

Synthesis and Characterization of Chlorine-Containing Flame-Retardant Polyurethane Nanocomposites via *In Situ* Polymerization

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ABSTRACT: We have developed flame-retardant polyurethanes (FRPUs) and polyurethane (PU) nanocomposites via *in situ* polymerization. Three series of thermoplastic elastomeric PUs were synthesized to investigate the effect of incorporating 3-chloro-1,2-propanediol (CPD) and nanoclay on mechanical, thermal properties, and also resistance to burning. PU soft segments were based on poly(propylene glycol). Hard segments were based on either CPD or 1,4-buthane diol (BDO) in combination with methyl phenyl di-isocyanate named PU or FRPU, respectively. In the third series, CPD was used as chain extender also nanoclay (1% wt) and incorporated and named as flame-retardant polyurethane nanocomposites (FRPUN). Mechanical properties and LOI of PUs and nanocomposites have been evaluated. Results showed that increasing the hard seg-

ment (chlorine content) leads to the increase in flame retardancy and burning time. Addition of nanoclay to CPD-containing PUs leads to obtain self-extinguish PUs using lower CPD contents, higher Young's modulus, and strength without any noticeable decrease in elongation at break. Investigation of the TGA results showed that copresence of nanoclay and chlorine structure in the PU backbone can change thermal degradation pattern and improve nanocomposite thermal stability. X-ray diffraction and transmission electron microscopy studies confirmed that exfoliation and intercalation have been well done. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 437–447, 2012

Key words: flame retardant; polyurethane; chlorine compound; nanocomposites; *in situ* polymerization

INTRODUCTION

Polyurethanes (PUs) form a very wide family of polymeric materials (paints, adhesives, elastomers, flexible, and rigid foams) and thus play an important and increasing role in our daily life. Like other organic materials, one of the major drawbacks of PU is their flammability.^{1,2} Flame-retardant additives are usually needed, among which halogenated compounds are most widely used. It is reported that brominated additives represent 25–30% of the total flame-retardant consumption in the United States and the Western Europe.¹ From the point view of flame retardancy, the halogenated flame retardants are most effective and cannot be substituted in many applications to date; but, in certain cases, they may give rise to environmental problems.^{1,3} Replacing carbon and hydrogen atoms in the polymer with inorganic atoms such as chlorine,^{4–6} silicon,^{7–9} nitrogen,^{10,11} sulfur,³ or phosphorus^{7,12,13} results in a polymer with reduced flammability due to increased

heat resistance and lower fuel value.¹¹ Bonding flame-retardant groups to PU backbone (i.e., using a reactive flame retardant) have attracted much attention.^{4,14,15} Using a reactive flame retardant has the advantage of permanent attachment of the flame retardancy. This will lead to the acquirement that a much smaller amount of flame retardant is required to reach a certain degree of flame retardancy. Consequently, a much smaller influence is brought upon the physical and mechanical properties of PU. Halogenated reactive flame retardants have been studied frequently, but there has been a debate about the evolution of dichloroethane.¹⁶ Therefore, emitting of poisoning gases has been considered a disadvantage for halogenated flame retardant. On the other hand, nanoclay has been used for improving flame retardancy.^{17,18} For getting special level of flame retardancy and less environmental hazards, it can be used with nanoclay with lower amount of halogenated flame retardant. Modified or organophilic clay could be dispersed in an appropriate polymer matrix by variety of methods. These methods can be broken down into three categories: intercalation of prepolymer or polymer from solution, melt intercalation, and *in situ* intercalative polymerization. A wide range of nanocomposites have been formed by melt

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mixing, solution casting, and *in situ* polymerization.^{18,19} Melt mixing and solution casting primarily result in intercalated nanocomposites, and *in situ* polymerization provides a range of dispersion from intercalated to exfoliated.^{18,20–22} There are few reports on using a reactive flame retardant to improve flame-retardancy of PU nanocomposites via *in situ* polymerization. In this work; attempts have been made to reduce flammability of PU through introducing chlorine-containing chain extender in the main chain and incorporating nanoclay via *in situ* polymerization.

According to previous studies, chlorine compound generates chlorine-containing heavy gases, which suppress the access of oxygen, and consequently suppresses flammable combustion of PUs.⁴ However, increasing the chain extender content increases hard segment and reduces soft segment content in unit volume of polymer. Accordingly, stiffness of polymer increases and elongation at break decreases. On the other hand, nanoclay can create a barrier layer in the surface of samples, which have prevented effect on diffusion of volatile decomposition products, consequently, flammability of PU reduces.¹⁷ Furthermore, nanoclay has an important role in strengthening nanocomposites by transferring the stress between nanoclay and PU matrix effectively, and so incorporating nanoclay into the FRPU samples increases modulus and strength.

In fact, both nanoclay and chlorine chain extender affect on bulk properties as well as flame retardancy of synthesized PUs. Incorporating of nanoclay and using of chlorine chain extender imparts desirable and undesirable changes on final properties individually. It means that nanoclay increases modulus, decreases elongation at break, forms barrier layer, and reduces flammability. Chlorine chain extender increases modulus, decreases elongation at break, and suppresses flammable combustion. Using both could lead to some unknown phenomena, for example, a synergistic effect.

How will the flammability and mechanical properties of PUs change via addition of chlorine chain extender or nanoclay? It seems that chlorine compound causes inherent flame retardancy, while nanoclay improves mechanical properties.

To verify the expected properties, three series of PUs were synthesized: PU using 1,4-butanediol (BDO), chlorine-containing polyurethane (FRPU) using 3-chloro-1,2-propanediol (CPD), and polyurethane nanocomposites using CPD-nanoclay (FRPUN). Various PUs and nanocomposites containing 1% nanoclay with different hard segment contents (41–68%) have been synthesized. Then, some of important properties such as mechanical properties, resistance to burning behavior, and thermal stability have been investigated using tensile, TGA, and LOI

tests, respectively. Finally, intercalation has been investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses.

EXPERIMENTAL

Materials

Polypropylene glycol (PPG) with $M_n = 425$ as soft segments, CPD, BDO as chain extender, methyl phenyl di-isocyanate (MDI) as isocyanate, dibutyltin dilaurate (DBTDL) as catalyst, and dimethylformamide (DMF) as solvent were from Merck. All the materials were used as received.

Cloisite 30B, from Southern Clay Products, was used as organically modified layered silicate. The Cloisite series of organosilicates are based on a natural montmorillonite with a cation exchange capacity of 0.92 meq/g and has a 0.9 meq/g organic quaternary ammonium ions $[N(CH_2CH_2OH)_2(CH_3)T]$, where T represents an alkyl group with $\sim 65\%$ $C_{18}H_{37}$, 30% $C_{16}H_{33}$, and 5% $C_{14}H_{29}$. Cloisite 30B was dried in a vacuum oven at 70°C for 12 h before use.

The oral LD₅₀ of CPD was reported to be 152 mg/kg bodyweight in rats. CPD is considered to be carcinogenic to rodents via a nongenotoxic mechanism.²³ It has a Sigma Hazard Code of T (toxic material) and soluble in cold water with a vapor pressure of less than 0.1 mm Hg @ 20°C. Two hydroxyl groups in the chemical structure of 3-chloro-1,2-propanediol $[ClCH_2CH(OH)CH_2OH]$ could be participated in chain extension reaction during PU chains formation.

Characterization techniques

FTIR spectra of the PU thin films (obtained of solution in DMF) coated on dry KBr disc were obtained using a BOMEM (Canada) spectrometer. The sample was scanned 21 times with a resolution setting of 4 cm^{-1} . Spectra were in the range of 400–4000 Cm^{-1} .

XRD patterns of FRPUN2 were obtained using a diffractometer (EXPERT. Philips) with Cu K α radiation ($\lambda = 0.154$ nm, 40 kV, and 40 mA). All experiments were carried out in the reflection mode at ambient temperature with a scanning speed of 0.02°/s and 2 θ varied from 1.01° to 9.99°.

TEM measurements were performed using a (TEM, model: CEM902A, company of Zeiss) at a voltage of 50 kV. Samples were in the form of thin films, which placed on a Cu grid. Wave length dispersive X-ray (model: 3PC-USA) was used for the analysis of Si in the polymer matrix.

TGA analysis was carried out using DU Pont TGA 951 thermogravimetric apparatus at air with a heating rate of 10°C/min. The scanned temperature range was from ambient temperature to 600°C, and reference material was calcium oxalate.

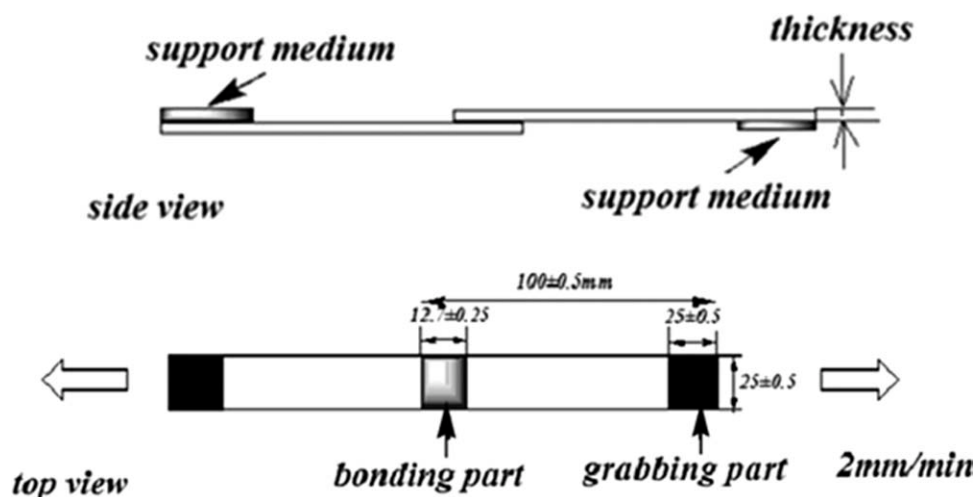


Figure 1 Set-up for tensile shear strength testing.

To study burning behavior, LOI and ignitibility tests were used. LOI test was carried out according to ASTM 2863-09 method. To measure burning times of various samples, 40 mm × 10 mm × 2 mm bars were prepared, and burning time to 2 Cm-mark lines was measured according to Clause 6.2.5 of DIN 4102 standard (ignitibility test).

To study mechanical properties, the samples were cut into dumb-bell shape and measuring carried out according to ASTM D 683 test method by Cesare Galdabini SPA tester (GALDABINI SUN 2500). The crosshead speed was 50 mm/min. All tests were performed at room temperature on two specimens.

The tensile shear bond strength of samples was measured using of Cesare Galdabini SPA tester (type: GALDABINI SUN 2500) with a crosshead speed of 2 mm min⁻¹ according to standard ASTM D 1002. Shear stress was applied across the adhesive bond; the bonded materials were forced to slide over each other with the adhesive bond layer providing the resistive force (Fig. 1). Substrates (25 × 100 mm²) were glasses with a thickness of 2 mm. PU, FRPU-63, and FRPU-68 were used as an adhesive to bond substrates. After applying of the polymer on the substrates, assemblies were fixed with special grips and kept at 70°C for 72 h.

Synthesis of polyurethanes (FRPU and PU)

Flame-retardant polyurethanes (FRPUs) were synthesized by two-step method according to the following general procedure. A 250-mL round-bottomed flask was equipped with a temperature-controller, mechanical mixer, reflux condenser, and N₂ inlet. It was charged with isocyanate, polypropylene glycol, and DMF. After the addition, reaction was continued for 3 h at 80°C. The obtained prepolymer was then subjected to react with 3-chloro-1,2-propanediol for

FRPUs in the presence of catalyst (1 wt %). The reaction time was 2 h at 60°C. The mixtures were then immediately cast on Teflon plates and were kept in an oven for 72 h at 45°C. In the case of PU, all conditions were similar, but BDO was used instead of CPD. Molar ratio of isocyanate groups to hydroxyl groups was constantly equal to 1.05. Detailed descriptions of synthesis are given in Table I. PU-XX and FRPU-XX indicate PU-containing XX % hard segment based on 1,4-butane-diol and CPD, respectively.

Synthesis of FRPUN

Flame-retardant nanocomposites were synthesized similar to above-mentioned method. At first, nanoclay platelets (1 wt % of total weight of polymer, by using a high shear mixer at 3500 rpm) have been dispersed in polypropylene glycol for 2 h at room temperature.

It is worth mentioning that 1 wt % nanoparticle was chosen due to our previous experience, which results in an exfoliated dispersion of nanoparticle in PU matrix. Stability after the addition of the nanoclay was acceptable.

Obtained mixtures were then used as polyol and added to the reactor. Other steps and conditions were similar to the procedure for the synthesis of PUs. Detailed descriptions of synthesis of nanocomposites are given in Table I.

Hard and soft segment content of the PUs has been calculated according to formula 1²⁴:

$$\text{hardsegment concentration(\%)} = \frac{M_{\text{OH}} + M_{\text{iso}} + M_{\text{ce}}}{M_{\text{total}}} \times 100 \quad (1)$$

where M_{OH} is the mass of hydroxyl group of polyol, that is, PPG, M_{iso} is the mass of isocyanate compound

TABLE I
Description of Polyurethane Samples Used in This Study

Sample	PPG425 (mol)	MDI (mol)	CPD (mol)	BDO (mol)	Chlorine (% wt) calculated	Hard segment content
PU-61	1	2.2	–	1	–	61
FRPU-41	1	1.42	0.29	–	1.25	41
FRPU-59	1	1.91	0.739	–	2.62	59
FRPU-63	1	2.2	1	–	3.22	63
FRPU-68	1	2.75	1.5	–	4.105	68
FRPUN-41	1	1.42	0.29	–	1.24	41
FRPUN-59	1	1.91	0.739	–	2.60	59
FRPUN-63	1	2.2	1	–	3.19	63

used, that is, MDI, M_{ce} is the mass of chain extender, that is, CPD, and M_{total} is the total mass. The calculations were carried out based on the 1.1 : 1M ratio of NCO/OH used in the capping reaction, and, accordingly, the amount of moisture required for completed

reaction. The calculated hard segment contents are given in Table I. FRPUN-XX indicates PU nanocomposite based on CPD containing XX % hard segment.

Chlorine (% wt) of the samples was determined by Formula 2:

$$\text{Chlorine}(\% \text{wt}) = \frac{(\text{mol})_{\text{CPD}} \times 35.5}{(\text{mol})_{\text{polyol}} \times M_{\text{polyol}} + (\text{mol})_{\text{diiso}} \times M_{\text{diiso}} + (\text{mol})_{\text{CPD}} \times M_{\text{CPD}} + m_{\text{nanoclay}}} \quad (2)$$

where 35.5 is molecular weight of chlorine.

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectrum of FRPU-63 and FRPUN-63 is shown in Figure 2. The bands between 2800 and 3000 cm^{-1} are due to the C–H stretching vibrations (asymmetric CH_3 stretching: 3032 cm^{-1} ; asymmetric CH_2 stretching: 2971 cm^{-1} ; symmetric CH_3 stretching: 2869 cm^{-1} ; and symmetric CH_2 stretching: 2851 cm^{-1}), C–H asymmetrical bending at 1459 cm^{-1} , C–H symmetrical bending at 1379 cm^{-1} , ether group (1052 cm^{-1} , C–O–C stretching vibration). The broad band between 3000 and 3650 cm^{-1} is due to the N–H stretching vibrations, and carbonyl groups due to urethane (1708 and 1735 cm^{-1} , C=O stretching vibrations) are observed; the peaks at 1535 and 1418 cm^{-1} are due to the N–H, C–N of urethane group, also C–Cl stretching at 768 and 535 cm^{-1} are observed. The observed peaks and absence of peak in 2270 cm^{-1} verify that PUs have been synthesized successfully.

Moreover, it is possible to calculate the degree of phase separation (DPS). The 1733 cm^{-1} band is due to the free-of-hydrogen-bonding carbonyl groups, and the band at 1703 cm^{-1} is associated with the hydrogen-bonded carbonyl groups. The degree of the carbonyl groups participating in hydrogen bonding can be described by the carbonyl hydrogen bonding as given in Formula 3.²⁵

$$\text{DPS} = \frac{C_{\text{bonded}}}{C_{\text{bonded}} + C_{\text{free}}} \quad (3)$$

The degree of hydrogen bonding of carbonyl groups and constituency DPS has been determined by using of the formula values as 0.4 and 0.59 for FRPU-63 and FRPUN-63, respectively. Therefore, phase

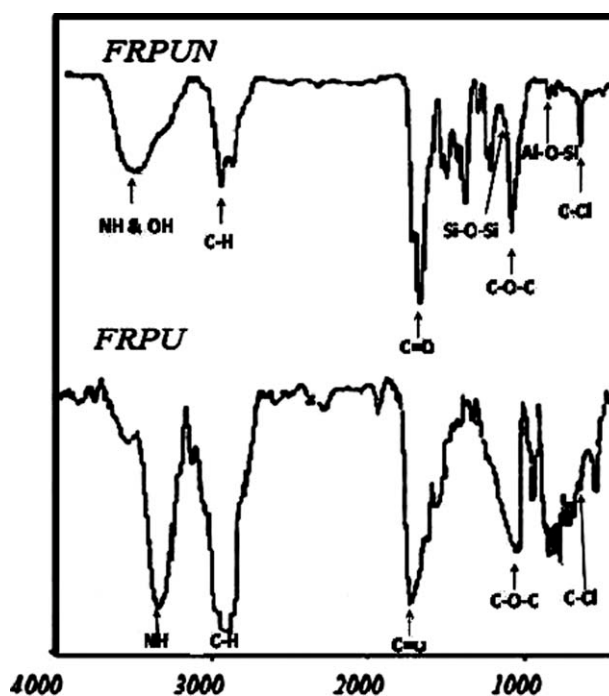


Figure 2 FTIR spectra FRPU and FRPUN.

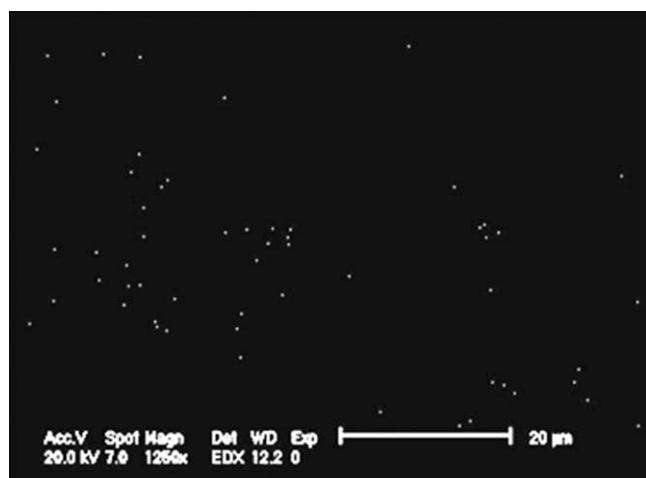


Figure 3 Si-mapping of FRPUN-63.

separation increases through the incorporating of nanoclay into the nanocomposites.

Studies on nanostructure of nanocomposites

Results of wave length dispersive X-ray test were used to verify existence of Si in the nanocomposite, because there is not any Si atom in the structure of polymer, existence of the Si is only due to montmorillonite in the polymer matrix. As shown in Figure 3, for FRPUN-63, Si spreads in entire of polymer matrix, which indicates no aggregation in nanoclay particles.

XRD and TEM, which are two complementary techniques, were used to characterize the nanocomposites structure. Figure 4 shows the XRD patterns of FRPUN-68. It is reported that when the extensive layer separation connecting with exfoliated structures disrupts the coherent OMMT layer stackings, there is no more diffraction peaks visible in XRD patterns because of the much too large spacing between the layers or because the nanocomposites present disordering.²⁶

As shown in Figure 4, FRPUN-68 shows only a small diffraction peak at $2\theta = 2.832^\circ$. This peak is related to $d = 3.116$ nm. This confirms that almost whole of Cloisite 30B has been exfoliated well.

However, only XRD patterns are not persuasive enough to characterize the structure of the nanocomposites, especially if some layered silicates do not exhibit well-defined basal reflections. Thus, TEM technique provides a qualitative understanding of the internal structure in real space in a localized area.²⁷ Montmorillonite platelets have a higher electron density than the PU, thus generating a higher resistance to electron transmission. This effect is seen in the TEM images as darker shapes.²⁸ The XRD result is confirmed by the TEM microphotographs of FRPUN-68 shown in Figure 5. As shown in Figure 5, exfoliated/intercalated has been accrued in nano-

composite. This may be related to several reasons such as better dispersion of the clay in polymer due to tethering that takes place during *in situ* polymerization, polar nature of PU chains,²⁹ and Cloisite 30B that has enlarged intragallery caused to the decrease of electrostatic interaction between adjacent Cloisite 30B layers, which provide an occasion for polyol chains to diffuse into the Cloisite 30B intragalleries during high shear mixing.

Thermal stability of PU nanocomposites

Polyurethane (PU) degradation usually starts with the dissociation of the urethane bond, carbon dioxide, and isocyanate evulsions. Figure 6 shows TGA curves of FRPU-63, FRPU-59, and FRPUN-63. Results show that degradation behavior of PUs under investigation depends on the structure of macromolecules and could be described with different values of thermal parameters, which are collected in Table II.

It is obvious that the IDT (initiation degradation temperature) of FRPUN-63 is higher than that of FRPU-63 and FRPU-59. As illustrated in Table II, FRPUN-63, FRPU-63, and FRPU-59 started being degraded at 160°C , 157°C , and 148°C , respectively. The IDT temperature of degradation for FRPUN-63 is 3 and 12°C higher than that of FRPU-63 and FRPU-59, respectively. This difference for PUs became more distinguished in higher temperatures; for example, in 70% weight loss, the difference is 69 and 72°C , respectively. Introduction of chlorinated diol caused an increase in thermal stability. Similar results have been reported in some other works^{5,30}

As shown in Figure 6, the thermal degradation patterns of FRPU-63 and FRPUN-63 have exhibited two steps. The differential thermogravimetric analysis (DTGA) curve reveals that these steps are composed reactions. An initial weight fraction loss at about 210 – 280°C can be explained by the degradation started

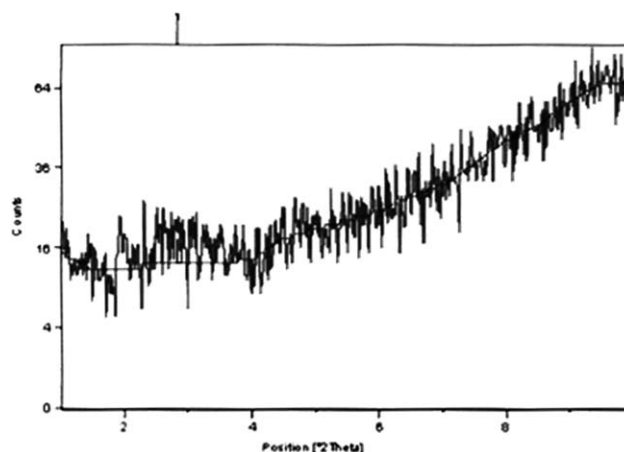


Figure 4 XRD pattern of FRPUN-68.

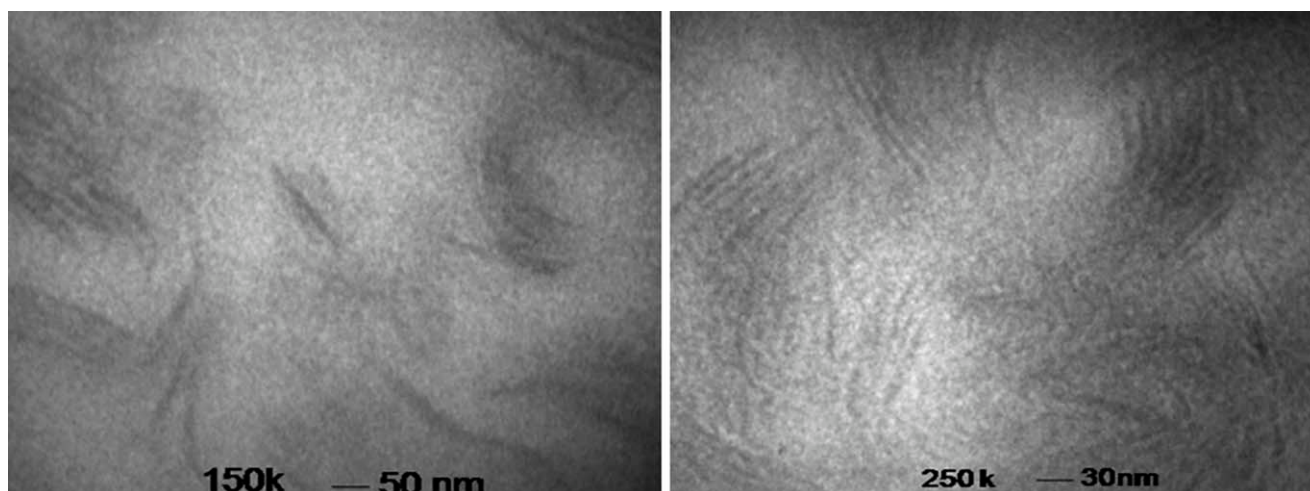


Figure 5 TEM microphotographs of FRPUN-59 with different magnification that show exfoliated and intercalated nanocomposite.

with HCl, CO₂, amines and HCN formation by loss of the chlorine, carbonyl, amine groups of the main chain.³¹ In the second step, a sharp peak occurs at 300°C for FRPUN-63. The weight loss in this range of temperature responds to chain scission of urethane linkages and PPG soft segments.³² This peak isn't sharp and extended to higher temperatures for FRPUN-63 due to presence of nanoparticles act as barriers which results delay in degradation process. In fact, presence of nanoparticles affects on the value of weight loss percent per 1°C (%/°C), from 2%/°C in FRPU-63 reduces to 1%/°C in FRPUN-63, depicted in Figure 6(b).

Moreover, as shown in Figure 6, the thermal degradation pattern of FRPU-59 has exhibited three steps. An initial weight fraction loss at about 170°C can be explained by the degradation started with started with HCl, CO₂, amines, and HCN formation by loss of chlorine, carbonyl, and amine groups of the main chain. In the second step, a peak occurs at

270°C for FRPU-59. The weight loss in this range of temperature responds to chain scission of urethane linkages. The last step of the degradation takes place at a temperature about 320°C, a sharp peak occurs, and this can be attributed to chain scission of PPG soft segments.

Comparison of FRPU-59 with FRPU-63 shows that the curve, 50°C, shifts to higher temperatures. It could be concluded that increasing of hard segment content about 4% caused to impose increased thermal stability of PU. Chlorine-containing hard segments are responsible for the improved thermal stability. Figure 6 depicts DTGA curves for FRPU-59, FRPU-63, and FRPUN-3.

Suggested mechanism to be operating during the thermal decomposition for segmented PUs based on 4,4-diphenylmethane diisocyanate, polyoxypropylene-diol, and low-molecular chain extenders: 3-chlor-1,2-propanediol is shown in Figure 7.³¹

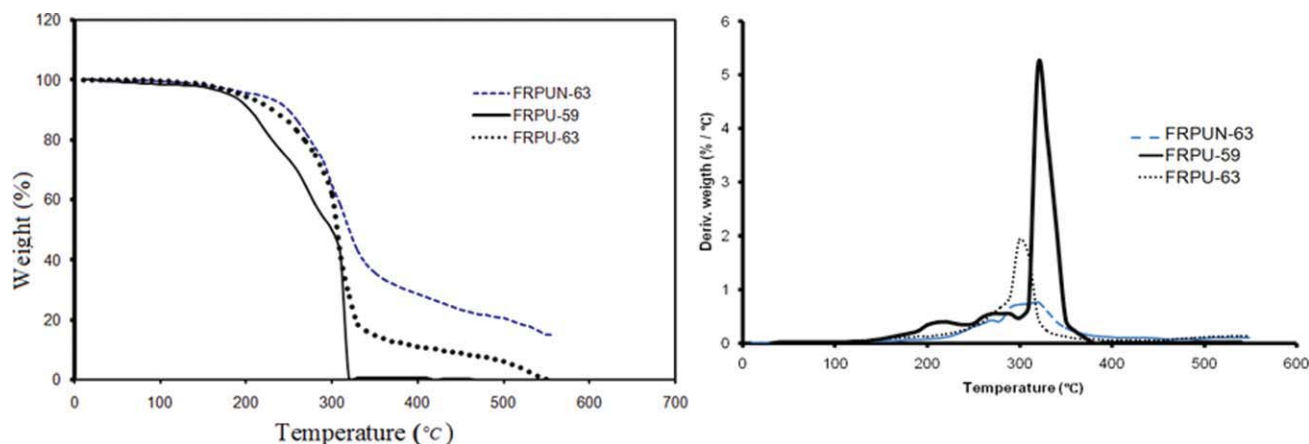


Figure 6 TGA and DTG thermograms for FRPUN63, FRPU63, and FRPU59. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Results of the Thermogravimetric Analysis of Samples

Sample	IDT (°C)	T _{20%} (°C)	T _{30%} (°C)	T _{50%} (°C)	T _{70%} (°C)	Char residue (%)	DTG max-temp. (°C)
FRPU-63	157	269	287	304	315	8.788	292
FRPU-59	148	231	259	299	312	0.268	313
FRPUN-63	160	274	294	321	384	23.48	321

It could be concluded that thermal stability of PUs has been improved via introducing of Cloisite 30B. This phenomenon is due to the presence of nanoparticles, which could possibly help prevent heat transfer quickly; therefore, further degradation has been limited. The thermal stabilization effect of nanoclay is explained by the so-called Labyrinth barrier effect generated by the highly anisotropic-layered silicate platelets dispersed on the nanometer scale in the

nanocomposite, which hinders the diffusion of the volatile degradation products (carbon dioxide, carbon monoxide, water molecules, etc.) from the bulk of the polymer matrix to the gaseous phase.³³

Moreover, in higher temperature, this phenomenon is related to the decomposition of PU and OMMT, which could be caused by the formation of a glassy coating and stable carbonaceous charred layers. This stable physical protective barrier on the

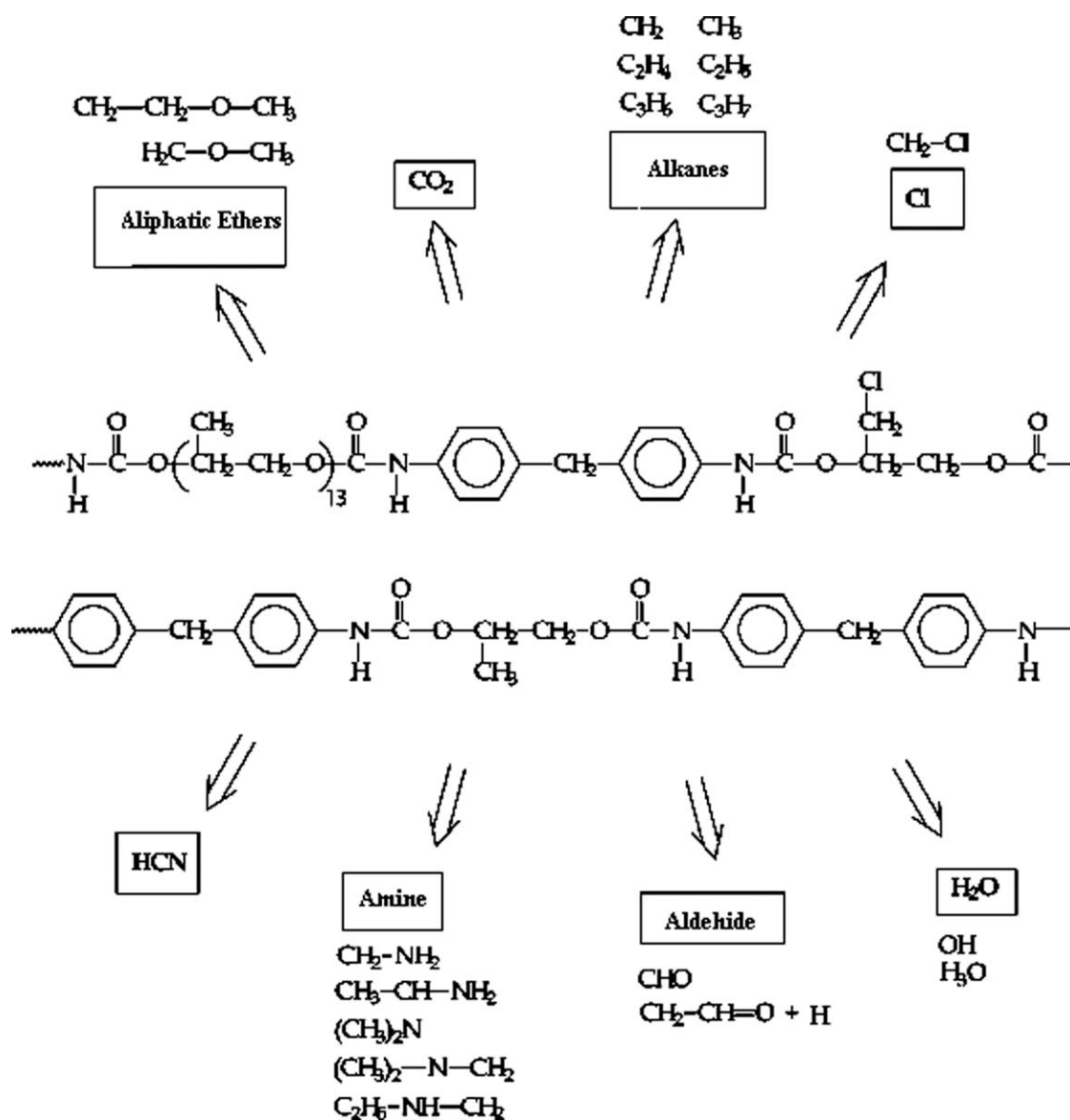


Figure 7 Mechanism of decomposition reaction.

TABLE III
Description of LOI and Ignitibility Tests

Samples	Environmental condition		LOI values	Char content	Time of burning (s)
	temperature (T : °C)	humidity (H: %)			
FRPU-68	T = 18.3	H = 35%	23	Low	Self-extinguished
FRPU-63	T = 18.3	H = 35%	22.2	Low	Self-extinguished
FRPU-59	T = 18.3	H = 35%	21	Low	54
FRPU41	T = 18.3	H = 35%	20.3	Low	45
PU-61	T = 19.3	H = 36%	18.2	Low	30
FRPUN-68	T = 19.3	H = 36%	23.8	High	Self-extinguished
FRPUN-63	T = 19.3	H = 36%	23.1	High	Self-extinguished
FRPUN-59	T = 19.3	H = 36%	22.3	High	Self-extinguished
FRPUN-41	T = 19.3	H = 36%	21.4	High	Self-extinguished

surface of PUs may insulate the underlying FRPU matrix from the heat source and slow down heat and mass transfer between the gas and condensed phases.^{34,35} Thus, formation of this layer causes broadening of TGA curve for FRPUN-63.

Char residue contents of all samples at 450°C are illustrated in Table II. Char residue of RPUN-63 is significantly higher compared to that of FRPU-63 and FRPU-59; FRPU-59 and FRPU-63 matrices completely decompose into gas products without any char residue in 480 and 550°C, respectively.

Effect of chlorine content and nanoclay in burning behavior

Chlorine compounds usually have low flammability in the gaseous state. The presence of chlorine affects chemical reactions during combustion; chlorine compound generates chlorine-containing heavy gases, which suppress the access of oxygen and consequently suppress the flammable combustion of PUs.⁴ Results of LOI and ignitibility tests are shown in Table III. Figure 8 shows that flame retardancy increases with increase in chlorine content. Chlorine-containing gases such as HCl and $-\text{CH}_2\text{Cl}$ ³¹ compounds are generated during thermal decomposition of CPD—including PU chains that are responsible to reach a self-extinguish composite or nanocomposite PU according to Table III. As shown in Table III, increasing of CPD content leads to higher LOI as well as higher burning times for FRPU and FRPUN samples following to self-extinguishability. It could be concluded that lower limit of hard segment to impart flame resistance in FRPUs is 60%, which is reduced to 40% in FRPUNs. Therefore, using nano-

clay, beside CPD, improves flame retardancy and LOI of PU.

Results in Figure 8 show that addition of nanoclay to PUs decreases flammability. This phenomenon may be related to the formation of a barrier layer in the surface of samples, which has prevented of diffusion of volatile decomposition products.¹⁷ Upon heating, the viscosity of the molten polymer/layered silicate nanocomposite decreases with increasing temperature and facilitates the migration of the clay nanolayers to the surface. Moreover, heat transfer promotes thermal decomposition of the organomodifier and the creation of strongly protonic catalytic sites onto the clay surface, which can catalyze the formation of a stable char residue. Therefore, accumulation

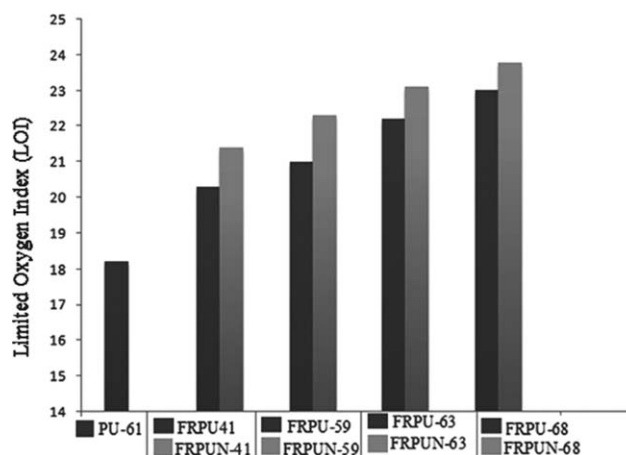


Figure 8 Limited oxygen index of FRPU-68, FRPU-63, FRPU-59, FRPU41, PU-61, FRPUN-68, FRPUN-63, FRPUN-59, and FRPUN-41.

of the clay on the surface of the material acts as a protective barrier that limits heat transfer into the material, volatilization of combustible degradation products, and diffusion of oxygen into the material. Furthermore, nanoclay migration is enhanced by the formation of gas bubbles, initiated by the decomposition of both the quaternary ammonium organomodifiers and the polymer chains. Such gas bubbles may in fact be nucleated by the surface of the MMT. These gas bubbles could also help in the convection of the MMT sheets to the surface.³⁶ According to TGA analysis, reduction in mass loss rate in case of nanocomposites indicates that flame retardancy mechanism of nanoclay is occurring in the solid and not gas, phase.³⁵

Mechanical properties

Mechanical properties of PU, FRPUs, and FRPUNs are shown in Table IV and Figure 9. The results indicate that with increasing of chain extender content, stiffness of polymer increases and elongation at break decreases. This phenomenon happens due to increasing hard segment content and reducing soft segment content in unit volume of polymer. Accordingly, urethane linkages in unit volume of polymer increase and subsequently hydrogen bonding increases. As a

TABLE IV
Mechanical Properties of FRPU and NFRPU with Different Chain Extender

Sample	Young's modulus (N/mm ²)	Max stress (N/mm ²)	Elongation at break (%)
FRPU-41	37	4.7	274
FRPU-59	75	10.85	145
FRPUN-41	92	7.9	159.2
FRPUN-59	144	16	32.1

result stiffness of polymers increases. For example, modulus increases from 37 to 75 N/mm² for the samples FRPU-41 and FRPU-59, respectively.

Incorporating of nanoclay into the FRPU samples increase modulus and strength. For example, modulus increases from 75 to 144 N/mm² in the samples FRPU-59 and FRPUN-59, respectively. Such an improvement can be attributed to clay polymer tethering and hydrogen bonding between clay particles and the polymer.³³ In fact, the nanoclay has an important role in strengthening nanocomposites by transferring of stress between nanoclay and PU matrix effectively. Furthermore, higher DPS of FRPUN rather to FRPU; according to FTIR results; is effective and leads to higher modulus. However,

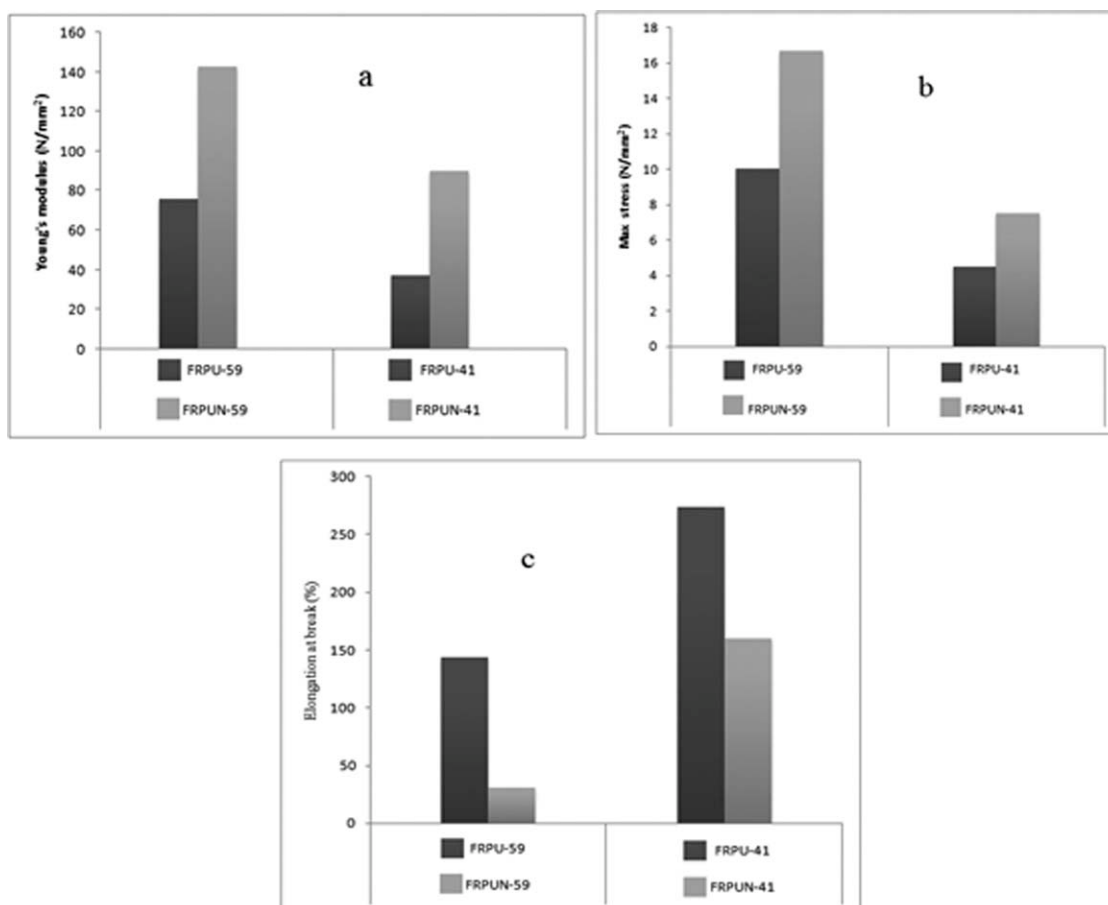


Figure 9 Modulus, max stress, and elongation via hard segment content in diagrams a, b, and c, respectively.

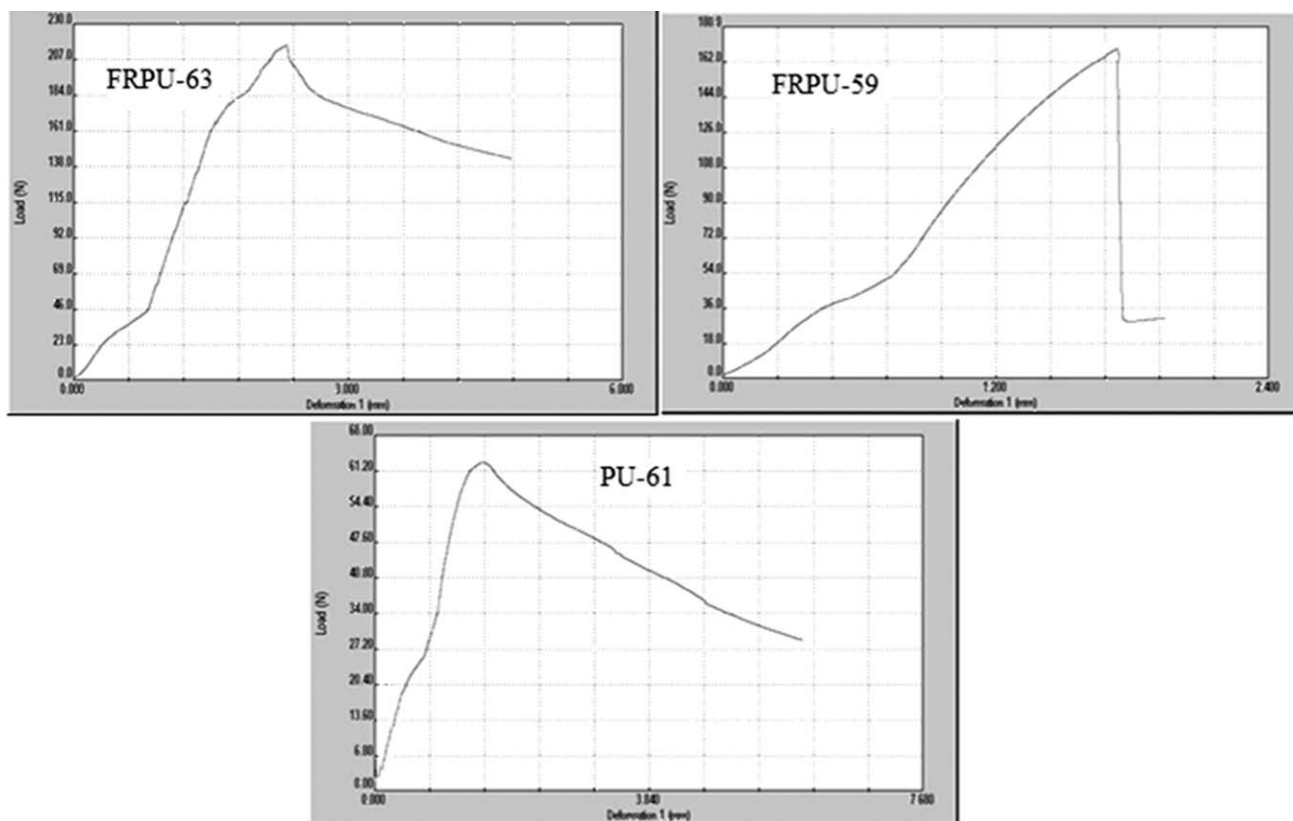


Figure 10 Load–deformation curves for FRPU-63, FRPU-59, and PU-61 on glass–glass substrates.

elongation at break value decreases with the incorporation of nanoclay, which is due to the restricted mobility of the polymer chains.³⁷

Comparison of results in Table III shows that incorporating of 1% nanoclay to FRPU-41 with 45-s burning time leads to a self-extinguish FRPUN-41. Furthermore, comparison of results in Table IV shows that increasing the hard segment as 18% to FRPU-41 leads to increasing of modulus as 38 MPa in FRPU-59. Moreover, incorporating 1% nanoclay into FRPU-41 caused a modulus of 50 MPa higher in FRPUN-59. Addition of 1% nanoclay leads to obtain self-extinguish PUs using lower hard segment contents, higher Young's modulus, and strength without any noticeable decrease in elongation at break.

Tensile shear bond strength

In this test, we are interested to know the effect of chlorine content of PUs on shear bond strength. Figure 10 shows load deformation curves for FRPU-59, FRPU-63, and PU-61. Measured strength as maximum load (F_m) of samples FRPU-63, FRPU-59, and PU-61 (applied on glass substrates) are 218N, 166N, and 63N, respectively. As can be seen, with increasing of chain extender content, the F_m is increased. Strong bond between the surface of the glass and PU films, such as hydrogen bonds, is likely to be

due to urethane groups. In samples that have higher chain extender, amounts of capable sites for formation of hydrogen bonds in unit volume of polymer matrix are more and thus F_m increases. In other point of view, existence of chlorine atoms in polymer structure caused increasing of adhesion, which reported in other studies.^{4,16,38}

As can be seen from Figure 10, the highest value of F_m , 218N and the lowest F_m value, 63N are observed for samples FRPU-63 and PU-61, respectively. Because both samples have equal urethane groups, thus, difference in amount of F_m shows effect of chlorine atoms on shear bond strength. Of course, other parameters such as NCO/OH ratio, evaporation of solvent, moisture, surface preparation method, and type and value catalyst, can affect on F_m .

CONCLUSIONS

FRPUs and PU nanocomposites have been synthesized via *in situ* polymerization in which exfoliation of 1% nanoclay has occurred well. Addition of Closite 30B results in decrease in elongation at break and increase in tensile strength and Young's modulus. Either nanoclay or CPD increases flame retardancy but using of nanoclay beside CPD improves flame retardancy and LOI of PUs. Addition of 1% nanoclay to CPD containing PUs leads to obtain

self-extinguish PUs using lower CPD contents, higher Young's modulus, and strength without any noticeable decrease in elongation at break. Results of LOI tests and ignitability test show that flame retardancy increases with increasing of CPD content as well as nanoclay.

Addition of nanoclay to PUs increases thermal stability, and char residue also creates protective barrier layer in the surface of nanocomposites; consequently, the flammability is decreased. According to TGA results, it seems that all thermal properties of nanocomposites are related to this fact that presence of nanoclay changes thermal degradation pattern of PUs from three steps to two steps. In fact, the value of weight loss percent of nanocomposites is half as much as pristine PUs due to the presence of nanoparticles. Increasing of chlorine content leads to improve adhesion of FRPUs to glass substrates.

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