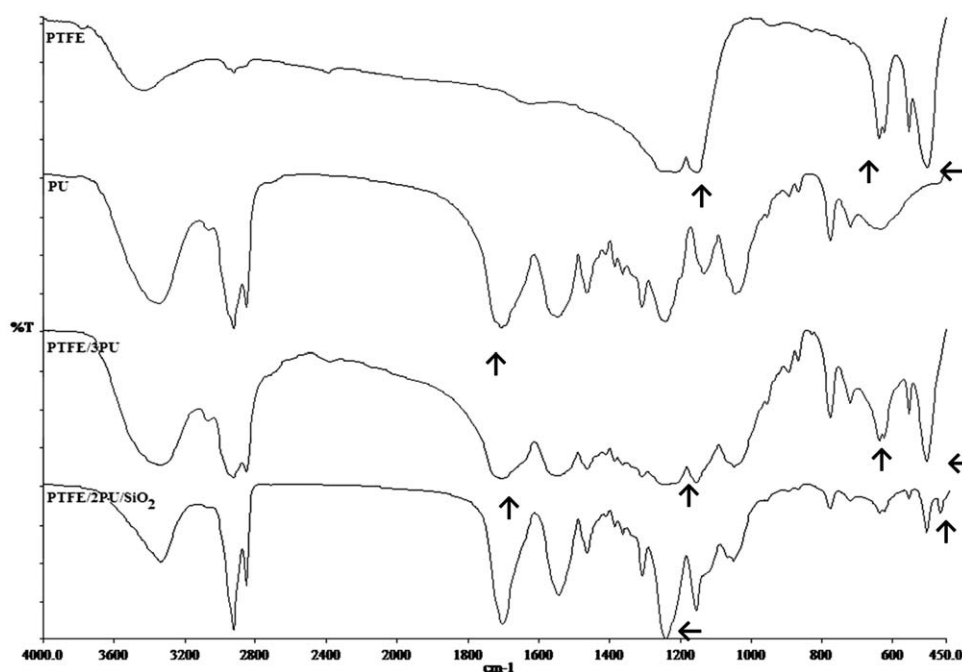


Figure 1. FTIR spectra's of PU, PTFE and its composites.

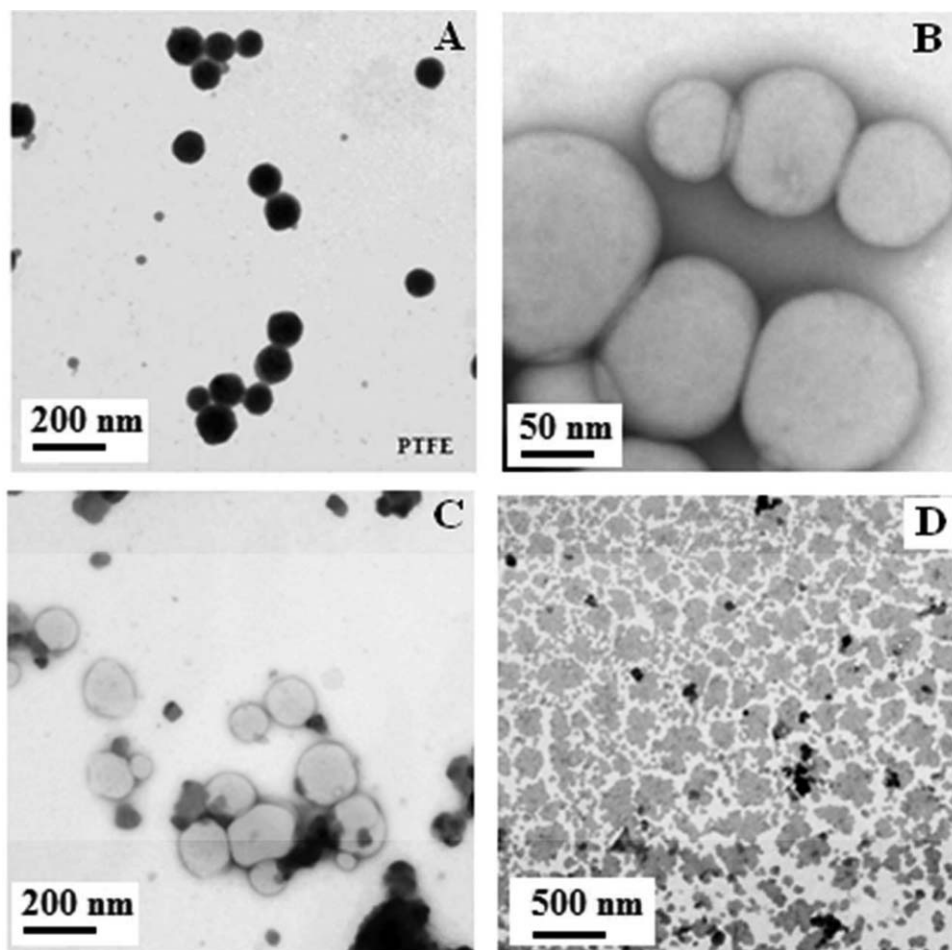


Figure 2. TEM pictures of (A) PTFE, (B) PU, (C) PTFE/2PU, and (D) PTFE/5PU Nanocomposites.

micrographs were obtained using a Philips Technai instrument, transmission microscope at an accelerating voltage of 200 kV. The samples were prepared by wetting a carbon-coated copper grid with a small drop of the dilute latex. Upon drying, it was stained with a small drop of Uranyl acetate for 5 min and dried at room temperature before analysis. Differential scanning calorimetric (DSC) thermograms were recorded on a DSC Q 100 Universal instrument. The samples were placed in sealed aluminum pans and initially heated at a heating rate of 10°C/min from room temperature to 200°C in a nitrogen atmosphere; they were quenched immediately from 200 to -70°C at a cooling rate of 50°C/min to remove the previous thermal history. The samples were subsequently rescanned at a heating rate of 10°C/min from -70 to 200°C. The instrument was calibrated with indium standards before the measurements. The average sample size was 10 mg, and the nitrogen flow rate was 20 cm³ min⁻¹. From these thermograms, the glass-transition temperature (T_g) was determined. Perkin Elmer thermo gravimetric analysis (TGA) 7 instrument was used to study the thermal decomposition profile of composite particles under non-isothermal conditions at a constant heating rate of 10°C/min in nitrogen atmosphere from room temperature to 800°C. For TGA analysis, composite particles about 8–10 mg of solid sample was taken for analysis purpose. Static contact angles were measured on a Contact Angle Goniometer

(Kruss GMBH German G10MK2) by the sessile drop method at 25°C. Deionized water was dropped, with a micro-syringe on the surface of the latex films. Average of the angles obtained at more than 10 different locations on each sample surface was reported.

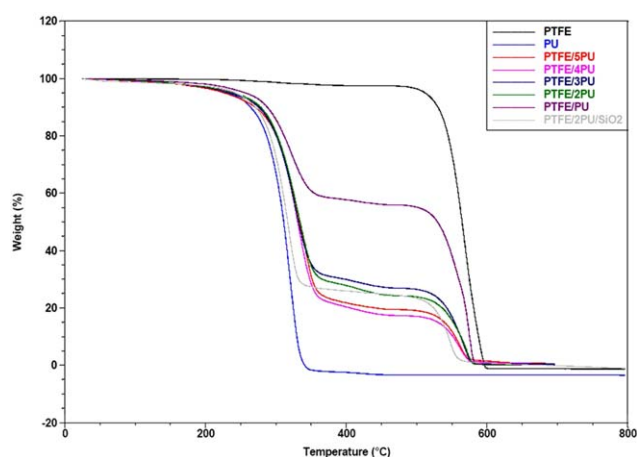


Figure 3. TGA graphs of PU, PTFE and its composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. TGA Values of PTFE, PU, PTFE/PU Nanocomposites

Sample code	T I (°C)	T II (°C)
PTFE	-	569.02
PU	319.78	-
PTFE/PU	323.12	574.73
PTFE/2PU	331.90	570.29
PTFE/3PU	326.60	567.64
PTFE/4PU	332.78	561.46
PTFE/5PU	338.08	562.34
PTFE/2PU/SiO ₂	317.76	546.82

RESULTS AND DISCUSSION

Structural Properties

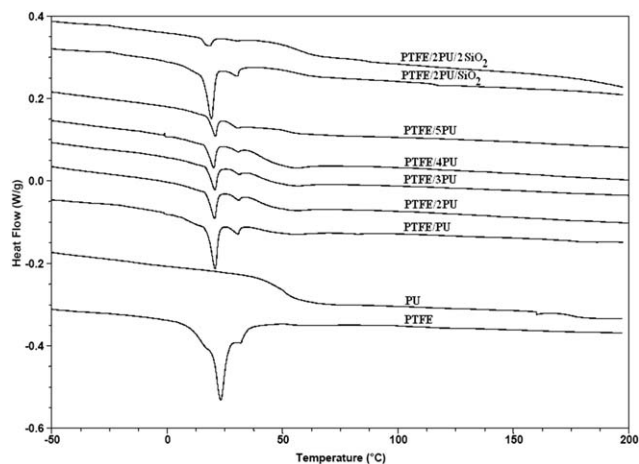
The Fourier transform infrared (FTIR) spectra of the PTFE, PU, PTFE/PU, and SiO₂/PTFE/PU nanocomposites are shown in Figure 1. In FTIR spectrum of PTFE, the characteristic absorption peaks of the CF₂ groups at 1155 cm⁻¹ (C—F asymmetric stretching mode) and 1218 cm⁻¹ (C—F symmetric stretching mode), and at lower wave numbers of 507 cm⁻¹ (CF₂ wagging mode), 548 cm⁻¹ (CF₂ deformation mode), and 634 cm⁻¹ (CF₂ rocking mode) are detected.⁵ It is shown by IR spectroscopy that the reaction of the diisocyanate with the diol is the main reaction, whereas the reaction with water is only a side reaction as the peak at 1640–1690 cm⁻¹ corresponding to ν (C=O) of urea formation is absent. Absence of isocyanate peak at 2300 cm⁻¹ indicates the formation of PU for all the composites. Similarly, the characteristic peaks of PTFE as mentioned above can be surveyed in the spectrum of all the PTFE/PU composites along with peaks corresponding to PU at 3330 cm⁻¹ [ν (NH)], 2855–2955 cm⁻¹ [ν (CH₂) and ν (CH₃)], 1705 cm⁻¹ [ν (C=O)], 1538 cm⁻¹ [δ (NH)] and 1110 cm⁻¹ [ν (C—O—C)] are strong evidence for the formation of PTFE/PU composites. SiO₂/PTFE/PU spectrum shows intensive bands in the region of 1000–1140 and 477 cm⁻¹ because of Si—O—Si vibration, which are specific to silica nanoparticles.

Size and Morphology of the Nanocomposites

The TEM photographs for plain PTFE and nanocomposites are shown in Figure 2. The average size of the PTFE particles is around 120–130 nm and are spherical in shape. PU particles were also spherical in shape but had size 200–250 nm. The composites have shown uniform distribution of PTFE nanoparticles in the PU matrix but interspersed with negligible domains

Table III. Composition Data of the PTFE/PU Nanocomposites

Sample code	Theoretical ratio of composite	TGA ratio of composite
PTFE/PU	1 : 1	1 : 0.76
PTFE/2PU	1 : 2	1 : 2.01
PTFE/3PU	1 : 3	1 : 2.96
PTFE/4PU	1 : 4	1 : 4.06
PTFE/5PU	1 : 5	1 : 4.71

**Figure 4.** DSC graphs of PU, PTFE and its composites.

of PTFE agglomerates indicating blending but with clear demarcation of both phases at few places.

Thermal Properties

TGA. Thermograms of PU, PTFE, PTFE/PU, and SiO₂/PTFE/PU are shown in Figure 3. PTFE and PU shows a clean single degradation at 569°C (T II) and 320°C (T I) whereas the nanocomposites show a two-step degradation pattern which shows PU (T I) and PTFE (T II). An increase in the thermal stabilities of nanocomposites was noticed when compared with corresponding unmodified PU and PTFE. The maximum derivative peak degradation temperatures T I and T II corresponding to PU and PTFE, respectively, are listed in Table II. However, in previous reports of PTFE blends with PU⁹ and PTFE-Poly amide imide,¹² a single degradation peak was noticed for the blends irrespective of their ratio and proportion. In the present case, except for the PTFE/PU (50% blend) all the other blends have shown T II that is not proportional to their ratio in the blend. Presence of silica nanoparticles in the composite slightly decreased the heat resistance for SiO₂/PTFE/PU nanocomposite samples. The composition of PTFE and PU in nanocomposites was estimated theoretically and gravimetrically (TGA) and are listed in Table III.

Table IV. T_g values of PTFE, PU, and PTFE/PU Nanocomposites

Sample code	PTFE first order transition (°C)	PU T _g (°C)
PTFE	21	-
PU	-	51
PTFE/PU	20	41
PTFE/2PU	20	41
PTFE/3PU	20	42
PTFE/4PU	19	42
PTFE/5PU	20	51
PTFE/2PU/2SiO ₂	16	56
PTFE/2PU/3SiO ₂	16	56

Table V. Water Contact Angles of PU, PU/PTFE and Si@PTFE/PU Nanocomposite Films

Sample codes	Water contact angle (°)
PU	70
PTFE/PU	94
PTFE/2PU	94
PTFE/3PU	92
PTFE/4PU	85
PTFE/5PU	82
PTFE/2PU/SiO ₂	97
PTFE/2PU/2SiO ₂	95
PTFE/2PU/3SiO ₂	98

DSC. The DSC curves of PU, PTFE/PU, SiO₂/PTFE/PU nanocomposites are given in Figure 4. Glass transition data of all the as synthesized PTFE/PU nanocomposites are listed in Table IV. The dried PU nanoparticles showed a glass transition temperature at 51°C and PTFE being a semicrystalline polymer as expected showed a crystal–crystal transition at 21°C and a specific endothermic peak at 337°C, which corresponds to melting peak of the fluoropolymer (this peak was not shown in DSC spectrum).⁹ On increasing the content of PTFE, decrease in T_g for the PTFE/PU nanocomposites was noticed, which is unlike the PAI/PTFE nanocomposites¹² wherein no change in glass transition has been reported with increase in the content of PTFE owing to absence of interactions between the two regions. Whereas, the decrease in T_g of PU in the present case can be attributed to some form of cooperative motion between the two polymer phases thus resulting in lowering of T_g . T_g of SiO₂/PTFE/PU nanocomposites increased by >10°C when compared with PTFE/PU nanoparticles which could be due to hydrogen bonding of silica with fluorine that may hinder chain segmental mobility.

Wettability. Before measuring contact angle the films of latex particles were casting on glass plates and dried at 50°C for 24 h, then the contact angles were measured at room temperature. The water contact angles of PU and PTFE/PU nanocomposite films with varying amounts of PTFE contents are shown in Table V. The contact angle of the PU films (70°) increased with increasing PTFE content in the nanocomposites upto 94° which had shown a further improvement to 98° for the SiO₂/PTFE/PU samples. The modification of PU to improving the hydrophobic surface increases with increasing the PTFE latex and the optimize ratio of PTFE/PU is 1 : 2 and shown 94° water contact angle. Further increase of 4° for the SiO₂/PTFE/PU nanocompo-

sites could be due to the contribution of roughness from silica nanoparticles.¹¹

CONCLUSIONS

A facile method for uniform modification of PU at molecular level using commercially available PTFE latex for improving its hydrophobic property has been reported. Miniemulsion polymerization of PU was done in the presence of PTFE latex to achieve hybrid nanoparticles of 200–300 nm as confirmed by using TEM. Water contact angle (WCA) of PU increased from 70° to 94° for 1 : 2 of PTFE/PU nanocomposites and an additional improvement to 98° for the SiO₂/PTFE/PU (1 : 2 PTFE/PU) nanocomposites without affecting their thermal stabilities. Such a modification of PU to improve hydrophobicity is simple, cost effective to the optimize ratio of PTFE/PU is 1 : 2 and can be used for top coat applications on leather or metal substrates.

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