Development of Polyamide Based Blend and Their Nanocomposites – A Review

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Abstract. Polymer blend nanocomposites have been recognized as a promising path to developing a different material with high-capacity that comprises benefits of hybrid polymers with advantages of composites made of polymers. The use of nanofillers to enhance certain properties (e.g., mechanical, chemical, thermal, etc.) of a polymer mixture, as well as to stabilize and modify the blend morphology, has sparked a lot of interest in nanocomposites with multiphase matrices. In this review, recent breakthroughs in polyamide (PA), acrylonitrile–butadiene–styrene (ABS), and polypropylene (PP) blend-based nanocomposites are studied. Polyamide 6 (PA6) (rich) blend-based nanocomposites made by blending various thermoplastics with nanofillers are highlighted. The production and characteristics of nanocomposites containing nanofillers made from a PA blend are described. A survey revealed that the volume and size percentage of the nano-filling materials affect wear resistance and friction coefficient. Multi-functional fillers can also be used to create composite materials with high performance that cannot be obtained with a single filler.

Keywords: Polymer blends and alloys · Nanocomposites · Compatibilizaer · Nanofillers

1 Introduction

Homopolymers may not always meet all of the criteria for a variety of practical uses. As a result, the first trend was to create novel polymers from a wide range of monomers. Copolymerization has proven to be a useful approach for customizing or altering the characteristics of polymers. However, due to the economic and technical uncertainties associated with developing new polymers, recent efforts have focused on multiphase polymeric systems to acquire materials with improved chemical and physical properties, and these considerations have been the foundation of polymer blends.

Blending two or more polymers together to make blends is a more cost-effective technique to manufacture novel polymeric materials with higher performance qualities than copolymerization. Polymer blending is one of the fastest-growing categories of polymer technology in terms of commercial uses and breakthroughs, thanks to the recognition that new materials with superior qualities can be created to fulfill specific

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end-user needs. As a result, the polymer mixes market has risen consistently during a previous couple of years and is expected to rise more in the coming decade. Polymer mixes are extensively used in the automobile sector, electrical and electronic equipment, packaging, construction, and home goods [1, 2].

2 Polymer Nanocomposite

In the past several years, Because of their multifunctional nature, adaptability, low cost, high-strength, and light-weight polymer nanocomposites have drawn a lot of interest in a variety of fields. The polymer nanocomposites have excellent thermo-mechanical characteristics, making them suitable for use in the automotive and aerospace, coatings/paints, and electrical and electronics sectors. Nevertheless, as building costs fall, there is an increasing need to enhance nanocomposite materials. Blending is one method for enhancing polymers' characteristics with another polymer in addition to nanofillers reinforcements. Thus, the polymer blends with nanofillers have the potential to design the new material for the intended applications [3].

Superior qualities of polymer blends are influenced by the molecular compatibility or miscibility of the constituent polymers. Majority polymer pairings, however, are immiscible and hence create phase-separated morphologies in blends due to the unfavorable enthalpy of mixing due to their intrinsic mismatch in terms of thermodynamics. Multiphase polymeric material characteristics are determined by the microstructure of the blend as well as the properties of the component polymers. As a result, microstructure control becomes a crucial aspect when it comes to evaluating the performance of polymer mixes. Minimizing interfacial tension and increasing interfacial adhesion between blending components has traditionally been the most efficient strategy to achieve adequate performance in incompatible polymer blends. By causing entanglement or bridging distinct polymer chains along with connection, the employment of a graft copolymer or block as a compatibilizer during the process is critical. In polymer mixes that are incompatible, the compatibilizer enhances the miscibility of the component polymers, reducing the typical region widths of disperse section during blend's matrix phase. The usage of polymeric compatibilizer in various immiscible polymer blends is limited by the production of various graft or block co-polymers based on the blend components [4–9].

3 Multiwall Carbon Nanotubes (MWNT)

Based on the literature, the extraordinary features of MWNTs are generating a great deal of curiosity for use in many nanotechnology applications. In the domain of MWNT exploration and application, there is a lot of research going on right now. Carbon nanotubes with many walls can be used in numerous applications, such as composite materials with polymer, metal, or ceramic matrices, chemical sensors, catalytic system components, electromagnetic shielding materials, and biological applications including selective drug delivery. The production of novel multi-functional composite materials with better and tailorable features is one of the most promising uses of MWNTs and graphene's

exceptional capabilities. Construction materials, anti-static coatings, low-weight electromagnetic shielding, conductive polymers, and other applications can all benefit from such composites. Polymer matrices are often used in the creation of such composites due to their lightweight, low cost, high processability, predictable physical, chemical, and mechanical properties, as well as great scaling prospects [31–33].

Several types of polymer matrices have been studied so far for the fabrication of MWNT- and Single Wall Carbon Nanotube (SWNT) composites of loaded polymers. Polyurethanes, epoxy resins, polyolefines, polystyrene, polymethyl methacrylate, polyamide, polypropylene, and other materials fall under this category. To understand and enhance the characteristics of innovative multifunctional composite materials incorporating carbon nanotubes, graphene, and their hybrids, a systematic analysis of their properties is required. As a result of varying the primary features of polymer matrices and including nanotubes, it is possible to produce composite materials with projected tailorable qualities that may be used in a range of applications. As a result, further research into the wear behavior of polyamide-based blends and related nanocomposites is required [34–36].

4 Processing of Polymers and Their Composites

Polymers and its composites are a type of tribo-engineering material commonly utilized in mechanical parts like cams, gears, bearings, bushes, bearing cages, and so on, where non-lubricated wear performance is a vital requirement for material selection. Wear of equipment that comes into interaction with an abrasive substance, seal wear, and component deterioration that enable harsh elements to pass through, and wear induced by abrasives entrained in fluids are all examples of abrasive wear. Metal abrasion wear has already been studied extensively [1–3]. Specialized polymers are rapidly being employed across a range of applications where wear resistance is critical, for example bearing materials and joint replacements that are biomedically based. Abrasive wear can occur in various applications, resulting in the loss of function. Because of their corrosion resistance, tolerance for tiny misalignments and stress loads, and low coefficient of friction, polymers are appropriate for use of bearing materials. To explore the 3-body wear behavior of polyurethanes, abrasion test (with a dry-sand rubber wheel) were employed [4]. Polymers and polymer-based composites [5–8] were examined for abrasive wear. The Seven polymers were tested in four different wear regimes: abrasive, adhesive, reciprocating, fretting, and found that the ranks of polymers differed substantially [9]. In various wear scenarios, no one polymer performed better or worse than the others. It is also a well-known truth that, while fibre reinforcement, solid lubrication, or both can considerably improve polymer performance, this is not always the case. It can sometimes degrade the performance of a clean polymer [10]. The thermal conductivity and storage modulus of polyamide 66 (PA66) was improved when Carbon Nanotube (CNTs) were introduced. The friction coefficient of PA66 with CNTs decreased, and the CNT length had a greater impact at higher temperatures. The rate of wear increased rapidly at surface temperatures above 110 °C, and CNTs' length had a significant impact on high-temperature wear [38].

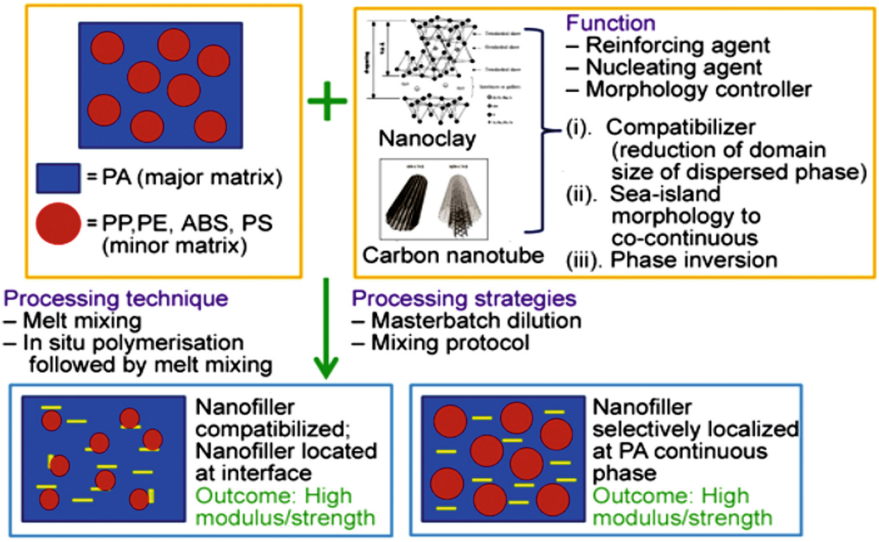

Fig. 1. Structure-properties-processing relationship of PA blend-based nanocomposites [40]

Although the binary polyamide 6 (PA6)/polypropylene (PP) mix had a morphology of coarse-scale and lesser cohesion between the two phases, the drop in PA6 concentration resulted in a loss in ductility of the composites. Composite's flexural and compressive strengths grow to their maximum, then decline as the filler mass fraction rises. The maximal compressive and flexural strength is achieved at 15% filler mass. Composite deflection and toughness improve as the filler mass fraction rises. Incorporation of PA6 particles, the friction factor and wear frequency of PP are decreased. Mechanical microploughing, plastic deformation are the two basic wear processes in dry sliding. When the volume of PA6 is 15%, the friction and wear attributes may be increased by increasing the PA6 percentage [39].

Hybrid polymer nanocomposites sliding wear behaviour is investigated under varied loading circumstances and counterface roughness. Two unique polymer matrices, polyamide 66 (PA66) and epoxy, were examined TiO2 (with and without) reinforcing nanoparticles as tribo-fillers, as well as typical micro-sized short carbon fibre and flakes of graphite. The tribological system was shown to be responsible for the synergistic effect of micro-sized fillers and nanoparticles on wear and friction performance [40]. The structure properties processing relationship of PA blend-based nanocomposites Fig. 1 illustrates this.

Researchers investigated PA6 (rich) blend-based nanocomposites with various compatibilizers (like MAH-g-PP, EPR-g-MA, MAPP, SMA, SEBS-g-MA, PE-g-MA, EnBACO-MAH) also nanofillers (like modified MMT (4 wt%), organoclay (4 wt%), MWNT, SWCNTs-COOH, Modified montmorillonite (5 wt%)) and these are processed with melt compounding/mixing and in situ bulk polymerization technique which is tabulated in Table 1 and Table 2.

Table 1. Current research on PA6 (rich) blend based-nanocomposites (Part A).

Sr. No.	Nanocomposites system based on a PA6 blend	The role of the dispersed span in the PA matrix	Nanofiller	Method of processing	Authors
1	PA6/PP/MAH-g-PP/Organoclay	PP: provides superior processability and moisture resistance; MAH-g-PP: compatibilizer	Organoclay (4 wt%)	Melt compounding	[11, 12]
2	PA6/PP/EPR-g-MA/Organoclay	PP: provides superior processability and moisture resistance; EPR-g-MA: Impact moderator and compatibilizer	Organoclay (4 wt%)	Melt compounding	[13]
3	PA6/PP/SEBS-g-MA/Modified MMT	PP: provides superior processability and moisture resistance; SEBS-g-MAH: Impact moderator	Modified MMT (4wt%)	Melt compounding	[14, 15]
4	PA6/PP/MAPP/Organoclay	PP: provides superior processability and moisture resistance; MAPP: compatibilizer	Organoclay (3.7 phr)	Melt compounding (different mixing protocols)	[16]
5	PA6/HDPE/Organoclay	HDPE: insensitivity to moisture	Organoclay (3 wt%)	Melt compounding	[17]
6	PA6/HDPE/Organoclay	HDPE: offer high toughness and cost-effective	Organoclay (5 wt%)	Melt compounding (different mixing protocols)	[18]
7	PA6/HDPE/Organo-bentonite	HDPE: insensitivity to moisture	Organo-bentonite clay (1.2–2.4 wt%)	Melt compounding	[19]

(*continued*)

Table 1. (*continued*)

Sr. No.	Nanocomposites system based on a PA6 blend	The role of the dispersed span in the PA matrix	Nanofiller	Method of processing	Authors
8	Nylon6/HDPE/PE-g-MA/Nanoclay	HDPE: poor water vapour permeability; PE-g-MA: compatibilizer	Nanoclay (0.5–3 phr)	Melt compounding	[20]
9	Nylon6/HDPE/PE-g-MA/Modified clay	HDPE: offer high toughness and is cost-effective; PE-g-MA: compatibilizer	Modified clay (0.5–2.5 phr)	Melt compounding	[21]
10	PA6/LDPE/Organoclay	LDPE: poor oxygen (O2) and water permeability	Organoclay (0.5–4 phr)	Melt compounding	[22]
11	PA6/LDPE/PE-gMA/Clay	LDPE: poor O2 and water permeability; PE-g-MA: compatibilizer	Clay (3 phr)	Melt compounding	[23]
12	PA6/PS/Organophilized clays	PS: offers stiffness	Organophilized clays (5 wt%)	Melt compounding	[24]

Table 2. Current research on PA6 (rich) blend based-nanocomposites (Part B).

Sr. No.	Nanocomposites system based on a PA6 blend	The role of the dispersed span in the PA matrix	Nanofiller	Method of processing	Authors
1	PA6/PS/Organoclay	PS: offers stiffness	Organoclay (2–7 wt%)	In situ bulk polymerization followed by melt compounding	[25]
2	PA6/Polyimide/ Organoclay	Polyimide: applications that are high-temperature and high-performance	Organoclay (3 wt%)	Melt compounding	[26]

(*continued*)

Table 2. (*continued*)

Sr. No.	Nanocomposites system based on a PA6 blend	The role of the dispersed span in the PA matrix	Nanofiller	Method of processing	Authors
3	PA6/Thermotropic liquid Crystalline polymer (TLCP)/MAPPClay	TLCP: have outstanding anti-wear qualities, excellent thermomechanical properties; MAPP: compatibilizer	Clay (4 wt%)	Melt compounding	[27]
4	PA6/poly(epichlorohydrin-co-ethylene oxide) (ECO)/Organoclay	ECO: enhances ductility and impact strength	Organoclay (6 wt%)	Two-step melt blending process	[28]
5	PA6/ABS/Styrene-maleic anhydride copolymer (SMA)/Modified montmorillonite	ABS: offers high impact strength SMA: compatibilizer	Modifiedmont-morillonite (5 wt%)	Melt compounding (different mixing protocols)	[29]
6	PA6/ABS/Ethylene-n butyl acrylate-carbon monoxide- maleic anhydride (EnBACO-MAH)/Nanoclay	ABS: offers high impact strength EnBACO-MAH: compatibilizer	Nanoclay (2–4 wt%)	Melt compounding	[30]
7	PA6/PP/MPP/Multiwalled carbon nanotubes (MWNT)	PP: give strong moisture resistance and processability; MPP: compatibilizer	MWNT (0.4, 1, 2 phr)	Melt compounding	[31]
8	PA6/ABS/MWNT	ABS: excellent water resistance, impact strength, and mould shrinkage	MWNT (1–4 wt%)	Compounding in melt	[32]
9	PA6/ABS/MWNTs	ABS: excellent water resistance, impact strength, and mould shrinkage	MWNTs (0.1–1 wt%)	Compounding in melt and master-batch (by blending the solution)	[33]
10	PA6/ABS/Styrene maleic anhydride copolymer (SMA)/MWNTs	ABS: offers high impact strength SMA: reactive compatibilizer	MWNTs (2 and 5 wt%)	Melt compounding	[34]

(*continued*)

Table 2. (*continued*)

Sr. No.	Nanocomposites system based on a PA6 blend	The role of the dispersed span in the PA matrix	Nanofiller	Method of processing	Authors
11	PA6/PS/MWNTs	PS: offers stiffness	MWNTs (0.5–1.5 wt%)	Successive in-situ polymerization	[35]
12	PA6/PMMA/carboxylic acid-functionalized single-walled carbon nanotubes (SWCNTs-COOH)	PMMA: PA6 improves mixing and miscibility	SWCNTs COOH (1 wt%)	Melt mixing	[36]

(MAH-g-PP: maleated polypropylene; EPR-g-MA: maleated ethylene/propylene rubber; MAPP: maleic anhydride grafted PP; SEBS-g-MA: maleated styrene-ethylene butylene styrene; MPP: maleated polypropylene; PE-g-MA: maleic anhydride grafted polyethylene; SMA: styrene-maleic anhydride copolymer; EnBACOMAH: carbon monoxide-modified ethylene-nbutyl acrylate–maleic anhydride; MMT: montmorillonite; SWCNTs-COOH: carboxylic acid-functionalized single-walled carbon nanotubes; LDPE: low-density polyethylene; TLCP: thermotropic liquid crystalline polymer; HDPE: high-density polyethylene; ECO: polyepichlorohydrin-co-ethylene oxide; SMA: styrene-maleic anhydride copolymer; PMMA: polymethyl methacrylate; PS: polystyrene)

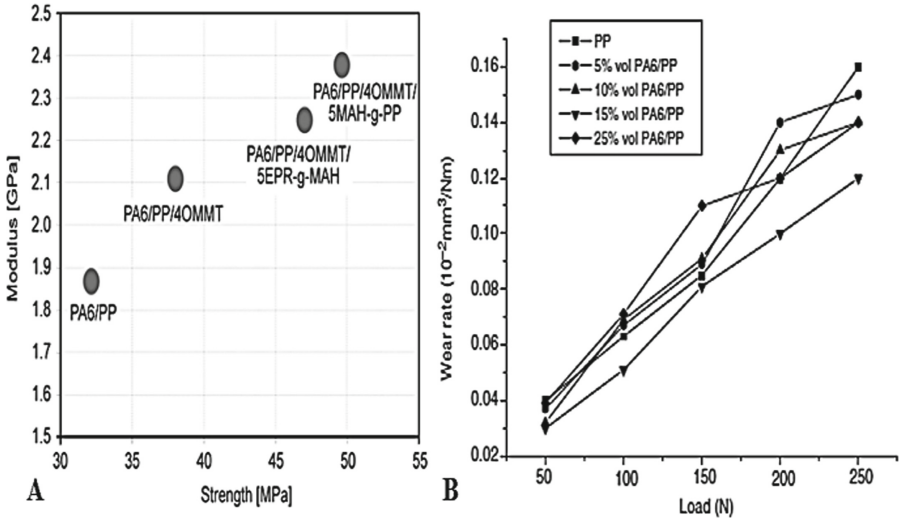

Fig. 2. A. Effects of compatibilizer (MAH-g-PP and EPR-g-MA) and OMMT on the modulus and strength improvement of PA6/PP blends **B.** Wear levels of PP and PA6/PP composites vs. load [39].

5 Effect on Mechanical Properties

According to Table 3 Mechanical characteristics of PA6-blend-based nanocomposites have improved.

Table 3. Mechanical properties of compatibilized PA6 mixture-based nanocomposites

Sr. No.	PA6-blend-based nanocomposites system	Types of nanofiller and their loading	Variety and loading of compatibilizers	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (EB)%	Ref.
1	PA6/PP (70/30) control	–	–	32.1	1.87	22.8	[11]
	PA6/PP/organoclay (70/30/4)	Organoclay intercalated by octadecylamine/4phr	–	38.0 (+17.4%)	2.11 (+12.8%)	4.2 (-81.5%)	
	PA6/PP/MAH-g-PP/organoclay (70/30/5/4)	Organoclay intercalated by octadecylamine/4phr	MAH-g-PP with 1.2 wt% of maleic anhydride (MA)/5phr	49.6 (+54.5%)	2.38 (+27.3%)	4.8 (-78.9%)	
2	PA6/PP (70/30) control	–	–	32.1	1.87	22.8	[13]
	PA6/PP/organoclay (70/30/4)	Organoclay intercalated by octadecylamine/4phr	–	38.0 (+17.4%)	2.11 (+12.8%)	4.2 (-81.5%)	
	PA6/PP/EPR-g-MA/organoclay (70/30/5/4)	Octadecyl amine intercalated organoclay/4phr	EPR-g-MA contents 1 wt% MA/5phr	47.0 (+46.4%)	2.25 (+20.3%)	6.7 (-70.6%)	
3	PA6/PP (70/30) control	–	–	44.0	–	–	[31]
	PA6/PP/MWNT (70/30/0.4)	Multiwalled carbon nanotube/0.4 phr	–	57.1 (+29.8%)	–	–	
	PA6/PP/MPP/MWNT (70/30/5/0.4)	Multiwalled carbon nanotube/0.4 phr	Maleate polypropylene (MPP)/5 phr	60.1 (+36.6%)	–	–	
4	PA6/HDPE (80/20) control	–	–	24.5	2.26	13.4	[37]
	PA6/HDPE/Nanoclay (80/20/0.5)	Nanoclay/0.5 phr	–	29.6 (+20.8%)	2.82 (+24.8%)	11.8 (-11.9%)	
	PA6/HDPE/PE-g-MA/Nanoclay (80/20/0.5/0.5)	Nanoclay/0.5 phr	PE-g-MA/0.5 phr	32.8 (+33.9%)	2.98 (+31.8%)	13.6 (+1.49%)	

Note: The value in parentheses denotes the % of properties that have changed compared to the control sample (i.e., PA6 blends)

Influence of compatibilizer (MAH-g-PP and EPR-g-MA) and organo-montmorillonite (OMMT) on modulus improvement of the PA6/PP blends and Wear levels of PP and PA6/PP composites vs. load (N) shown in Fig. 2 (A), (B) respectively. Friction coefficients w.r.t. load (N) of PP and PA6/PP composites is shown in Fig. 3.

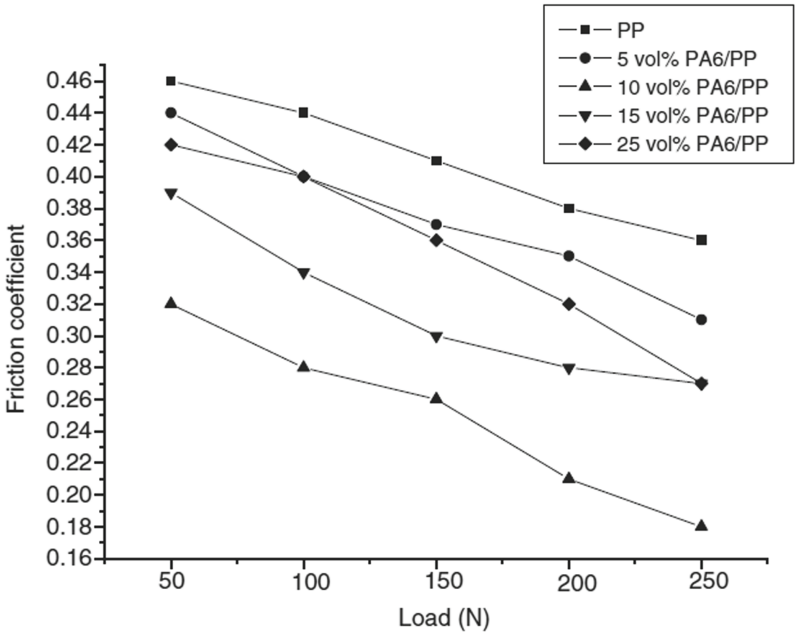

Fig. 3. PP and PA6/PP composites frictional coefficients [39].

6 Worn Surface Morphologies

Scanning electron micrographs (SEM) of a PP/PA6 mix, 5 to 25 vol percent PA6 are shown in Fig. 4 (a) to (e). In all of the compositions studied, visual proof of the interference among PP and PA6 can be found in the blends (Fig. 4(a) (c)), where PA6 is scattered as rounded particles in constant PP matrix. As a result of the spheres coalescing during melt processing, the scattered phase is unstable and acquires a morphology that is coarse. Additionally, there is proof of weak interfacial bonding, with PA6 particles detached from the PP mixture laying free across the worn surfaces and little micro gaps around PA6 nodules.

Fragments of the dispersion span in uncompatibilized mix appear, securely integrated into the mixture with the addition of PA6, and the scattered phase boundaries are becoming indistinct, as shown in Fig. 4 (a) and (b). When the PA6 level is 15 vol%, the. Blends' structural morphology and stability are considerably enhanced.

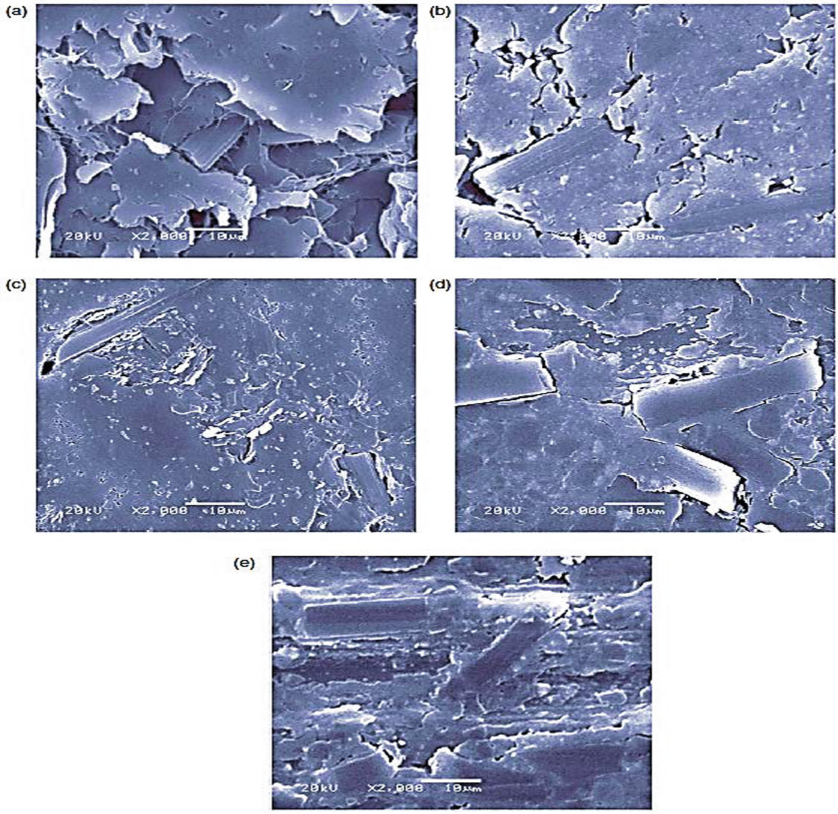

Fig. 4. PP/PA6 blend SEM micrographs **(a)** 5 vol% PA6/PP composite, **(b)** 10 vol% PA6/PP composite, **(c)** 15 vol% PA6/PP composite, **(d)** 20 vol% PA6/PP composite, and **(e)** 25 vol% PA6/PP composite [39].

7 Conclusions

Nanofillers, as studied in this review, are a promising way to improve and extend the characteristics of PA blends in order to create high-performance PA blend-based nanocomposites. Compositions, interfacial interactions, morphologies, nanofillers, and processing techniques all have an effect on the characteristics of PA blend-based nanocomposites. The better characteristics obtained by combining PA blends and nanofiller presents in manufacture of materials for a variety of uses.

The electrical and thermomechanical properties of composites created by the incorporation of nano-scale particles into a polymer matrix are improved. Polymers loaded with nano-scale fillers have better tribological characteristics than those containing micro particles. The wear resistance and friction of these composites are enhanced as the filler concentration increases. Multi-functional fillers can also be used to create composite materials that work well yet cannot be made with only one filler.

A survey revealed that there is growing interest in polymer-based composites for technical applications requiring low friction and low wear. The addition of nano-particles improved the composite's mechanical qualities significantly, according to the survey. Nano-filling materials such as Titanium dioxide (TiO2), Silicon carbide (SiC), Zirconium dioxide (ZrO2), Silicon dioxide (SiO2), Calcium carbonate (CaCO3), Silicon nitride (Si3N4), Zinc oxide (ZnO), Aluminum oxide (Al2O3), and nano copper oxide (CuO) have been employed in a variety of polymers including Polytetrafluoroethylene (PTFE), Poly Ether Ether Ketone (PEEK), Poly methyl methacrylate (PMMA), and epoxy. Tensile strength, Fatigue resistance, wear resistance, fracture toughness, and friction coefficient are among the mechanical qualities that have been improved. According to the study's findings, wear resistance has significantly increased and the coefficient of friction has decreased. A survey revealed that the volume and size percentage of the nano-filling materials affect wear resistance and friction coefficient. Multi-functional fillers can also be used to create composite materials with high performance that cannot be obtained with a single filler.

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