A short review on polyurethane-based nanocomposites for various applications

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Abstract. In recent years, polyurethane (PU) has attracted researchers’ attention due to their easily tailored properties to meet specific application requirements. PU and PU-based composites are being developed to be applied in various demanding fields such as aerospace, automotive, and electronics. This is because PU-based nanocomposites have numerous types of functional nanofiller integration. This has led to the advancement of polymer nanocomposite of PU with the inclusion of nanosised fillers for various specific purposes. In this short review article, the authors have reviewed the fundamental or basic understanding of PU and several types of nanofillers used such as clay, carbon nanotubes, and graphene for PU-based nanocomposites development, as well as its potential applications.

1 Polyurethane (PU) and its potential applications

Polyurethane (PU) is accessible in both thermoset and thermoplastic form. Historically, Otto Von Bayer and his co-workers discovered PU in 1937. Then, commercial PU was first developed at the beginning of World War II (WWII) as a replacement for rubber [1]. PU belongs to a block copolymer which contains low molecular weight of polyester or polyether segment that is covalently attached to urethane the group (-NH- C (=O) –O-).

Polyester-based polyurethanes is more biodegradable than polyether-based PU [2]. These polymers are synthesised by step-growth polymerisation through the reaction with three basic components which are isocyanate, polyol, and low molecular weight of chain extenders [3]. Fig. 1. shows the reaction occurred between the polyols and isocyanate in a standard PU synthesis. The properties of the PU end product depend on the composition of isocyanate and polyol. The PU structure may consists of a hard and soft segment which can organised alternately as shown in Fig. 2. The hard segment is generally formed by the isocyanate which resulted in the rigid and fragile properties of PU, while the soft segment is formed by the polyols group which characterised the flexible polymer chain. Whether it is

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an aromatic, cyclic or aliphatic compound, the reactivity of the isocyanate differs [4]. Aromatic isocyanate is more reactive than aliphatic isocyanate [5] because aliphatic isocyanate does not have enough reactivity for foam application but could be used for other urethane application such as coating [6]. Diphenylmethane diisocyanates (MDI) and toluene diisocyanates (TDI) are the commonly used aromatic isocyanate in rigid PU production [5]. Rigid PU is obtained from low molecular weight polyols which have a few hundred units, while flexible PU are produced from high molecular weight polyols which possessed more than 10,000 units [6]. Table 1 summarised the physical form of PU foam using different types of isocyanate and polyol. The types of polyols used to manufacture polyurethane are polyester and polyether. Polyol is a monomer which contain two or more hydroxyl groups in their structure for an organic reaction [4].

It was found that the selection of isocyanate crucially influenced the end properties of PU. This situation may possibly open a very wide opportunity to design PU for various specific applications. Other than manipulating the use of isocyanate that are basically toxic, nowadays to design green PU, researchers have started to employ composite strategy. One of the method to design green PU with composite are by using Design of Experiment (DOE) [7] and Taguchi [8,9]. The following section summarised the effort to produce PU-based nanocomposite by utilising various types of nanofillers for various possible applications.

![Formation of PU linkage pathway](image)

**Fig. 1.** Formation of PU linkage pathway [10].

![Cross-linked PU elastomer](image)

**Fig. 2.** Cross-linked PU elastomer [11].
Table 1. Comparison of different type of isocyanate and polyols for PU production.

| Types of polyol                                      | Isocyanate                                      | Physical form | Reference |
|------------------------------------------------------|-------------------------------------------------|---------------|-----------|
| Recycled PU                                          | Polymeric methylene-diphenyl disocyanate (PMDI) | Flexible      | [12]      |
| Waste Cooking Oil (WCO) and post-consumer polyethylene terephthalate (PET) | Polymeric methylene-diphenyl disocyanate (PMDI) | Rigid         | [13]      |
| Copolymerization of carbon dioxide                   | Diphenyl-methane disocyanate (MDI)              | Flexible      | [14]      |
| Rapeseed oil-based polyl                            | Polymeric methylene-diphenyl disocyanate (PMDI) | Rigid         | [15]      |
| Soybean oil-based polyl                             | Toluene disocyanate (TDI)                       | Flexible      | [16]      |

PU can be classified into several categories based on their desired properties and mechanical performances as summarised in Fig. 3. For instance, due to its remarkable mechanical properties and low density, rigid PU is widely used for domestic appliances and building insulation [17]. Other applications of PU involved building and construction, automotive, marine, coating, medical, apparel, wood composites, packaging and appliances [18]. The next section specifically summarised the PU-based nanocomposites and its potential application.

![Fig. 3. Types of PU and their example application [3, 12, 14, 15, 19].](image)

2 PU-based nanocomposites and its application

Nanocomposites possessed dimensions of at least one solid phase and are in nanometer size range (1-100 nm) [20]. According to M. Bhattacharya [21], nanoparticles plays an important role as reinforcing fillers in the polymer matrix. Thus, the nanofiller should have (i) outstanding mechanical properties in terms of strength and Young’s modulus, (ii) high
surface area and high aspect ratio to interact with the polymer, (iii) and should dispersed well to avoid agglomeration.

Nanoscale fillers that are utilised in PU-based nanocomposites have superior properties over conventional composites in terms of electrical, thermal, and chemical properties [22]. Table 2 shows some examples of nanofillers, previously used in the PU matrix. Common carbon-based nanomaterials used are carbon nanotubes (CNTs) [23] which consists of single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) [24], nanoclay [25] such as montmorillonite, nanosilica [26] and bentonite [27], carbon nanofibers (CNFs) [28], and graphene [29]. They can be divided according to their dimension; one dimension such as nanotubes and nanowires [30, 31], two dimension such as graphene [32] and clays such as montmorillonite [33]. Graphene and nanotubes possessed excellent properties due to their high aspect ratio and high mechanical strength [23]. To further enhance the performance of PU-based nanocomposites, several effective chemical functionalisation strategies were performed. This resulted in excellent mechanical properties but destructive to electrical properties due to harsh treatment of carbon nanofiller surfaces [22].

The existence of nanoscale filler has intrinsically provide nanocomposites with unique properties and superior characteristics compared to conventional composites. Cell morphology improvement enhances the thermo mechanical properties of nanocomposites. Numerous nanoparticles were added to PU foams to improve thermal properties, heat distortion temperature, mechanical properties, foaming behaviour, barrier properties, biodegradation, electrical conductivity, and crystallisation kinetics such as nanoclay, nanosilica, graphene, and CNTs [34]. Physical and mechanical properties of carbon-based nanoparticles are relatively high and have the potential to increase material performances [35].

**Table 2.** Example of nanofiller used in PU matrix.

| Matrix         | Nanofiller                  | Particle size | Dispersion technique | Response                                                                 | Reference |
|----------------|-----------------------------|---------------|----------------------|--------------------------------------------------------------------------|-----------|
| PU             | rod-shaped CNFs             | 0.20 µm       | sonication           | high strength, stiffness, thermal degradation                             | [19]      |
| PU             | Bentonite Cloisite® Na⁺ (MNa) | 88 nm         | waterborne dispersion | efficient as gas barrier                                                 | [27]      |
| Shape-memory PU (s-PU) | graphene nanosheets (flake form) | 10 µm          | magnetic stirrer     | electrical conductivity increase, mechanical and shape memory improved | [28]      |
| Rigid PU (r-PU) | montmorillonite nanoclay (NCL) | 50 nm          | homogenizer          | Flame retardancy increase                                                 | [36]      |
| PU             | MWCNTs                      | 5–20 nm       | solution casting     | CNTs loadings dépendances                                                 | [37]      |

PU-based nanocomposites are used in various applications due to their versatile properties such as aerospace [38] and automotive industry, radar absorbing and EMI shielding, fire proof material, shape memory appliances, PU foam sensor [39], and biomedical [40]. Due to the versatility of PU-based nanocomposites and the ability for us to modify its properties, there are various possible demanding applications that could be actualised as shown in Fig. 4.
Bahrami et al. (2019) [42] used graphene as the nanofiller for tissue engineering application including cardiac patch development and spinal cord injury treatment in which the main factor of the product’s success is the scaffold conductivity. In this study, they discovered that the electroconductivity of the material increased significantly after using 2% of graphene concentration with electrospun mats. The results showed that the electrospinning technique distributed better compared to the solvent casting of graphene into the PU matrix.

On the other hand, Awad et al. (2018) [43] discovered that the most efficient solar thermal converter of water desalination is Plasmonic Graphene Polyurethane (PGPU) nanocomposite using 0.2 wt% Au and Ag nanoparticles. The solar thermal performance of Au/Ag-PGPU foams increased by 63%, 88%, and 96.5% under 1, 5 and 8 sun illumination where the water evaporation average rates were 1.00, 6.59, and 11.34 kg m⁻² h⁻¹ respectively. The results also showed that after the evaporation cycles were repeated 10 times, the PGPU foams displayed very stable evaporation rates without any failure. It can be concluded that PGPU nanocomposites is the best method for seawater desalination and solar-steam generation as they have a very high thermal evaporation efficiency, longer durability, and high solar thermal evaporation efficiency.

3 Conclusions

Overall, PU properties could be modified by manipulating the composite development strategy. Due to this factor, the utilisation of PU based composites could be diversified in accordance to specific applications based on the performance requirement. Various potential fillers can be used for this purpose. However, carbon-based nanofillers are highly preferable since they could offers outstanding improvements to PU-based nanocomposites likes enhancing mechanical, physical, and electrical properties. Hence, from this short review, it can be said that the future exploration for PU based nanocomposites are promising.

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