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A B S T R A C T

Components such sensors, aerospace, heat exchanger, armour, storage, automobile and other electronics devices are continuously subjected to fluctuating thermal and mechanical stresses which consequently affect their performance, reliability and lifespan. Aerospace industry, for instance, is also in constant quest for weight reduction to attain fuel efficiency in terms of cost. It is because of these factors that engineering polymers are gaining research prominence in heat management systems, where simultaneous high strength and thermal property with significant low weight are crucial. Meanwhile, montmorillonite and carbon nanotubes are mostly used as reinforcing particles to improve physico-chemical, mechanical and thermal properties of thermoplastic matrices. This review discusses the thermoplastics-based nanocomposites reinforced with the hybrid of montmorillonite and carbon nanotubes, for high-performance applications. Influence of the nanoclay on carbon nanotube dispersion and vice versa were revealed and discussed, while used duo as hybrid in thermoplastic matrices. Consequent interaction of the hybrid nanoparticles within the host matrix influences the bulk properties of nanocomposite: Rheology, morphology, thermal stability, flame retardancy, electrical, mechanical as well as tribology. The hybrid nanofillers synergy favours efficient dispersion without destroying nanoparticles structures, leading to optimized percolation threshold and better properties of the ternary nanocomposites. Prominently, the dependency of bulk properties on nanocomposite morphological characteristics is recognised.

Keywords: Montmorillonite; thermoplastic; hybrid nanocomposite; synergy; morphology; high-performance

1. Introduction

As at year 2013, engineering plastics has already recorded a market share of more than 19.6 million-metric-ton and forecasted to hit more than 29 million-metric-ton by 2020 (Das et al., 2018). Three decades back, (McCrum et al., 1988) gave two reasons for the unending and the continuous expansion to the use of polymers in Engineering: their robust properties (lightness, toughness, chemical and corrosion resistance); and versatility combined with the speed of shaping operations (Arrigo et al., 2018; Nayak, 2019) at which the raw polymers (and other additives) are transformed to functional hardware products. This is currently witnessed in terms of their applications in aerospace (Kausar et al., 2017; Pitchan et al., 2017), packaging, automobile (Shirvanimoghaddam et al., 2018), defence (Kurahatti et al., 2010; Liu et al., 2016; Venkategowda et al., 2018), anti-corrosion (Kumar et al., 2018), marine, sports, vibration control (Geng et al., 2012), piezoelectric sensor (Hosseini and Yousefi, 2017a) and numerous thermomechanical applications (Shabanian et al., 2016; Yuan et al., 2018).

Polymeric nanoparticle-filled composites are currently receiving tremendous attention as they are promising engineering materials with varying properties enhancement courtesy of the various nanoparticles incorporated into the polymer matrix (Mohammed, 2014; Cicco et al., 2017; Klonos and Pissis, 2017; Yuan et al., 2018; Nayak, 2019). The nanoscale particles have exceptional high aspect ratio (surface to volume ratio) that provides the needed engineering features required from polymeric composites (Yue et al., 2014; Klonos and Pissis, 2017). The properties impacted on polymers by these nanofillers focus directly on strengthening mechanical, electrical, optical and thermal behaviours as well as barrier features to temperature and fluids (Marquis et al., 2011; Yuan et al., 2017; Kumar et al., 2018). For few decades back, nanofillers include diatomite, carbon black and pyrogenic silica have been used in polymers as additives without understanding their real influence (Marquis

et al., 2011). However, the work of (Usuki et al., 1993) from Toyota Research and Development Group brought limelight and definite roles of nanoclays (typical nanofiller) in polymeric polyamide-6 matrix. Multi-walled carbon nanotubes (CNT), graphene (G), graphene oxide (GO), carbon nanoribbon, nanoclays including halloysite nanotubes (Chiu, 2016, 2017a; Raee and Kaffashi, 2018; Ren et al., 2018; Zhu et al., 2018; Aguzzi et al., 2019), make the recent list of commonly used nanofillers (Marquis et al., 2011; Nayak, 2019).

Therefore, researchers and industries are in constant quest of designing cost-effective, multipurpose and robust nanocomposite system for advanced material applications, especially the primary thermomechanical systems: aerospace, automobile, sensors, conductors, petroleum processing facilities (Kausar et al., 2017). For instance, aircraft industry requires low weight nanocomposites for fuel efficiency without jeopardizing strength, stiffness, thermal conductivity, impact and corrosion resistance as the system is continuously exposed to fluctuating harsh environment (Anbusagar et al., 2018). Moreover, polymer applications in modern thermal and high energy-related fields (electronics, storage and energy transportation, medicines) emphasis great attention to fire safety. This is a subset of heat management that is crucial in improving/securing the service life of a system as well as reduction of hazards by quick transfer of generated heat, which ensures maintenance of practically low temperature on the course of operational service (Chen et al., 2016; Xiao et al., 2016).

Nanoclay, a two-dimensional (2D) nanofiller, has been fused into polymer matrices with due mechanical, barrier and fire retardancy properties improvement. Clay platelet structure affords it the formation of protective barrier, once high degree of exfoliation with good dispersion is attained, leading to improved polymer physical performances. At this condition, low loading of clay is required. Clay's high rich intercalation chemistry affords it easy chemical modification and compatibility with polymers. Besides, it can be gotten

uncontaminated as mineral with little cost (Santangelo et al., 2011). Similarly, one-dimensional (1D) carbon nanotubes (CNT) continues to impact an exceedingly high electrical (Fang et al., 2019), flame retardancy (Lee et al., 2019), mechanical and thermal properties when incorporated in polymers (Khan et al., 2018; Abidin et al., 2019). The superior aspect ratio, lightweight and thermal conductivity of 2000-6000 $Wm^{-1}K^{-1}$ (Cao et al., 2019) give CNT its uniqueness.

In an attempt towards achieving the polymeric nanocomposite high-performance goal, hybrid/combination of these two dissimilar but distinctive nanofillers is being introduced into polymer matrix to produce ternary nanocomposites. Optimal electrical and thermal conductivities, lowered flammability, high barrier system, corrosion inhibition while improving the mechanical properties are targeted (Kumar et al., 2018; Zhou et al., 2018). Hence, the review provides up-to-date information on high-performance nanocomposites developed strictly with incorporation of hybrid of montmorillonite (nanoclay) and carbon nanotubes in thermoplastic matrices. The influence of the nanoclay on carbon nanotubes and vice versa was discussed. Consequent interaction of the hybrid nanoparticles in nanocomposite was analysed on each of the bulk properties of the nanocomposite such as rheology, morphology, thermal and flame retardancy, electrical and mechanical properties. Finally, a summary of the review and other perspectives were presented.

2. The need for hybrid of nanofillers

Nanofiller roles in the mitigation of the deficiencies of polymers give rise to more novel academia researches and subsequent progressive industrial demands for the composite of thermoplastics, thermosets and elastomers (Marquis et al., 2011; Arrigo et al., 2018; Boumbimba et al., 2018; Aydoğan and Usta, 2019). A little percent of nanofillers significantly changes the physicochemical, thermal, mechanical, optical, magnetic and

electrical properties of the hosting matrix (Papageorgiou et al., 2017a; López-Barroso et al., 2018).

Sizable number of researchers (Bray et al., 2013; Moghri et al., 2015; Kim et al., 2015; Bischoff et al., 2017; Ramazanov et al., 2018; Yuan et al., 2018; Radmanesh et al., 2019) have worked on the benefits of incorporating a single nanoparticle type into selected polymeric matrix (homopolymer, copolymers or mixed polymers), especially in the areas of attaining well dispersed nanofillers for toughening or improving polymeric nanocomposite. However, efficient and effective dispersion without agglomeration of the nanofillers in a polymer remains a challenge (Papageorgiou et al., 2017a; Pitchan et al., 2017; López-Barroso et al., 2018). Another impediment is the incompatibility of the constituent materials (Prashantha et al., 2014).

Meanwhile, nanocomposites property enhancement is directly related to the interfacial bonding formation that exists between the reinforcement phase and the matrix (Shirvanimoghaddam et al., 2017). Researchers in their varying efforts of proffering solutions resorted to the use of chemicals (either to modify the filler or as dispersing agent) (Navidfar et al., 2017), which are usually expensive, environmentally demeaning and sometime detrimental to the structure and surface of the nanofiller and/or lowering the properties expected from the bulk nanocomposite (Marquis et al., 2011; Tjong, 2014; Szeluga et al., 2015; Punetha et al., 2017). Other means of realizing an efficient dispersion is through high shear rate, which de-agglomerates the clustered nanofiller particles, and prevents further agglomeration resulted from van der Waals forces of interaction. However, high shear can cause breakage of some CNT or nanofibres particles (Levchenko et al., 2011). Moreover, conductive polymer composite (CPC) is gaining high relevance in the electromagnetic interference (EMI) shielding and carbon-material reinforced CPC is popular in this field. EMI is usually protected by reflection and absorption processes. However, single carbon-

144 reinforced CPC releases secondary EMI pollution because, in this case, the conductivity
145 stems from reflection (Zhao et al., 2018).

146 Hybridization of nanofillers in a matrix provides safe and effective means of ensuring
147 dispersability of certain nanofiller using other nanofiller (Levchenko et al., 2011; Szeluga et
148 al., 2015; Papageorgiou et al., 2017a). Combination of nanofillers could bring about
149 synergistic effects between nanoparticles (Nurul and Mariatti, 2013), offset deficiency in any
150 of the fillers as well as improving and/or aiding dispersion and interaction of the fillers within
151 the polymeric matrix (Safdari and Al-Haik, 2013; Papageorgiou et al., 2017a). Ultimately,
152 benefits of the constituents' fillers are brought together in creating advanced, cost-effective
153 (Pandey et al., 2014; Szeluga et al., 2015) and innovative materials.

154 *2.1. Hybrid fillers in ternary nanocomposites*

155 Hybrid nanocomposite is a system of material that involves the combination of two or
156 more different nanofillers in a single or multiphase polymer matrix with the purpose of
157 achieving better material properties. Hybrid nanocomposite is pivoted on three rules: (1)
158 economic effect by which expensive nanofiller can be combined with less expensive filler;
159 (2) achieving a combined functional and properties enhancement; and (3) efficient
160 preparation method (hybrid effect) (Jaafar, 2017).

161 Researchers used various combinations of fillers in different polymer matrices to achieve
162 properties improvements. Zhao et al. (2018) used both 7 wt% (CNT and Nickel (Ni)) and 13
163 wt% (graphene (G) and Ni) in enhancing heat dissipation for electromagnetic shield. Zhou et
164 al. (2018) recorded over 126% enhancement in thermal conductivity on incorporating 20 wt%
165 of GO and CNT in poly (methyl methacrylate) (PMMA). Edenharter et al. (2016) used a total
166 of 5.5 wt% (GO and layered double hydroxide (LDH)) to realize 47% reduction in peak of
167 heat release rate (PHRR). Xiao et al. (2016) attained 602% in thermal enhancement at hybrid

filler load of 22 wt% (G and CNT). With optimum combined nanofillers (ZnO and CNT) of 40.5 wt% in poly (butyl methacrylate), Han et al. (2016) reported high thermal stability of the ternary composite with improved tensile strength (42%), elastic modulus (19%) and hardness. Shao et al. (2016) also employed 8.4 wt% (boron nitride (BN) and G) in achieving 350% thermal conductivity improvement. Oliveira et al. (2016) used polyetherimide and CNT doped with sodium alanate ($NaAlH_4$) for hydrogen storage.

Sa et al. (2018) added only 0.8 wt% of CNT and G; and Chatterjee et al. (2012) used 0.5 wt% of G and CNT nanofillers to achieve prime mechanical property. Kumar et al. (2010) reported an enhanced thermomechanical properties with just 0.5 wt% of CNT and G. Yang et al. (2011) developed CNT/G/epoxy nanocomposite filled with hybrid of 0.9 wt% G and 0.1 wt% CNT. They reported improvement of 35.4, 27 and 146% in tensile strength, Young modulus and thermal conductivity, respectively. Prasad et al. (2009) used 0.6 wt% total loading CNT and nanodiamond in achieving more than 400% stiffness and hardness boost.

From these cited works, carbon-based nanofillers, most especially carbon nanotubes, seem to be consistently used in polymer nanocomposite. CNT is unequal in impacting high mechanical, electrical and thermal properties in polymers (El Rhazi et al., 2018; Li et al., 2018), at comparatively low loading, due to its high aspect ratio leading to its unique capacity in formation of interconnectivity. Yet, combination of nanomaterials at high loading (7-47 wt%), which might favour some features (e.g. electromagnetic shielding and flame retarding) (Pan et al., 2014), significantly hamper mechanical properties, processability and hike cost (Alshammari and Wilkinson, 2016; Edenharter et al., 2016).

Again, all the excellent features of CNT are worthless in isolation because the high aspect ratio and inter-tubular van der Waals forces keep the CNT nanoparticles together as large clusters (Punetha et al., 2017). Secondly, the solubility of CNT in most organic solvents is exceptionally challenging (Vyas and Chandra, 2018). Szeluga et al. (2015) emphatically

193 stated in their review that the main problem with CNT is cost and quantity of production for
194 industrial applications. This is in agreement with (Roes et al., 2007; Almasri et al., 2018).
195 Other effective carbon-based nanofillers, like graphene and graphene oxide (GO), have
196 similar associated challenges (Punetha et al., 2017). These are some of the reasons that
197 prompted and necessitated the research for hybridizing CNT with other nanofillers.

198 Similar to carbon-based nanofiller, application of small amount of layered clay, like
199 montmorillonite (Mt), gives superior properties impact than larger percent of traditional
200 fillers (e.g. glass fibre, calcium carbonate) (Aït Hocine et al., 2008; Prashantha et al., 2014;
201 Raji et al., 2018) in the enhancement of the hosting matrix (Raji et al., 2016; Rahmaoui et al.,
202 2017). Low loading of clay nanofiller attracts improved barrier performance, easier
203 processability and provide excellent surface appearance (Prashantha et al., 2014). Shabanian
204 et al. (2016) combined Mt and hydrogel in achieving high thermal and mechanical properties
205 simultaneously. Clay has also been effectively used in enhancing tribological property
206 (Golgoon et al., 2015; Azam and Samad, 2018a; Wani et al., 2018). Kausar (2016) used
207 combination of nanogold (Au) and Mt to reinforce polyamide in developing flame retardant
208 composite. There are reports on non-conducting nanoclays aiding CNT's dispersion and
209 assisting in creating volume exclusion (conductive nanoparticles free zone) inside polymeric
210 matrix and consequently led to a reduced percolation threshold (Liu and Grunlan, 2007; Wu
211 et al., 2012; Al-Saleh, 2017; Paszkiewicz et al., 2017). More importantly, apart from being
212 the most reported nanofiller, nanoclay is economically and industrially viable for use as nano-
213 reinforcement in polymeric matrices (Ahamed et al., 2016; Surendran et al., 2018).

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216

2.2. Carbon nanotube and nanoclay

2.2.1. Structure and properties of carbon nanotubes

Carbon nanotubes (CNT) exhibit unique mechanical, thermal, electric conductivity, electromagnetic interference properties (Zhang et al., 2018) that are impacted onto its hosting polymer matrix. CNT has a ring structure featuring strong bond that is made up of C-C covalent type. This gives CNT its exceptional physical properties but resulted into low affinity to chemical reactions that makes it difficult to interact with other nanofillers as well as polymer matrix molecules (Punetha et al., 2017). Consequently, CNT most often requires surface modifications in enhancing its physicochemical interactions with other molecules and improve its processability (Shirvanimoghaddam et al., 2017). High interfacial relations within polymer nanocomposite brings about effective stress transfer to improve physical, thermal, mechanical, electrical or multifunctional features (Papageorgiou et al., 2017b; Avilés et al., 2018). There are two forms of functionalization, covalent and non-covalent, to get better orientation and improved bonding with matrix (Shirvanimoghaddam et al., 2017, 2018). CNT are available as single, double and multi-walled carbon nanotubes obtained through rolling up of a single or multiple of graphene along its axis. CNT can be produced by arc discharge, laser vaporization, chemical vapour deposition (Manikandan et al., 2013; Safdari and Al-haik, 2018). CNT reported in this review is strictly restricted to multi-walled nanotubes

2.2.2. Structure and properties of montmorillonite nanoclay

Generally, all nanoclays have the same structural description but are distinguished by their hydroxyl bond relations, positions and interlayer water numbers in each of the clay (Ray and Okamoto, 2003; Raji et al., 2018). They possess two outer tetrahedral ($[SiO_4]^{4-}$) plates coordinated by silicon atoms and sandwiched on an inner octahedral ($[AlO_3(OH)_3]^{6-}$) plane, i.e., 2:1 phyllosilicate layered silicate mineral (Barick and Tripathy, 2011). For engineering

polymers, montmorillonite (Mt) is crucial and the most reported for polymer nanocomposite preparation because of its unique interfacial reactivity and high specific surface area (Seghar et al., 2011; Bunekar et al., 2018). Mt is a natural phyllosilicate from bentonite and has raw chemical formulae $(Na, Ca)_{0,3}(Al, Mg)_2Si_4O_{10}(OH)_2$, nH_2O (Marquis et al., 2011).

The presence of the compensating charge cations and the polar molecule on the gallery basal planar makes the nanoclay to display the hydrophilic properties, and determines the interlayer space of an expansible clay mineral (Raji et al., 2016). The expansion of the interlayer space with respect to non-expansible clay affords better cation exchange capacity (CEC). Mt has high CEC (Almasri et al., 2018) which is an advantage over other clays. The hydrophilic nature makes clay difficult to be dispersed in polymer and the challenge is addressed through replacement of the interlayer cations by quarternized phosphonium or ammonium cations (Ray and Okamoto, 2003) and sol-gel technique (Bunekar et al., 2018). In short, the interlayer d-value needs to be enlarged in order to allow the penetration of the polymer molecules and/or other nanofiller into clay platelets (Fig. 1).

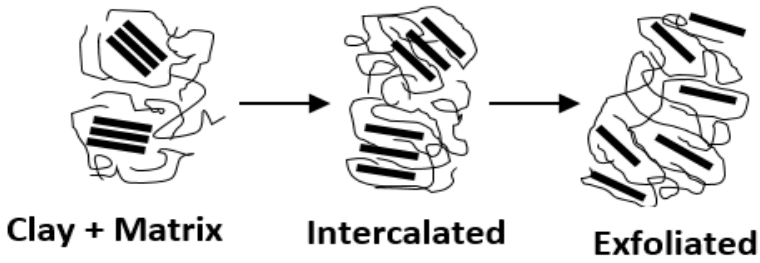

Fig. 1. Three phases of layered clay in polymer matrix

2.2.3. Prepared Mt-CNT hybrid nanofiller

Aside physical addition of Mt and CNT into a matrix as regards to this review, the use of Mt-CNT hybrid filler, prepared by growing CNT over Mt via catalytic chemical vapour deposition (CCVD) (Fig. 2) that aids homogenous dispersion within polymer (Manikandan et al., 2013), is also cited. Details on CCVD process can be accessed in (Madaleno et al., 2012).

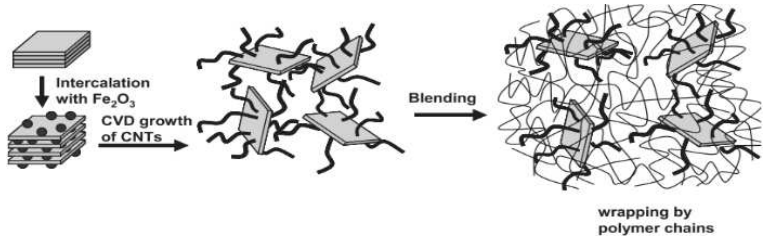

Fig. 2. Route of growing CNT on Mt and blending with polymer (Zhang et al., 2006)

3. Preparation techniques of ternary nanocomposites

Polymer nanocomposite properties are dependent on the processing technique adopted for its production and ultimately dispersion of the nano-reinforcements in terms of effective distribution and exfoliation in the matrix (Zaferani, 2018). Besides the conventional melt blending, solution blending and in-situ polymerization, electrospinning and high-energy ball-milling were recently reported. Table 1 lists the reviewed thermoplastics polymers specifically filled with hybrid of CNT and clay (Mt) for high-performance applications.

Table 1

Summary of thermoplastics polymer filled with hybrid of CNT and Mt.

Matrix	Optimum filler concentration (wt%)			Dispersion Technique	Focused Application	Reference
	CNT	Mt	CNT/Mt**			
ABS	1	1		Melt-mixing	Flame retardant	Ma et al. (2007)
EVA	1	3		Melt-mixing	Thermo-mechanical	Peeterbroeck et al. (2004)
EVA	2.5	2.5		Melt-mixing	Flame retardant cable	Beyer (2005)
EVA	2.5[$]	2.5[$]		Melt-mixing	Flame retardant cable	Beyer (2006)
Nafion			2	Solution-mixing	Fuel cell	Manikandan et al. (2012)
HDPE	1	1		Solution- and melt-mixing	Thermo-mechanical	Silva et al. (2014)
HDPE	0.6	0.4		Melt-mixing	Flame retardant	Rao et al. (2015)
UHMWPE	1.5	1.5		Solution-mixing	Tribology	Azam and Samad (2018b)
PA-6			1	Melt-mixing	Mechanical	Zhang et al. (2006)
PCL			0.5	Melt-mixing	Thermo-mechanical	Terzopoulou et al. (2016)
PET			3	Melt-mixing	Thermo-mechanical	Gorrasi et al. (2014)

PLA			3	Centrifugal ball milling	Sorptive and electrical	Santangelo et al. (2011)
PLA			3	Melt-mixing	Irradiation	Gorrasi et al. (2013)
PLA	2	10[£]		Melt-mixing	Flame retardant	Hapuarachchi and Peijs (2010)
PP	NS	3		Melt-mixing	Mechanical	Olalekan et al. (2010)
PP	0.5*	0.5*		Melt-mixing	Electrical conductor	Levchenko et al. (2011)
PP	1	1		Melt-mixing	Mechanical	Prashantha et al. 2014)
PP	0.3	3		Melt-mixing	Thermal and flame retardant	Pandey et al. (2014)
PP	0.5	0.5		Melt-mixing	Electrical and thermo-mechanical	Al-Saleh (2017)
PS-b-PI-b-PS			1	Solution-mixing	Mechanical	Enotiadis et al. (2013)
PU			0.25	In-situ polymerization	Polymer foam	Madaleno et al. (2013)
PVA			3	Solution-casting	Thermo-mechanical	Zhao et al. (2009)
PVB	0.2	2		Solution-mixing	Impact resistance	Stern et al. (2018)
PVDF	1.9	3		Melt-mixing	Vibration	Geng et al. (2012)
PVDF	0.5	0.5		Melt-mixing	Electrical and thermo-mechanical	Chiu (2014)
PVDF	0.5	1		Melt-mixing	Charge storage	Khajehpour et al. (2014)
PVDF	0.05	0.1		Electrospinning	Piezoelectric	Hosseini and Yousefi (2017b)
PVDF	0.05	0.1		Electrospinning	Sensor Piezoelectric	Hosseini and Yousefi (2017a)

*%volume; [$]part per resin

[£]sepiolite nanoclay; NS not stated

**Hybrid CNT/clay produced via CCVD. ABS-acrylonitrile-butadiene-styrene ; EVA-ethylene-vinyl acetate; HDPE-high-density polyethylene; PA-polyamide; PP-polypropylene; PET-poly(ethylene terephthalate); PLA-polylactide; PS-b-PI-b-PS-polystyrene-b-poly(isoprene)-b-polystyrene; PU-polyurethane; PVA-polyvinyl alcohol; PVB-polyvinyl butyral; PVDF-polyvinylidene fluoride; PCL-poly(ε-caprolactone); UHMWPE-ultra-high molecular weight polyethylene.

3.1. Melt-mixed nanocomposites

Melt mixing is a process of applying both high temperature and shear force in order to prepare nanocomposites with well-dispersed nano-reinforcement. It is highly popular for industrial/academic research and development as it supports various forms of polymer that are not suitable for other methods. It requires no solvent/chemical, supports high volume of bulk polymer and it's low cost with the least environmental issues (Bunekar et al., 2018). With regards to the thermoplastics reinforced with hybrid CNT/Mt, many researchers (Zhang et al., 2006; Hapuarachchi and Peijs, 2010; Olalekan et al., 2010; Levchenko et al., 2011;

Geng et al., 2012; Chiu, 2014; Khajehpour et al., 2014; Pandey et al., 2014; Prashantha et al., 2014; Terzopoulou et al., 2016; Al-Saleh, 2017) have reported properties enhancement with melt-mixing method. Few of the works that draw substantial attention are discussed below.

Peeterbroeck et al. (2004) employed melt-blending approach in developing a ternary nanocomposite using CNT and organo-modified Mt in EVA. In the binary system of EVA/Mt, degradation temperature was delayed by 52˚C while EVA/CNT composite had only 37˚C delay. On incorporating hybrid of 3 wt% Mt and 1 wt% CNT nanofillers into the EVA, 56˚C highest delay was reported. The flammability behaviour was also studied by comparing binary systems (each filled with 4.8 wt% Mt or CNT) and the ternary having the same combined nanofillers loading. All recorded enhanced flame retardancy but ternary EVA/CNT/Mt (CNT:clay; 2.4:2.4) recorded the highest PHRR reduction of 36% with an accompanying lessening of Mt detrimental effect on time to ignition which improved from 67 s (Mt/EVA) to 71 s. The ternary supremacy was associated with formation of synergistic uniform crust by Mt/CNT over the burning composite that limited the heat and gas diffusion, and consequently lessened its flammability. Well-dispersed clay platelets, in the presence of CNTs, was reported thus aided the barrier effects.

Ma et al. (2007) prepared the hybrid of organoclay and CNT via melt mixing in enhancing ABS flame retardancy. In studying the influence of CNT on clay, morphological state of dispersion of the clay in the composites were analyzed, using X-ray diffraction, in both ABS/2clay (loaded with 2 wt% clay) and ABS/1clay/1CNT (1 wt% clay; 1 wt% CNT). They achieved 3.77 nm interlayer space of the clay in ternary ABS/1clay/1CNT against 3.67 and 1.92 nm for binary ABS/2clay and ordinary clay particle respectively. This meant that clay in the ternary attained better exfoliation in the presence of CNT. They also assessed and compared the distribution of filler(s) in both binary and the hybrid-filled ABS. The reported transmission electron microscopy (TEM) affirmed that binary systems prepared with clay,

ABS/2Mt, produced composite with insignificant clay exfoliation; and ABS/2CNT with more CNT aggregations within matrix. However, the ternary system revealed CNT intercalated into the Mt interlayer spaces, which produced good interaction between the fillers and matrix structures, and CNT was able to form structured network with the clay platelets. Hence, the superiority of ternary fire retardancy over binary ones.

In determining the susceptibility of the residual ash to further heating, they calculated graphitization degree. Ternary ABS/1clay/1CNT reportedly produced ash with higher graphitization than ABS/2CNT, which asserted lower vulnerability of the ternary residual ash to further thermal oxidation on prolonged exposure. They also performed rheological characterizations to further probe into the establishment of 3D network structure by the hybrid fillers, with respect to the single-filled composites. In relation to both storage and loss moduli, the ABS/1clay/1CNT recorded highest values followed by ABS/2CNT and ABS/2clay, while ABS matrix had the least property. They explained the behaviour from nanomaterials' dimensional perspective that the incorporation of high aspect ratio 1D nanotube and 2D nanoclay formed an efficient confined space and created a 3D structure that restricted polymer chains movement. Consequently, enhanced the rheological and flame retardancy characteristics of hybrid-filled nanocomposite over individual nanofiller inclusion.

By comparing the processing behaviour of ternary CNT/clay/PP and binary CNT/PP during melt-mixing, Al-Saleh (2017) was able to substantiate reduction in the amount of CNT required for the ternary CNT/clay/PP to attain percolation threshold concentration compared to binary CNT/PP with the same 1 wt% CNT loading. Every two seconds, he monitored the mixing-torque of the nanocomposite against time. It was found that the mixing torque of the binary with only 1 wt% CNT loading was higher than that of ternary system with 1 wt% CNT and 1 wt% clay loading. He concluded that the additional incorporated clay in the ternary

served as plasticizers and lowered viscosity, which promoted a reduced shear on the CNT particles. Meanwhile, increase of mixing energy/torque is said to degrade CNT particles.

3.2. Solution-mixed nanocomposites

Solution mixing method gives effective nanofiller dispersion and it involves three main steps: introduction and dispersion of nanofiller(s) into a suitable solvent, mixing with the parent matrix (magnetic, heating, sonication), and drying of the material. Few challenges are inherent with this method: cost and environmental issues linked with chemicals, and the use of ultrasound in aiding polymer solution mixing that may result in reduction of polymer molar mass (Isitman and Kaynak, 2010). Zhao et al. (2009), Manikandan et al. (2012), Azam and Samad (2018b) reported high properties enhancement by adopting this approach in incorporating CNT-Mt hybrid, while Stern et al. (2018) is discoursed for its discovery.

Stern et al. (2018) used the hybrid of Mt and CNT to produce PVB-based nanocomposite through solution mixing. In aiding filler(s) dispersion, they applied and varied sonication power (100 W, 700 W), and then studied the effect on morphological and mechanical properties. They reported better dispersions of CNT, clay or hybrid of the fillers in PVB at higher sonication power. Fracture toughness of both hybrid and single-filled matrices affirmed this. At 700 W, ternary PVB/CNT-0.2/nanoclay-2 recorded 176% peak fracture energy improvement while PVB/CNT-0.2 and PVB/nanoclay-2 had 104 and 118% respectively. However, scanning electron microscopy (SEM) and small-angle X-ray scattering (SAXS) employed in studying the nanoclay state of exfoliation revealed a surprise. At 100 W power application, PVB/nanoclay-1wt% and PVB/CNT-0.1wt%/nanoclay-1wt% had interlayer d-values of 17.58 and 17.62 nm; while having 18.36 and 18.34 nm at 700 W sonication respectively, but both were lower than 20.31 nm of the clay particles. This implies a lack of intercalation or exfoliation of the incorporated clays despite the high fracture toughness property of the composites. After that, they found that high surface roughness

362 value of fractured ternary composite surface, caused by the hybrid fillers synergism, was
363 responsible for the high mechanical property. Consequently, they termed surface roughness
364 as a determinant of fracture toughness aside the famous stress transfer mechanism. Two, high
365 sonication power generates more filler(s) particles which support improved fracture strength.

366 *3.3. Comparing solution-mixing and melt-mixing methods*

367 Silva et al. (2014) compared nanocomposite of HDPE using the hybrid of 1 wt% CNT (C)
368 and 1 wt% of either natural clay (N) or organoclay (30B) by both melt-mixing (m) and
369 solution-mixing (s) methods. The two mixing methods, to prepare binary unmodified natural
370 clay/HDPE, reportedly caused no clay exfoliation in the matrix. Equally, modified clay
371 reportedly remained as agglomerates in HDPE with melt-mixing but well exfoliated with
372 solution method, owing to its organophilic character of swelling to allow HDPE matrix-clay
373 interaction in the presence of solvent. On the contrary, melt-mixing produced better CNT
374 dispersion in HDPE/CNT binary composite than solution method (although inefficient
375 magnetic stirring was reported as the cause of the re-agglomeration of CNT particles). For the
376 ternary nanocomposites by solution blending (Figs. 3a, b, e, f), irrespective of the nanoclay
377 hybridized with CNT, the nanotubes were well dispersed but preferentially formed structure
378 with organoclays (PE/C/30B-s) (Figs. 3a, b). However, ternary composites prepared by melt
379 blending (Figs. 3c, d, g, h) showed agglomerates of nanoclays enclosed by dispersed CNT
380 with some clusters.

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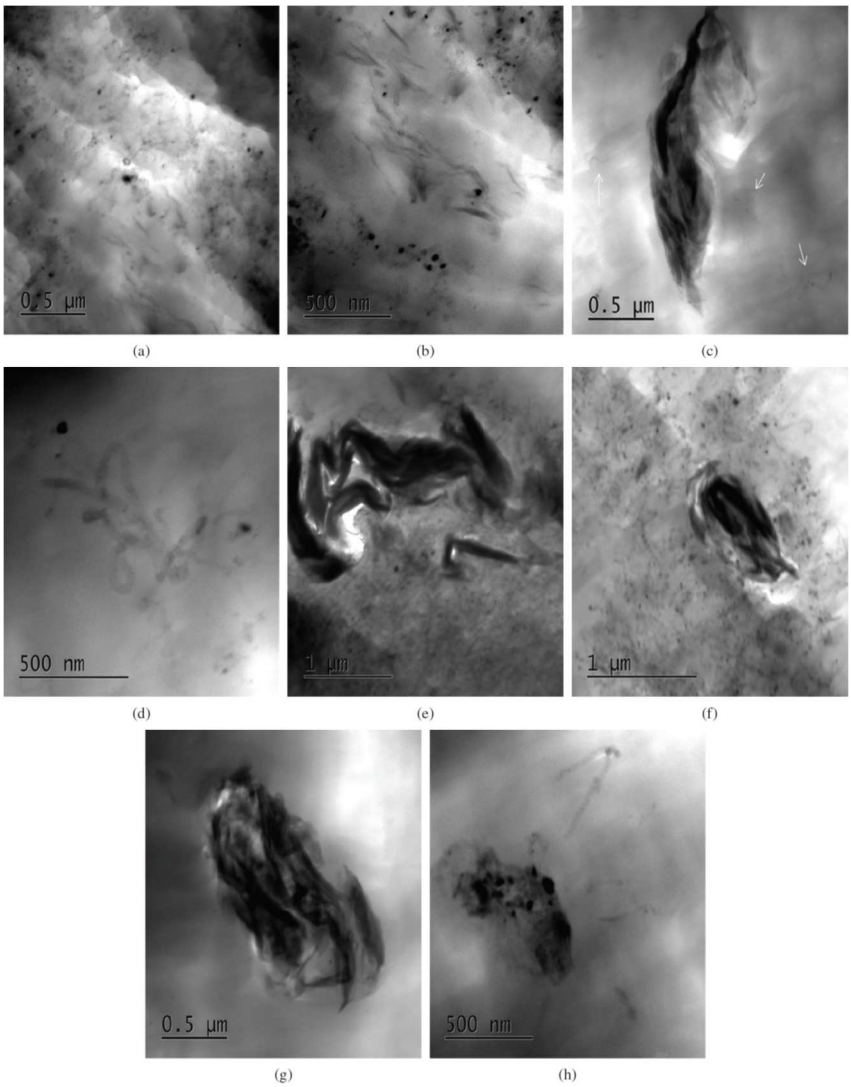


Fig. 3. TEM images at different resolutions for: PE/C/30B-s (a) and (b); PE/C/30B-m (c) and (d); PE/N/C-s (e) and (f); PE/N/C-m (g) and (h) (Silva et al., 2014)

The mechanical study revealed improved Young's modulus irrespective of the preparation method or clay. Melt-mixed ternary composites got 16% peak enhancement, while binary and ternary samples with nanoclay via solution mixing only attained 9% modulus improvement. For hardness, ternary composite (PE/C/30B-s) prepared with organoclay through solution-mixing recorded 28% peak enhancement but 20% for PE/C/30B-m (melt mixing). They established the superiority of using organo-modified nanoclay over natural clay as it is more compatible with CNT in effecting synergistic reinforcement. They explained that the solution

mixing offered an easier diffusion of the nanoparticles within the matrix, which contributed to homogenous dispersion of clay/CNT and making them as nucleating agents/sites for crystallization. They also restrained the polymer chains mobility, thus requiring higher load to induce plastic deformation.

3.4. In-situ polymerization method

Although it was adopted to prepare binary poly(ethylene terephthalate)/clay (Tsai et al., 2014), polyimide/graphene oxide (Wang et al., 2011), nylon-6/graphene (Xu and Gao, 2010), and poly(methyl methacrylate) incorporated with graphene (Potts et al., 2011), in-situ polymerization is rarely compatible with latest techniques of polymer processing (Dlamini et al., 2019) and commonly employed for low viscous matrix like liquid epoxy (Safdari and Al-haik, 2018). To the best of our review, Madaleno et al. (2013) have only applied the method for clay/CNT-filled high-performance thermoplastics polymer nanocomposite.

Madaleno et al. (2013) utilized Mt-CNT prepared by CCVD to develop PU nanocomposite foam with varying loading of Mt-CNT (0.25, 0.50, 1.00 wt%). They reported that hybrid fillers at lower concentrations showed no agglomeration, but higher inclusion produced more agglomerates due to the closeness of particles that are of high surface energy and area. All the composites attained improved compressive strength and thermal stability over the neat matrix. Yet, prepared Mt-CNT significantly increased degradation rate of the nanocomposite, associated with metallic particles used in exfoliating clay in CCVD process.

3.5 Electrospinning and high-energy ball milling methods

Electrospinning method can be defined as a process of drawing continuous polymeric fibre from either a polymer solution or polymer melt, based on an electrohydrodynamics phenomenon, using electrostatic force in a liquid-jet form to fabricate polymer composite (Brown et al., 2016). Fig. 4 shows a schematic melt electrospinning system.

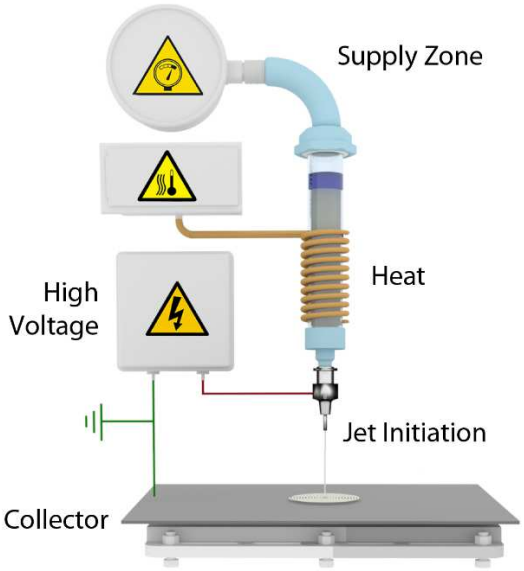


Fig. 4. Melt electrospinning system set up (Brown et al., 2016)

Hosseini and Yousefi (2017a, b) prepared a ternary of PVDF (A), CNT (CN) and modified clay. 0.15 wt% total fillers loading were varied (A/0.05CN/0.1clay, A/0.075CN/0.075clay and A/0.1CN/0.05clay) in studying the effects on PVDF's crystalline structure; and invariably on the piezoelectric performance of the resulting nanocomposites. They observed high level of nanofillers exfoliation in the matrix, for instance, the Mt d-value peak from the XRD disappeared in all composite formulations that connoted a high level of dispersion. They reported reduced composite fibre diameter as the quantity of clay increased (while CNT reduced), that favoured lower viscosity with reduced nanotubes tangles and formation of β-phase crystal, which enhanced the PVDF piezoelectric behaviour. Mt interacted with $-CH_2$ group in the PVDF, after being stretched by the high electric field during electrospinning, leading to stabilization of targeted β-phase crystals and prevented its transformation to α-phase.

The significant of β-phase content and polarization achieved was verified by piezoelectric impact sensory of neat PVDF, A/0.1CN/0.05clay, A/0.075CN/0.075clay and A/0.05CN/0.1clay composites. They recorded 8.25, 8.4, 9.03 and 10.9 mV/N sensitivities,

434 respectively. They explained that the high sensitivity of A/0.05CN/0.1clay was due to the
435 little amount of the hybrid fillers (0.15 wt%) which was not sufficient to cause any PVDF's
436 polar dilution and detrimental effect on its mechanical flexibility. However, the widest sound
437 absorption by the composite was dependent on higher CNT content (A/0.1CN/0.05clay); and
438 it recorded the least electrical resistance, signifying established network formation at very
439 low loading.

440 Ball milling is another environmental-friendly method adopted by (Santangelo et al.,
441 2011) to developed PLA nanocomposite using clay-CNT nanofiller produced by CCVD
442 growth of CNT over nanoclay (muscovite). Enhanced sorptive and electrical conductivity
443 with 6-9 orders of magnitude in nanocomposite over the pristine matrix was reported. Gorrasi
444 and Sorrentino (2015) wrote a review on forms of mechanical milling for nanocomposite.

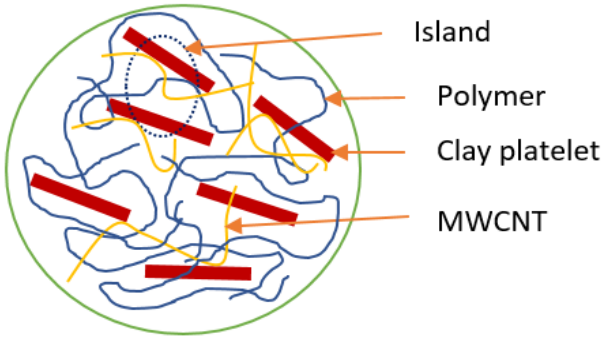
445 **4. Properties of polymeric nanocomposites reinforced with hybrid of nanoclay-CNT**

446 *4.1. Rheological properties*

447 Mixing torque depicts the composite viscosity variations coordinated by the instantaneous
448 microstructural rearrangements. Rheological investigation serves as the tool to evaluate the
449 existing network structure between matrix and the incorporated nanofiller(s) (Rueda et al.,
450 2017; Singla et al., 2017).

451 Pandey et al. (2014) developed ternary nanocomposite comprised of polypropylene (PP),
452 clay (C15A, 3 wt%) and CNT (0.3 wt%) by melt blending. They reported improved storage
453 and loss moduli of all composites over neat PP, while the ternary system had the highest
454 improvement. The same trend was reported for the viscosity of the composites but unlike
455 storage and loss moduli that improved with frequency, viscosity reduced with frequency
456 (non-Newtonian characteristics). The improved rheological behaviour of ternary system over
457 the binary was attributed to the high synergetic interaction of the clay platelets and CNT.

458 CNT has a high degree of affinity for nanoclay, thereby the presence of clay lead to
459 interruption of bundled CNT network and establishing an island of intact clay-CNT three
460 dimensional (3D) network structures that restrain polymer chains motion (see the mechanism
461 in Fig. 5), leading to enhanced viscosity and modulus. The formed intact network effected
462 improved thermal and flammability property of ternary by the formation of protective char
463 with a tight and continuous structure that prevented thermal and mass transfer.



464

465 **Fig. 5.** Clay platelet-CNT interaction mechanism in ternary system

466 Al-Saleh (2017) reported 50% reduction in the quantity of CNT needed for the ternary
467 CNT/clay/PP to attain electrical percolation threshold concentration (EPTC), compared with
468 binary CNT/PP that required 1 wt% CNT (Fig. 6a). The researcher further probed clay
469 influence on electrical resistivity of percolated composites, 0.5 wt% CNT/PP and 2.5 wt%
470 CNT/PP, by adding varying amount of clay. They reported negligible effect on 2.5-CNT/PP
471 because of an established conductive network, while clay increase beyond 0.5-synergistic
472 EPTC upset the "young" CNT-network in 0.5-CNT/PP, with observed resistivity growth (Fig.
473 6b). From rheological study, the researcher found that the mixing torque required by ternary
474 with clay/CNT (having total 2 wt% hybrid fillers) was lesser than the binary composite
475 without clay (only 1 wt% CNT), which was expected to require higher torque. Therefore, the
476 researcher established that the clay inclusion functioned as a plasticizing agent in the matrix
477 that facilitated viscosity and shear stress reduction thereby maintained CNT high aspect ratio,

478 influenced the composite crystallinity and improved CNT-networks formation. This resulted
479 in a 50% electrical percolation reduction in ternary system. Similarly, Hosseini and Yousefi
480 (2017b) reported higher dynamic viscosity, storage and loss moduli in electrospun
481 PVDF/CNT/clay ternary composite compared to neat or single-filled matrix.

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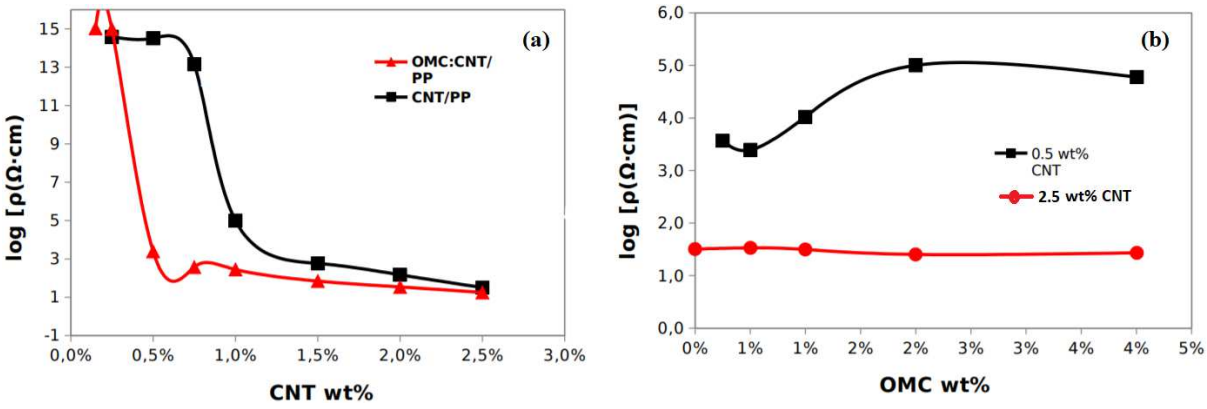

483

484 **Fig. 6.** (a) Percolation behaviour of CNT/PP with(out) clay (OMC); (b) influence of clay on
485 electrical resistivity of both 0.5-CNT/PP and 2.5-CNT/PP composites (Al-Saleh, 2017)

486 *4.2. Morphological Properties*

487 Several examinations are required for better understanding of the structure morphology,
488 interfacial interaction and nanofillers dispersion in a polymer matrix, like using Raman
489 microscopy, scanning electron microscopy (SEM), TEM, Fourier transform infrared
490 spectroscopy (FTIR), X-ray diffraction (XRD). It is worth noting that the morphology of a
491 nanocomposite dictates its overall performance (Mayeen et al., 2018).

492 Manikandan et al. (2012) utilized CCVD-prepared Mt-CNT fillers to achieve defect-free
493 homogenous Nafion (perfluoro-sulphnoyl-fluoride copolymer) nanocomposite for fuel cell
494 application. From microstructural study, strong adhesion in Mt-CNT-Nafion nanocomposite
495 was proven as broken CNTs particles reportedly remained stuck within matrix. The clay

496 layered-structure favoured the uniformity of Nafion over CNT resulted in high thermal
497 stability.

498 Chiu (2014) used the hybrid of Mt (C) and CNT (T) in developing PVDF nanocomposite
499 using melt-mixing approach. Binary and ternary composites of varying nanofiller were
500 prepared with the following designations: C1 (PVDF/Mt-1 wt%), T3 (PVDF/CNT-3 wt%);
501 and CT5 (PVDF/Mt-2.5 wt%/CNT-2.5 wt%). On comparing the morphology of C1 and
502 hybrid reinforced CT5, SEM revealed that the inclusion of CNT aided the dispersion of
503 nanoclay in CT5; unlike Mt aggregation found in C1. Chiu related the behaviour to increase
504 in the melt viscosity when CNT was added to binary PVDF/Mt, which led to intensive
505 dispersion of Mt (Fig. 7). Similarly, on combining CNT with Mt, XRD diffraction angle
506 reportedly shifted to the left and became sharpened, which indicated d-value increase and
507 perfect crystallite size respectively. The morphological study confirmed that the addition of
508 only Mt or the hybrid of the fillers created polymorphism in PVDF matrix. He found that low
509 crystallization cooling rate generated high β-form crystals.

510 He also described the thermal property (DSC) of the composite from the morphological
511 perspectives. It was observed that individual introduction of Mt or CNT and their hybrid
512 (Mt/CNT) significantly acted as nucleating agent for the matrix crystallization which led to
513 increase in both onset and peak crystallization temperatures (Figs. 8 a, b); and these increased
514 with nanofiller mass fraction. Fig. 8a also includes structure of each of the composites and
515 shows the uniformity of structure generated with the use of hybrid filler.

516 In terms of thermal stability, inclusion of CNT in the binary PVDF/CNT (T) improved the
517 thermal degradation of the composite, which suggested good CNT dispersion and protective
518 layer/char formation during heating. However, upsurge of Mt in PVDF matrix led to reduced
519 degradation temperature for the PVDF/Mt (C), while ternary system PVDF/CNT/Mt (CT)
520 displayed thermal stability that falls in between that of the improved binary PVDF/CNT and

the reduced binary PVDF/Mt (Fig. 8c). The reduction of thermal stability of Mt-included composite has been related to the effect of organic modifier on Mt particles. Nonetheless, CNT upturned the deficiency in Mt while hybridized in the ternary.

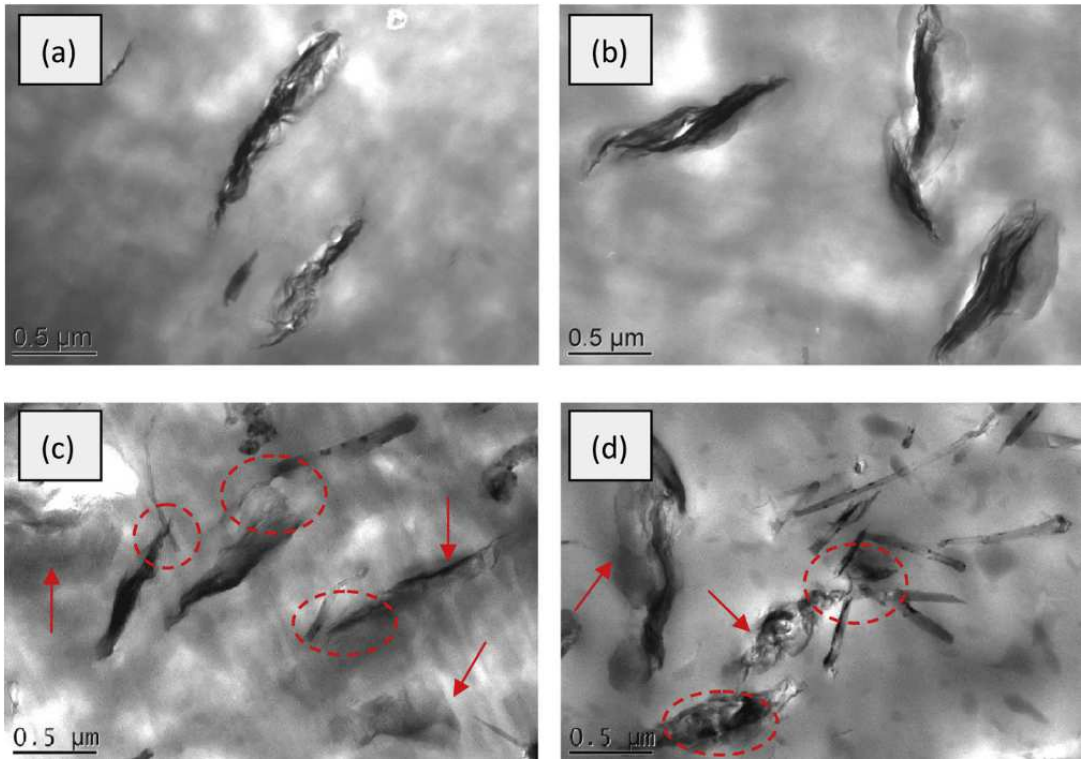

Fig. 7. TEM of PVDF composites containing (a) 1wt% Mt (b) 3 wt% Mt (c) 1.5wt% Mt/1.5 wt% CNT (d) 2.5wt% Mt/2.5wt% CNT (Chiu, 2014)

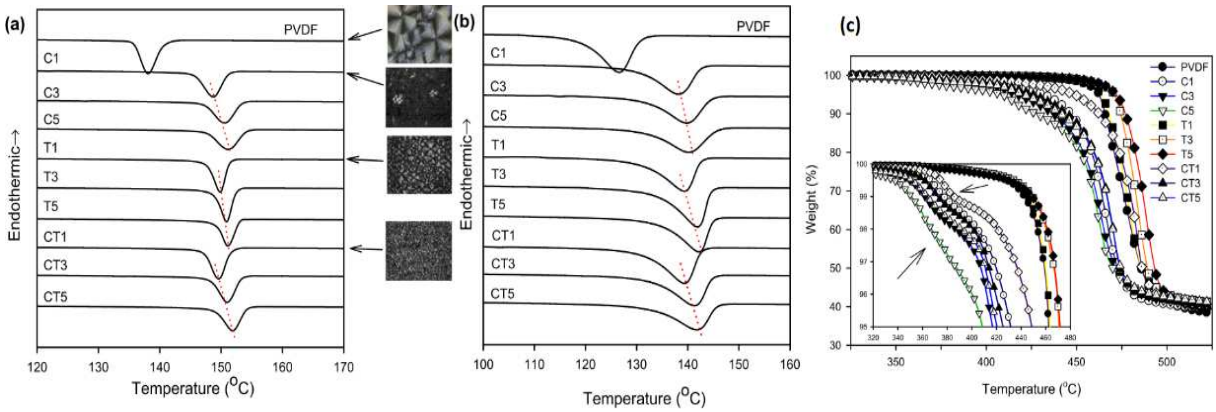

Fig. 8. (a) DSC cooling curve 15°C min^{-1}; (b) 40°C min^{-1} (c) TGA curves- N_2 of PVDF and its composites (Chiu, 2014)

530 *4.3. Thermal and flame retardancy properties*

531 Polymer combustion cycle involves thermal decomposition that yields volatile as well as
532 highly inflammable organic compounds, at comparatively low temperature, and emits large
533 quantum of heat that causes further polymer degradation and accelerates growth of fire
534 (Rothon and Hornsby, 1996; Dasari et al., 2013). Several approaches are used for protection
535 against fire by interrupting the combustion cycle: modification of thermal degradation
536 process, oxygen denial, or inhibition of back-flow of heat (Rothon and Hornsby, 1996; Dasari
537 et al., 2013). Flame retardants (Dasari et al., 2013) or intumescent flame retardants (Yuan et
538 al., 2017) are added to polymer to improve flame retardancy. However, environmental and
539 health-related concerns, aside high loading that has a deteriorating impact on processability
540 (Rothon and Hornsby, 1996; Bourbigot et al., 2019) and mechanical behaviour of resulting
541 nanocomposite (Feng et al., 2018), pose a major challenge.

542 Nanomaterials present eco-friendly flame, smoke and toxicity performances at a very low
543 loading percentage due to its high aspect ratio (Yuan et al., 2017). Few examples include
544 layered silicates (Liu et al., 2019; Zhu et al., 2019), carbon nanotubes (Ji et al., 2018),
545 graphene oxide (Fanga et al., 2019; Wang et al., 2019). Beyer (2005, 2006) attained about
546 57% reduction of PHRR on incorporation of 2.5 phr each of CNT and nanoclay in poly
547 (ethylene-vinyl acetate) copolymer. The heat release capacity was drastically reduced by 58%
548 on incorporation of 2 wt% CNT and 10 wt% clay in PLA matrix (Hapuarachchi and Peijs,
549 2010). Rao et al. (2015) prepared flame retardant nanocomposite of HDPE with blend of
550 modified clay and CNT. They reported improved thermal stability in the binary system with
551 CNT (1 wt%) over the neat HDPE; while with incorporation of only clay (1 wt%) thermal
552 stability fell below pristine HDPE. HDPE/clay binary composite recorded 123.2 and
553 132.16˚C for its onset and peak degradation temperatures respectively, while 127.5 and
554 135.34˚C for HDPE/CNT in the same order. Meanwhile, simultaneous addition of same ratio

555 of CNT (0.5 wt%) and clay (0.5 wt%) in the matrix showed the best thermal properties: 12%
556 char residue, highest delay in degradation temperatures (onset, 128.1˚C; peak, 137.94˚C) and
557 the least percentage crystallization that means efficient components interaction.

558 Also, in an effort to determine the optimum ratio of CNT to clay (total loading: 1 wt%) for
559 flammability resistance application in the ternary HDPE/CNT/clay, nanoclay was varied in
560 0.8 - 1 wt% (i.e., CNT 0.2 - 0 wt%) and vice versa. In comparison with neat HDPE, they
561 reported 66.8% reduction in peak heat release rate (PHRR) at optimum formulation of
562 0.6CNT/0.4clay/HDPE. They reported that CNT migrated faster than clay to the matrix
563 surface in forming insulating protective layer, which prevented gas or energy transport. Time
564 to ignition was said to be favoured with CNT increase, as formed char layers served as heat
565 sinks that deferred ignition and degradation. Ternary's mechanical property was also
566 enhanced through enhanced interfacial adhesion, clay exfoliation and CNT dispersion.

567 *4.4. Electrical Property*

568 Levchenko et al. (2011) adopted both experimental and theoretical approach in
569 determining the influence of clay (OC) inclusion on electrical percolation threshold of ternary
570 PP/CNT/OC nanocomposite. Electrical percolation threshold was reported to reduce by
571 28.4% (from 0.95 to 0.68 vol% of CNT) on incorporation of clay into PP/CNT. The
572 behaviour was ascribed to clay disentangling and prevention of CNT aggregations during
573 melt-mix processing, thereby interparticle-contact numbers were enriched to form conductive
574 network. They corroborated this explanation by morphological study that showed clusters of
575 clay or CNT in the singly filled PP/OC or PP/CNT composites, respectively (Figs. 9a, b).
576 Conversely, the SEM image of the ternary showed well-exfoliated CNT at the instance of
577 clay with an established network structure needed for conductivity (Fig. 9c).

On the contrary, Khajehpour et al. (2014) reported an increase of percolation threshold on addition of clay to CNT/PVDF from 0.3 to 0.5 wt% of CNT due to deterioration of the conductive network caused by the clay platelets barrier role.

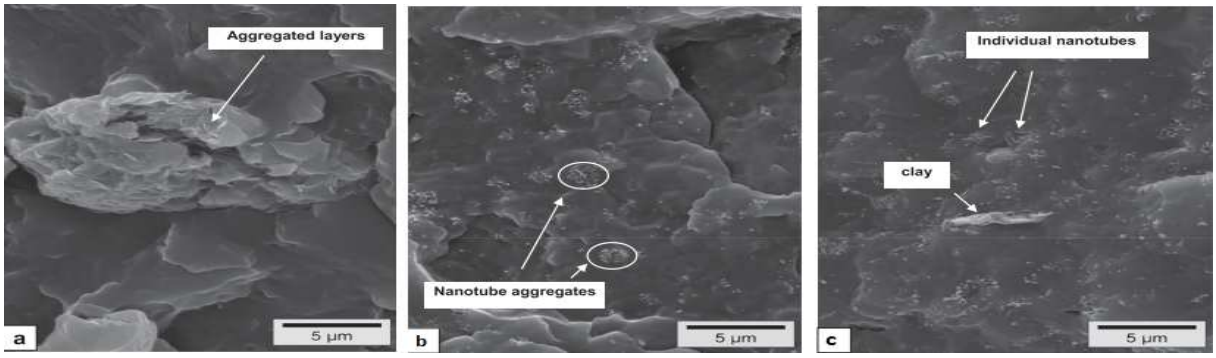

Fig. 9. SEM image of (a) PP/OC (b) PP/CNT (c) PP/CNT/OC (Levchenko et al., 2011)

4.5. Mechanical Properties

Zhang et al. (2006) incorporated CNT-clay nanofiller, prepared by CCVD process, into polyamide-6 (PA6) by melt mixing. Tensile modulus and strength were enhanced significantly by 289% and 153% respectively. Homogenous dispersion of CNT-Mt was reported and attributed to swollen and exfoliation of clay by iron ions intercalation into clay interlayers as well as CNT growth on clay platelets resulted in enhanced mechanical property of the ternary prepared with 1 wt% of CNT-clay. Olalekan et al. (2010) utilized masterbatch of polypropylene-clay (PP/clay) and CNT in preparing ternary composite. They reported PP/clay composite with tensile strength, Young's modulus and impact strength of 28.55 MPa, 1588.27 MPa and 5.55 kJ m^{-2}, respectively. With incorporation of CNT alongside Mt, they achieved improved tensile strength, Young's modulus and impact strength by 27, 42 and 13% respectively. It was related to higher aspect ratio and specific surface area of the incorporated CNT, and clay facilitated CNT superior dispersion in the matrix and in turn enhanced the mechanical properties of the ternary composite. Geng et al. (2012) reinforced PVDF with CNT and Mt. The mechanical properties of the ternary reportedly surpassed the neat PVDF

598 and single-filled nanocomposites. The reported dynamic mechanical analysis (DMA) showed
599 that the ternary PVDF/1.9CNT/3Mt had approximately twice mechanical loss factor (tan δ)
600 than binary composites, with an established conductive network and piezoelectric phase,
601 which made the ternary to be applicable for damping application.

602 Prashantha et al. (2014) developed polypropylene (P) nanocomposite reinforced with
603 hybrid (1:1) of Mt (C) and CNT (M). Both binary (MP-2, MP-4, CP-2, CP-4) and ternary
604 (MCP-2, MCP-4) composites showed increase in strength and modulus with nanofillers
605 loadings. Meanwhile, composites with the hybrid fillers recorded better improvements in
606 tensile strength (MCP-2, 37%; MCP-4, 54%) and tensile modulus (MCP-2, 40%; MCP-4,
607 50%). Also, ternary MCP-2 (CNT 1 wt%; Mt 1 wt%) was reported to have the least
608 elongation reduction when compared with neat PP due to increased polymer chains rigidity as
609 a result of nanofillers restriction effects. For hybrid-filled composites, positive synergy in
610 both flexural strength (MCP-2, 49%; MCP-4, 64%) and modulus (MCP-2, 58%; MCP-4,
611 65%) were also reported. The notched ternary composites MCP-2 and MCP-4 maintained
612 respective peak impact strength improvement of 50% and 53% above the neat matrix. The
613 high mechanical properties of the ternary nanocomposites were related to strong clay-CNT
614 and fillers-matrix interfacial adhesions revealed by morphology study. Uniform distribution
615 of retained broken CNT upon failure, instead of pull-out from the matrix, was cited as the
616 factor for property improvement.

617 Terzopoulou et al. (2016) studied the mechanical behaviour of poly(ε-caprolactone)
618 incorporated with clay-decorated CNT filler. The hybrid nanofiller was varied: PCL/clay-
619 CNT 0.5 wt%, PCL/clay-CNT 1.0 wt% and PCL/clay-CNT 2.5 wt%. They reported increase
620 in yield point and Young's modulus (stiffness) with the increase in fillers loading, which was
621 related to composite enhanced crystallinity. However, only PCL/clay-CNT 0.5 wt% recorded
622 increase in elongation with respect to the neat matrix. Also, PCL/clay-CNT 0.5 wt% and

PCL/clay-CNT 1.0 wt% had respective 5.5 and 3.7% increase in tensile strength but PCL/clay-CNT 2.5 wt% showed 15.9% reduction. Apparently, 0.5 wt% clay-CNT enhanced the composite strength, but higher loading led to weak fillers/PCL interfacial bonding because of agglomeration.

4.6. Tribology Property

Polymeric nanocomposites are fast replacing the traditional materials in fabricating mechanical elements (clutches, bush, gear, and bearing) and other electromechanical systems that solely depend on friction, wear and lubrication principles (Wani et al., 2018). Achieving high tribology efficiency requires homogenous distribution of fillers within matrix.

Azam and Samad (2018b) employed solution mixing in preparing UHMWPE nanocomposite using hybrid of Mt (C15A) and CNT for marine application. The samples were designated as Sample, Sample-1, Sample-2, Sample-3, Sample-4, Sample-5, and Sample-6 representing respectively 1.5wt%C15A/UHMWPE, 0.5wt%CNT/UHMWPE, 1.5wt%CNT/UHMWPE, 3wt%CNT/UHMWPE, 0.5wt%CNT/1.5wt%C15A/UHMWPE, 1.5wt%CNT/1.5wt%C15A/UHMWPE, and 3wt%CNT/1.5wt%C15A/UHMWPE. Cyclic sliding wear test was performed at 9 N load, underwater. Neat UHMWPE failed as early as 22000 cycles, while none of the binary and ternary composites failed at the condition. By increasing force to 12 N on composites, they found that only Sample-2 (1.5 wt% CNT) and Sample-5 (1.5 wt% CNT/1.5 wt% C15A) sustained wear life up to 150000 cycles. The earlier failure of neat matrix and other samples was either attributed to lack of CNT, inadequate CNT causing inept matrix chains anchoring, aggregation of CNT or formation of dual-phase structures. These caused weak filler(s)-matrix bonding and poor bridging of the polymer chains resulting in an inefficient loading transfer by the CNTs on the course of wear tests. Interestingly, SEM study of Sample-2 and Sample-5 was reported to reveal homogenous filler(s) dispersion that promoted matrix-filler interactions, polymer chains bridging, and thus

secured against any pull out during wear test. On further investigation of the two samples, ternary Sample-5 displayed its superiority up to 300000 cycles, which indicated the significant role of the hybrid nanoclay/CNT fillers over single-filled Sample-2 that failed at 170000 cycles.

For Sample-5 (with hybrid nanofillers), clay was said to create a torturous path, due to its platelet structure, which prevented water molecule absorption (transportation) while the CNT synergistically bridged the polymer chains together during wear test underwater. As hardness is a critical factor for high wear property, report of 17.14, 12.4 and 2.7% influence of water on the hardness of neat polymer, Sample-2 and Sample-5 respectively confirmed the synergy in ternary.

5. Polymer blend reinforced with Mt-CNT Nanofillers

Although this review focusses on a thermoplastic matrix reinforced with Mt-CNT nanofillers, it is worth considering that researchers have also incorporated the hybrid fillers into polymer blends (Table 2) and reported magnificent properties enhancement. Incorporation of Mt/CNT in blend reportedly led to co-continuous morphology formation (Potschke et al., 2007; Al-Saleh, 2015), mechanical (Chiu, 2017b) and flammability (Ambuken et al., 2014) properties augmentation.

Table 2

Summary of thermoplastics blends filled with hybrid of CNT and Mt.

Matrix		Optimum hybrid filler concentration (wt%)		Dispersion technique	Focused application	References
I	II	CNT	Mt			
PE	PP	1*	1*	Melt-mixing	Electrical & mechanical	Al-Saleh (2015)
PC	PP	2	3	Melt-mixing	Electrical	Pötschke et al. (2007)
PC	PVDF	2	1	Melt-mixing	Thermo-mechanical	Chiu (2017b)
PU	PA-11	3.5	3.5	Melt-mixing	Thermo-mechanical	Ambuken et al. (2014)

*%volume

6. Conclusion

This review has provided the advances on high-performance thermoplastics ternary nanocomposites specifically prepared by the sole incorporation of montmorillonite clays and carbon nanotubes. Preparation of nanocomposites through the conventional and the recent approaches was briefly summarized. Systematically, the reviewed studied each of the bulk properties of nanocomposite: rheology, morphology, thermal, mechanical, electrical, and tribology. Factors responsible for these properties enhancement were identified, and overall nanocomposite behaviour was found to be principally hinge on the resulting morphology.

The hybrid fillers influence high properties, though how efficient the influence is solely depended on their level of dispersion within the matrix because agglomeration of any or both of the nanofillers substantially reduce or cause more detrimental effect on the resulting nanocomposite. There is no gainsaying in the significant of rheological property of the composite emanating from right material selection, formulation and other processing variables.

The review established the effectiveness of clay in aiding the dispersion of CNT by lowering the viscosity of polymer thereby reducing the CNT percolation threshold, which significantly affects material cost. Clay interjects bundled CNT particles as CNT has a high degree of affinity for nanoclay. Consequently, aiding the formation of network structures that favour electrical and thermal conductivity, and restrict polymer chains movement thereby enhances flame retardancy and mechanical behaviour. Similarly, the presence of CNT facilitates clay d-value increase that leads to improved exfoliation of clay.

However, there is need for more research pertaining to the implications of processing behaviour on the ternary nanocomposites. Processing factors, such as temperature, shear and time residence that ultimately affect the resulting nanocomposite properties, should be further studied while using Mt and CNT as hybrid filler in polymers.

693 The superior reduction of the peak of heat release rate (PHRR) is mostly reported in the
694 ternary system, which is related to the formation of synergistic uniform crust by Mt-CNT
695 over the burning composite. Thus limits the heat and gas diffusion and consequently lessen
696 the nanocomposite flammability. Nanoclay modification processing/chemicals should be
697 carefully selected as it is majorly cited to be responsible for early degradation of ternary
698 nanocomposite.

699 For tribology application, clay creates a tortuous path (due to its platelet structure) that
700 prevents molecule absorption (transportation) by nanocomposite while CNT synergistically
701 bridged the polymer chains together resulting in improved wear resistance. Another key role
702 of clay is the creation of polymorph phase in polymer, and CNT inclusion is responsible for
703 the establishment of co-continuous morphological formation in polymer blend.

704 Thermal conductivity is vital in the design of material for heat management services: it
705 improves and guarantees the service life of a system as well as the reduction of hazards.
706 Concurrently, mechanical durability cannot be traded-off in advanced applications such as
707 aerospace, automobile, military and other thermomechanical facilities.

708 **Declarations of interest:** none

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