Rigid Polyurethane Nanocomposites Prepared by Direct Incorporation: Effects of Nanoclay, Carbon Nanotubes and Mixing Speed on Physical and Morphological Properties

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Abstract. Rigid polyurethane (PU) nanocomposites were fabricated via solution mixing of PU, nanoclay and multiwalled carbon nanotubes (MWCNT) according to full factorial DoE. The nanoclay and MWCNT concentration as well as mixing speed were varied. The effects of controlled variables on reduced compressive strength, fire retardancy, hardness and morphological properties were analyzed. In general, the results showed that incorporation of nanofillers into PU matrix successfully elevated nanocomposites performance. The properties changed from -12% to 45% for reduced compressive strength, 9% to 30% for reduced fire retardancy and -32% to 101% for reduced hardness. The results suggested that the improvements were affected by nanoclay dispersion that acted as nucleating agent which resulted in smaller close cells of PU structures.

1. Introduction
Polyurethane is a polymer commodity that has many applications and products in industry and daily life, including but not limited to flexible and rigid foam, adhesive, coating, thermal insulation and biomedical [1-5]. Among PU products, rigid PU foam contributes to more than 23% of total PU production globally [6]. However, the fact that rigid PU is combustible and has a low compressive strength, inhibits the use thereof for further applications for instance as wall in knock down and lightweight house [7]. Existing flame retardants for PU in the markets generally contain halogenated materials that harmful for health and environment [8]. To address this, a healthy and environmentally benign nanocomposite polymer is designed. Nanomaterials such as CNT and nanoclay are preferable due to their eminent thermal and physical properties at nano size [9]. However, the incorporation of nanomaterials especially CNT into polymer system, encounters agglomeration issue caused by Van Der Waals force [10]. In order to overwhelm the issue, a ternary system is chosen instead of secondary or hybrid polymer/nanomaterial system.

Synergistic dispersion of MWCNT and nanoclay was studied by several groups. Ma Et.al reported that the dispersion of ternary system between ABS/MWCNT/clay was higher as indicated by TEM and XRD result in comparison with hybrid ABS/MWCNT or ABS/clay alone [11]. Peeterbroeck Et.al studied synergetic effect of MWCNT and nanoclay on EVA copolymer nanocomposite. Excellence improvement of elongation at break was observed by the incorporation of nanofillers [12]. The effect of simultaneous incorporation of nanoparticles (MWCNT, nanoclay), and nanofibers (polyacrylonitrile, PU) on sound absorption of flexible PU nanocomposite was studied by Bahrambeygi Et.al, indicating better properties due to the concomitant addition of nanoparticles [13].
However, the research about simultaneous incorporation of nanoclay and MWCNT into PU nanocomposite is limited.

The effect of layer by layer assembly of MMT and CNT hybrid flame retardant on the surface of flexible PU was investigated by Pan et al. Chitosan wrapped CNT dispersed in acetic acid aqueous solution, MMT suspension and alginate solution were prepared followed by layer by layer deposition of mixture on the surface of flexible PU. 43% reduction on heat release peak was observed [14]. Lee et al. reported that the simultaneous incorporation CNT and MMT in thermoplastics PU via melt mixing slightly increased tensile properties [15]. Madaleno et al. synthesized PU nanocomposite using hybrid iron modified MMT/MWCNT. Increasing on compressive strength up to 31% compared with neat PU was observed. However, this route required additional step to hybridize MM/MWCNT via CVD technique [16].

This study aims to investigate the effect of direct incorporation of MWCNT and nanoclay as well as mixing speed on compressive strength, fire retardancy, hardness and morphological properties of rigid PU nanocomposite. Instead of modifying nanoclay and MWCNT, the nanofillers were directly mixed with polyol to produce PU nanocomposite via solution mixing.

2. Experimental

2.1 Materials
Polyether polyol (Bayfit 21 BT 001) and modified diphenylmethane-4,4'-diisocyanate (MDI) (Desmodur 26BM13) from Covestro GmbH were used as polyurethane precursors. Modified montmorillonite nanoclay (Nanomer 1.44PT) from Elementis Specialties Company was chosen as nanofiller due to its eminence thermal stability. MWCNT with diameter 50 nm and length 20 µm were obtained from Cheap Tubes Inc. Polyvinyl butyral (Mowital B60H) used as dispersing agent for MWCNT was supplied by Kuraray GmbH. All materials were used as received.

2.2 Instrumentation
Specimens for testing were cut from cured samples and pre-conditioned at 23°C and 50% for more than 40 hours. The compression strength was measured using Shimadzu AGS 10 kNG Universal Testing Machine, referring to ASTM D1621 with crosshead speed 2.5 mm/min and limited strain to 13%. Horizontal burning rate was determined referring to UL 94. Density was obtained by directly weighted cubic PU nanocomposite and divided by its volume. Hardness was measured according to ASTM D2240 using shore A durometer. SEM Image was taken using JEOL JSM-6510LA at 10 kV.

Reduced compressive strength, burning rate and hardness were calculated by dividing the properties by density. Reduced fire retardancy was calculated by reciprocating the reduced burning rate.

2.3 Procedure
Table 1 lists all variations in PU nanocomposite preparation. Mechanical stirrer with speed 1300 rpm and 1900 rpm was used to perform all mixings. Polyether polyol and MDI ratio was fixed at 45:55. Firstly, PU/nanoclay/MWCNT composite was prepared by mixing polyether polyol, MWCNT, PVB and nanoclay at room temperature for 10 minutes, followed by 30 minutes ultrasonication. The amount of nanofillers was varied according to total polyurethane weight, namely 1.5 and 2.5 phr for nanoclay, 0.015 and 0.025 phr for MWCNT. The resulted mixture along with MDI was conditioned at 10°C for 5 minutes prior to further mixing. The chilled materials were mixed for 30 seconds and immediately poured into the mould and left for curing.

3. Results and Discussion
Table 2 shows reduced compressive strength, fire retardancy and hardness for PU nanocomposite samples. The results show that the properties are affected by the incorporation of nanofillers and processing condition. In general, the properties changed from -12% to 45% for reduced compressive strength, 9% to 30% for reduced fire retardancy and -32% to 101% for reduced hardness in comparison with control sample. Our ultimate reduced compressive strength is higher in comparison...
with another group, suggesting more efficient route to produce PU/Nanoclay/MWCNT nanocomposite [16].

Figure 1 and Figure 2 show the effects of nanoclay and MWCNT concentration as well as mixing speed on reduced compressive strength, fire retardancy and hardness. Figure 1 show that increasing concentration of nanoclay and MWCNT tend to lower the properties. On the other hand, increasing compressive strength and hardness are observed by increasing mixing speed. Figure 3 shows morphological comparison between low and high nanoclay contained PU nanocomposite.

**Table 1.** Conditions of Nanocomposite Preparations

| Runs | Nanoclay (phr) | MWCNT (phr) | Mixing Speed (rpm) |
|------|---------------|-------------|-------------------|
| Control | 0             | 0           | 1900              |
| 1     | 1.5           | 0.025       | 1900              |
| 2     | 1.5           | 0.015       | 1300              |
| 3     | 1.5           | 0.025       | 1300              |
| 4     | 1.5           | 0.015       | 1900              |
| 5     | 2.5           | 0.015       | 1300              |
| 6     | 2.5           | 0.015       | 1900              |
| 7     | 2.5           | 0.025       | 1300              |
| 8     | 2.5           | 0.025       | 1900              |

**Table 2.** Resulted Properties of Nanocomposite Samples

| Runs | Density (g.cm\(^{-3}\)) | Reduced Compressive Strength (MPa/g.cm\(^{-3}\)) | Reduced Burning Rate (mm/s.g.cm\(^{-3}\)) | Reduced Fire Retardancy | Reduced Hardness |
|------|--------------------------|-----------------------------------------------|------------------------------------------|-------------------------|-----------------|
| Control | 0.0425         | 3.4471                                        | 93.9675                                  | 0.0106                  | 181.2           |
| 1     | 0.0506         | 4.9743                                        | 76.6239                                  | 0.0131                  | 191.7           |
| 2     | 0.0511         | 4.2701                                        | 77.2153                                  | 0.0130                  | 156.6           |
| 3     | 0.0519         | 5.0000                                        | 71.6525                                  | 0.0140                  | 260.1           |
| 4     | 0.0571         | 4.8284                                        | 64.5955                                  | 0.0155                  | 364.3           |
| 5     | 0.0545         | 3.7009                                        | 65.7061                                  | 0.0152                  | 196.3           |
| 6     | 0.0447         | 3.9508                                        | 65.7061                                  | 0.0117                  | 192.4           |
| 7     | 0.0508         | 3.3720                                        | 79.0860                                  | 0.0126                  | 196.9           |
| 8     | 0.0561         | 3.0143                                        | 78.0077                                  | 0.0128                  | 123.0           |
Figure 1. Main Plot of PU/Nanoclay/MWCNT Nanocomposite for Reduced:
(a) Compressive Strength; (b) Fire Retardancy; (c) Hardness
Figure 2. Interaction Plot of PU/Nanoclay/MWCNT Nanocomposite for Reduced:
(a) Compressive Strength; (b) Fire Retardancy; (c) Hardness
3.1 Compressive Strength and Hardness

Figure 1a shows that reduced compressive strength is less affected by MWCNT and mixing speed probably due to the deficient amount of MWCNT and low mixing speed. On the contrary, nanoclay alter the property. At 1.5 phr nanoclay concentration, the average reduced compressive strength is 4.78 MPa which is 38% higher than the neat PU. This is probably due to the dispersed nanoflakes served as nucleating agent for PU foam that produced small and condense cells [7]. However, the property decreases at higher concentration. At 2.5 phr, only 2% increase is obtained relative to the neat PU. Lower increment at higher concentration is probably due to the agglomeration of nanoflakes that resulted in larger and less populous cells in comparison with the lower one.

Figure 2a also shows the interaction between nanoclay and MWCNT. At low nanoclay concentration, the supplement of MWCNT managed to increase the reduced compressive strength. This is probably due to nanoclay assisted dispersion of MWCNT [17]. However, at higher nanoclay concentration, supplementary of MWCNT further deteriorated the property. Incorporation of agglomerated nanoclay and MWCNT created bigger nanoparticle that served as failure site. Figure 1c shows main effects of nanoclay, MWCNT and mixing speed on hardness. Similar to compressive strength, hardness decreases as nanofillers concentration increases. On the contrary, increasing mixing speed slightly harden PU nanocomposite. Figure 2c shows independency between nanoclay and MWCNT on hardness. However, interaction between nanofillers and mixing speed is observed. At low nanofillers concentration, accelerating mixing speed manage to harden PU nanocomposite. However, at high concentrations, PU nanocomposite is softer in spite of expediting the mixing speed.

3.2 Fire Retardancy

The effects of accretion of nanoclay and MWCNT concentration as well as mixing speed on fire retardancy are shown in Figure 1b and 2b. Figure 1b shows that increasing nanofillers concentrations and mixing speed tended to lower fire retardancy. The average fire retardancy of PU nanocomposite at low nanofillers concentration and mixing speed is 22% higher than the neat PU. While at high states, the average value is decreased 19%. Figure 2b shows less interaction between nanoclay and MWCNT for fire retardancy. However, there is an interaction between nanoclay concentration and mixing speed. At low concentration, rising the mixing speed better dispersed nanoflakes into PU matrix giving a good nucleation on PU foam that resulted in small and packed PU nanocomposite cells [7]. However, at higher concentration and high speed, fire retardancy is decrease due to agglomeration of nanoflakes giving a poor nucleation of PU foam which produced larger and less PU nanocomposite cells in comparison with low concentration one yielding shorter and less burning route.

3.3 Morphology

Figure 3 compares the morphology of low and high nanoclay contained PU nanocomposite. It shows that low nanoclay contained PU nanocomposite has smaller, numerous, more condense and structured cells that resulted in better properties in comparison with the high one.

![Figure 3. SEM of PU/Nanoclay/MWCNT Nanocomposite Cell; (a) Nanoclay 1.5 phr ; (b) Nanoclay 2.5 phr](image-url)
4. Conclusion

Rigid PU/nanoclay/MWCNT nanocomposite was fabricated successfully via solution mixing of the monomers, nanoclay and MWCNT. The effects of variables on physical and morphological properties were measured. Overall improvements on compressive strength, fire retardancy and hardness compared with neat PU were obtained. The dispersion of nanofillers especially nanoclay that served as nucleating agent for PU matrix yielding small, compact and structured cells was responsible for positive effects on the properties at low nanoclay concentration. However, the agglomeration of nanoclay at high concentration generating larger, less condense and poor structured cells declined the properties compared with the low one.

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