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Abstract Thermoplastic matrix polymer composites have gained commercial success in the semistructural and structural applications. Polyethylene (PE) is one of the most versatile and widely used thermoplastics in the world because of its excellent properties like toughness, near-zero moisture absorption, excellent chemical inertness, low coefficient of friction, ease of processing and unusual electrical properties. This review is designed for comprehensive source of PE-based polymer composites research, including structure and classification of PE manufacturing/processing techniques for PE composites, and it also described different characterization methods for

PE composites. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) characterization methods were used to describe the thermal properties of PE composites. Morphological studies were explained by using scanning electron microscope (SEM), transmission electron microscope (TEM) and atomic force microscope (AFM) techniques. Rheological properties and dynamic mechanical analysis (DMA) are also discussed in this review. X-ray diffraction (XRD) characterization was described in this review to explain crystallinity in PE composites. Hence, this review offers a comprehensive discussion on processing and characterization of PE-based composites.

Keywords Review, Polyethylene, Polymer composites, Processing, Mechanical properties

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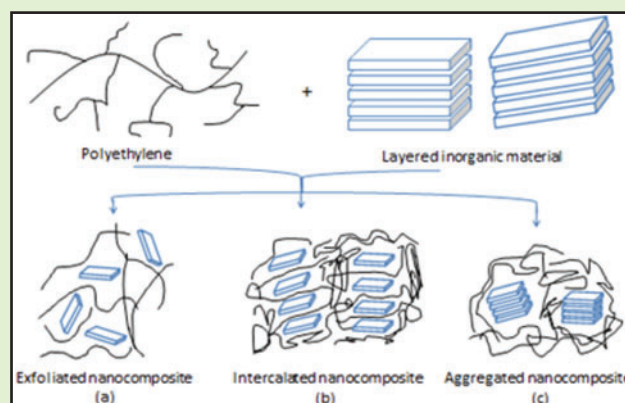
Introduction

During the last few decades, polymer-matrix composites (PMCs) have been of interest to industry and academia, especially in the areas of automotive, aerospace, electronic systems, medical products, civil construction, chemical industries, and other consumer applications. This is because of their superior properties such as high strength to weight ratio, good electrical insulation, ability to transfer load, and easy and inexpensive processing. In polymer composites, the matrix phase is the primary phase, which is more ductile phase and it holds the reinforcement that is the secondary phase. Reinforcements are usually stronger than the polymer matrix that improves the mechanical properties of the polymer composite.

When designed in a proper way, the new combined material exhibits good properties, which can be better than the individual material. Composite materials can be classified in different ways. Broadly, polymer composites can be classified into two groups on the basis of reinforcing material. They are fiber-reinforced polymer (FRP) and particle-reinforced polymer (PRP) composites.

Fiber-reinforced polymer materials consist of fibers, which have high strength and modulus. Fibers can be bonded to the matrix, the interface that is boundary between the fiber and the matrix, which has different physical and chemical identities. Particle-reinforced polymer composites used for reinforcing include ceramics, small mineral particles, metal powders such as aluminium and amorphous materials including polymers and carbon black. Particles are used to increase the modulus and to decrease the ductility of the matrix. They are also used to reduce the cost of the composites.

In the last decade, thermoplastic composite industry has shifted from the use of high performance advanced composites to cost-effective engineering composites by using different fibers. Polyethylene (PE) is one of the most widely used thermoplastic in the world because of its good properties that can be used such as toughness, near-zero moisture absorption, excellent chemical inertness, low coefficient of friction, ease of processing and low electrical conductivity.[1] Polyethylene is

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used in many applications such as pipes, sheets, containers and other products. Polyethylene is used as an electrical insulating material for wire and cable applications because of its high dielectric strength and very low electrical conductivity.[1] The mechanical and physical properties of PE depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight.

New composites that include PE as the matrix is widely used in many applications with better mechanical and physical properties compared to the polymer alone. Polyethylene composites can be used in packaging, electrical, thermal energy storage, automotive applications, biomedical and space applications.[2-9]

Much work has been done on developing the PE composites by using various additives. Improvement of the interfacial bonding strength is one of the major challenges that the scientists face especially for the natural fiber addition.

Polyethylene can be classified into several different categories but mostly do not depend on its density and branching. The main forms of PE are High-density polyethylene (HDPE), High molecular weight HDPE (HMW HDPE), ultrahigh molecular weight density polyethylene (UHMW-HDPE), linear low-density polyethylene (LLDPE), and very low-density polyethylene (VLDPE). These are divided based on density and branching. Generally, the most used PE grades are HDPE, low-density polyethylene (LDPE) and medium-density polyethylene (MDPE). Table 1 shows the density values for some types of PE.[10,11]

Properties of PE composites depend on the molecular weight of PE, experimental conditions and reinforcement types and amounts. It is important to know the structure and properties of PE composites to control and modify the needed properties of each application.

Low-density polyethylene is a branched thermoplastic, have many relatively long braches of the main molecular chain as seen in Fig. 1*a*. This prevents the molecules form packing closely together, irregular packing cause low crystallinity content. Low-density polyethylene is flexible and has low tensile and compressive strength compared to HDPE because of irregular packing of polymer chains. Generally, LDPE is used in food packaging materials, rigid containers and plastic film applications such as plastic bags and film wraps.[10,11] Medium-density polyethylene (MDPE) has mixed properties of LDPE and HDPE properties. Medium-density polyethylene has good impact and drop resistance, less notch sensitivity and has a better cracking resistance than HDPE, but it has lower hardness and rigidity than HDPE. It is softer than HDPE and never sleek as LDPE. Medium-density polyethylene has less branching than LDPE and more

Figure 1   Structure of *a* low-density polyethylene (LDPE), *b* linear low-density polyethylene (LLDPE) and *c* high-density polyethylene (HDPE) types

branches than HDPE. Medium-density polyethylene is typically used in gas pipes and fittings, sacks, shrink film, packaging film, carrier bags and screw closures.[10,11] High-density polyethylene consist of long chains, without major branching, less than 1 side chain per 200 per carbon atoms in the main chain. Long linear chains result in regular packing and high crystallinity because of stereoregularity of the PE molecules. High-density polyethylene is more rigid than LDPE because of the higher crystallinity content. High-density polyethylene is used in many products and in packaging such as milk jugs, detergent bottles, margarine tubs, garbage containers and water pipes.[10,11]

Additional subclasses of PE are LLDPE, VLDPE, UHMWE, etc. Comparison between the structure of some PE types are shown in Fig. 1*a–c*.

Polyethylene composites may contain fibrous and/or particulate rigid fillers. Polyethylene is usually used as a matrix material for preparing the composites with the fillers to improve the properties of the polymer. Natural[12-14] and synthetic fibers[15-17] or particles such as conductive additives[18-20] can be added. Improved properties may include strength, rigidity,

Table 1   Density and MFI of different PE

Type of PE	Density (g cm^{-3})	Melt flow index (g/10 min)
HDPE	0.941–0.965	0.2–3.0
MDPE	0.926–0.940	1–2.0
LDPE	0.915–0.925	0.3–2.6
LLDPE	0.915–0.925	0.1–10.0
VLDPE	0.870–0.914	0.026–0.1

PE: polyethylene; HDPE: high-density polyethylene; LLDPE: linear low-density polyethylene; VLDPE: very low-density polyethylene; LDPE: low-density polyethylene; MDPE: medium-density polyethylene.
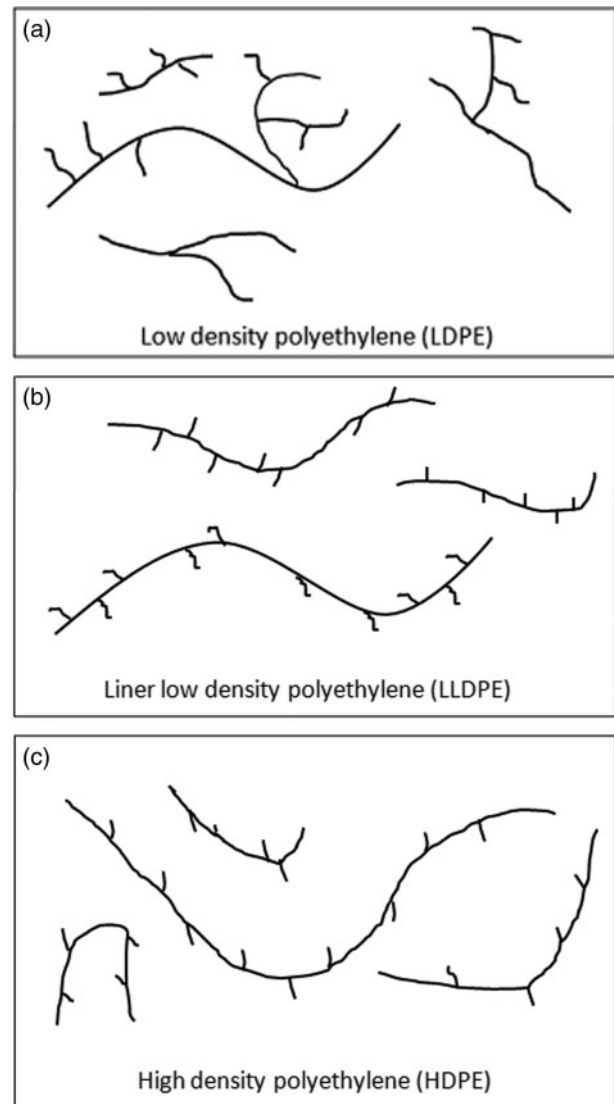
durability and hardness. By the addition of filler, the cost of material can also be reduced.

In this review paper, the authors discuss the different types of processing and characterization techniques used to analyze the PE composites and examples of using these techniques to understand the properties and structure of the composites.

Processing

The first step in preparing the PE composite is processing. Processing can be defined as the technology of converting raw polymer to materials in a desired shape. Polyethylene composites are processed by many techniques such as extrusion, injection molding, compression molding, and rotational molding.

A schematic representation of general processing technique is shown in Fig. 2.

Common methods in processing PE composites

Extruder

Extruder is a versatile machine, which forms thermoplastic items with a uniform cross-section such as pipe, hose, wire and cable. Extruder screws are designed for the polymers that being extruded. Melting, compression and metering sections are basic sections of a screw. In melting part, the solid pellets are conveyed from the hopper and converted into molten polymer. In compression section, the molten polymer is compacted and mixed with the additive (if required). The metering section is needed to produce the desired product cross-section. Twin-screw extruder and single screw extruder are basic types of extruders.

Extrusion process can be used for the compounding of the PE composites. Polyethylene granules or powder with fiber/filler are fed from the hopper to the screw and are then pushed along the barrel chamber to be heated. The processing temperature
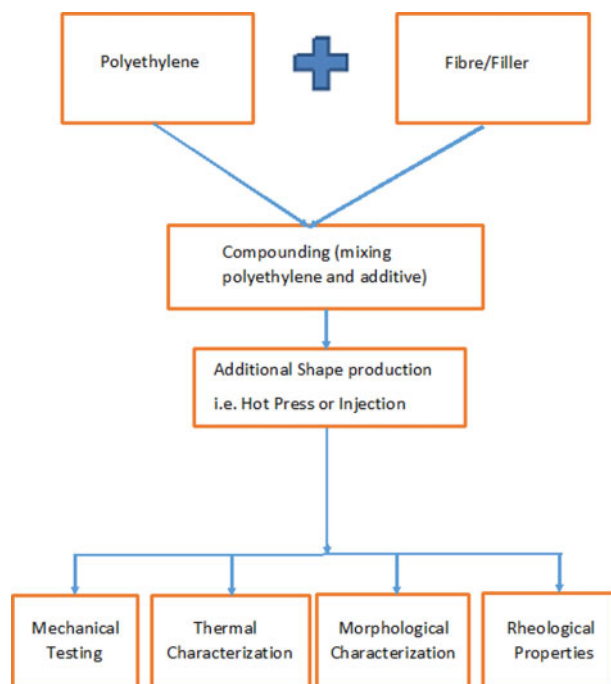
can be in the range of 190–230°C. The mixtures are fed into the hopper of the extruder, compounded, cooled and granulated. The compounded samples are prepared as test specimens by injection molding machine or hot press molding machine.

Injection molding

A large number of products are produced by injection molding. In injection molding process, the compounded samples are preheated in cylindrical chamber to a temperature at which it can flow and then it is forced into a cold, closed mold cavity by means of quite high pressure, which is applied hydraulically through the ram or screw type plunger. The screw rotates to pick up the PE and melt it, mix the melt and deliver it to the closed mold. The screw is then moved forward to force a fixed volume of the molten polymer into the closed mold. After melting, PE is solidified in the cool mold, the screw rotates and moves backward to charge the polymer for the next cycle.

Rotational molding

Rotational molding or rotomolding is one of the most important polymer processing methods for producing stress free, hollow plastic materials. In this process, PE is filled up in a half of mold then closed and subjected to biaxial rotation in an oven at a temperature of 200–400°C. The polymer starts to melt by heat, which is transferred through the mold wall. Once the polymer has melted, the mold is moved out of the oven with biaxial rotation. For cooling the mold, water or air fan can be used. Once the PE is cooled inside the mold, the mold opens and the product is removed. Rotational molding processing has many advantages in terms of product design like hollow products, stress free products, less production time and low cost. Despite the advantages, there are also some drawbacks in this processing method, i.e. the limited moldable material selection. Polyethylene can be used in rotational molding because of its low melting point, low cost and good thermal stability. Reinforcements can be incorporated into the rotationally molded components to increase their mechanical properties.

Compression molding

Compression molding is one of the processing techniques for preparing the PE composites, which contains stationary and movable molds. Polyethylene composite is placed between them and then the mold is closed, heat and pressure are applied to obtain a homogeneously shaped composite. Applied pressure and heat depend on the thermal and rheological properties of the polymer. A preheating time is needed to reduce holding time. Slow cooling or rapid cooling (quenching) can be applied at the end of holding time.

Casting

In this method, PE is dissolved in suitable solvents and mixed with filler by stirring. After the stirring, a continuous sheet of the polymer solution is formed and this liquid material is poured into the mold. A thin film of the polymer is formed on the surface of the mold, which is easily removed by stripping.

After processing, specimens can be cut into the desired size and shape before starting the characterization, i.e. testing the samples.

Figure 2 Flow chart of processing and characterization of polyethylene (PE) composites

Characterization

The following characterization techniques will be discussed in this review: mechanical properties, dynamic mechanical properties (DMA), thermal properties [Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA)], morphological properties [scanning electron microscopy (SEM), transmission electron microscopy (TEM)], surface analysis [atomic force microscopy (AFM)], rheological properties and X-ray diffraction (XRD) properties [small-angle X-ray scattering (SAXS) and wide angle X-ray scattering] of PE composites.

Mechanical properties

Polyethylene composite can be elastic, brittle or glassy depending on the temperature and timescale of the measurements. Mechanical properties depend on the testing conditions such as temperature, load and strain's amount.

Polyethylene-based polymer composites can be tested for mechanical characterization (tensile, flexural, impact and hardness). All tests should be carried out by using international standards such as ASTM standards. In this review paper, tensile, flexural, impact and hardness properties of PE composites will be discussed.

Tensile testing

Tensile tests are applied to observe the strength of the PE composites. A dog bone-shaped specimen (Fig. 3a) prepared according to international standard (i.e. ASTM: D638). The sample can be deformed with increasing tensile load, which is applied along the long axis of material at a constant rate. A stress *versus* strain graph is plotted for glass fiber (GF)-reinforced HDPE, which is shown in Fig. 3b. While stretching the sample, the amount of force (F) applied is measured, and then by dividing the force by the cross-section area (A) of the sample, stress (σ) is obtained.

$$\sigma = \frac{F}{A}. \tag{1}$$

Strain (E) is defined according to the equation below

$$\varepsilon = \frac{\Delta L}{L_o}. \tag{2}$$

$\Delta L =$ the change in gage length of specimen
$L_o =$ initial gage length
Percent elongation (%E) is the extension at break by the original gage length, multiplied by 100

$$\% \text{ Elongation} = \frac{\Delta L}{L_o} \times 100. \tag{3}$$

Universal testing machine (UTM) is suitable for many mechanical tests of PE composites. Tensile properties are usually measured at strain rate of $1–100\% \, \text{min}^{-1}$. The sample is elongated through moving crosshead. The load cell shows the magnitude of the applied load on the sample, where the extensometer measures the elongation of the sample. A standard tensile fractured sample of a PE composite is shown in Fig. 4. During the tensile testing, deformation occurs at the central region of the sample, which contains a uniform cross-sectional area along its length.

Polyethylene composites are used instead of PE in many applications to improve the mechanical properties (such as tensile strength, tensile modulus and flexural strength) of the PE. Various types of additives can be used to improve these properties. Fibers are considered to be effective reinforcing fillers for PE. Various kinds of fibers (such as natural fiber, GF, keratin feather fiber, and metallic fibers) have been widely used to improve the mechanical properties of PE.[20-26] Adding fillers can also reduce the cost of the material. Optimum amount of additive can be reached depending on the required application. Many research publications reported that adding fiber/filler to the PE, improves its tensile modulus and tensile strength.[20-26] Some brief reports are given below.

Thermally reduced graphite oxide (TRG) enhances the tensile strength and modulus of PE matrix.[27] Glass fiber increases the tensile strength of LDPE, HDPE and MDPE polymer matrix.[20] The tensile test results of HDPE/carbon nanocomposites showed that with increasing the carbon nanoparticles contents, the Young's modulus, yield strength of HDPE nanocomposite increased while the strain at fracture decreased. Similarly, the fracture toughness and the strain energy release rate decreased proportional to the carbon content.[28] Sisal fiber improves the tensile strength and tensile modulus of the LDPE.[29] Electrically and thermally conductive composites of PE made with HDPE matrix with nickel particles showed that Young's modulus increased significantly from 606 to 1057 MPa when composites were filled with 20 vol.-% of the filler. Further increasing of the filler content caused no further increase in Young's modulus, probably because of high aggregation of the filler. The stress at break of the composites behaved non-linearly; the low filler content suppressed necking, resulting in a decrease in stress at break, whereas higher filler content (higher than 10 vol.-%) lead to reinforcement of the composites and therefore increased the stress at break.[19]

Fiber dispersion and fiber–matrix adhesion play important role in the PE composites mechanical properties. During the mechanical loading, loads are not directly transferred to the matrix, but the load must be transferred from the matrix to the fibers. This requires good interactions between the fiber and the matrix. This can be controlled by surface treatment of the fibers or by using coupling agents. Chemical treatment of fibers improved the tensile properties of PE composites.[30-33] This is because of the improvement of maximum interfacial adhesion of natural fiber and PE matrix. Properties of PE composites improved with the increase of fiber loading with optimum fiber length.[34]

The most important factors for improving mechanical properties in PE are good interaction and good dispersion of fiber in the matrix.[20,26] This interaction between PE matrix and fiber can be developed without the coupling agents in some fibers/fillers such as E-GF, carbon nanotubes, carbon nanofiber, and graphite.[35-37] For natural fibers, coupling agents or fiber treatment is needed to develop the fiber–matrix interaction. Mechanical properties of pure PE can be improved by adding fiber with/without treatment. Fibers that have higher modulus are used to achieve optimum increase in properties. Integral of the polymer matrix interface needs to be high for efficient load transfer in short FRP composites. Generally, the molten polymer would spread
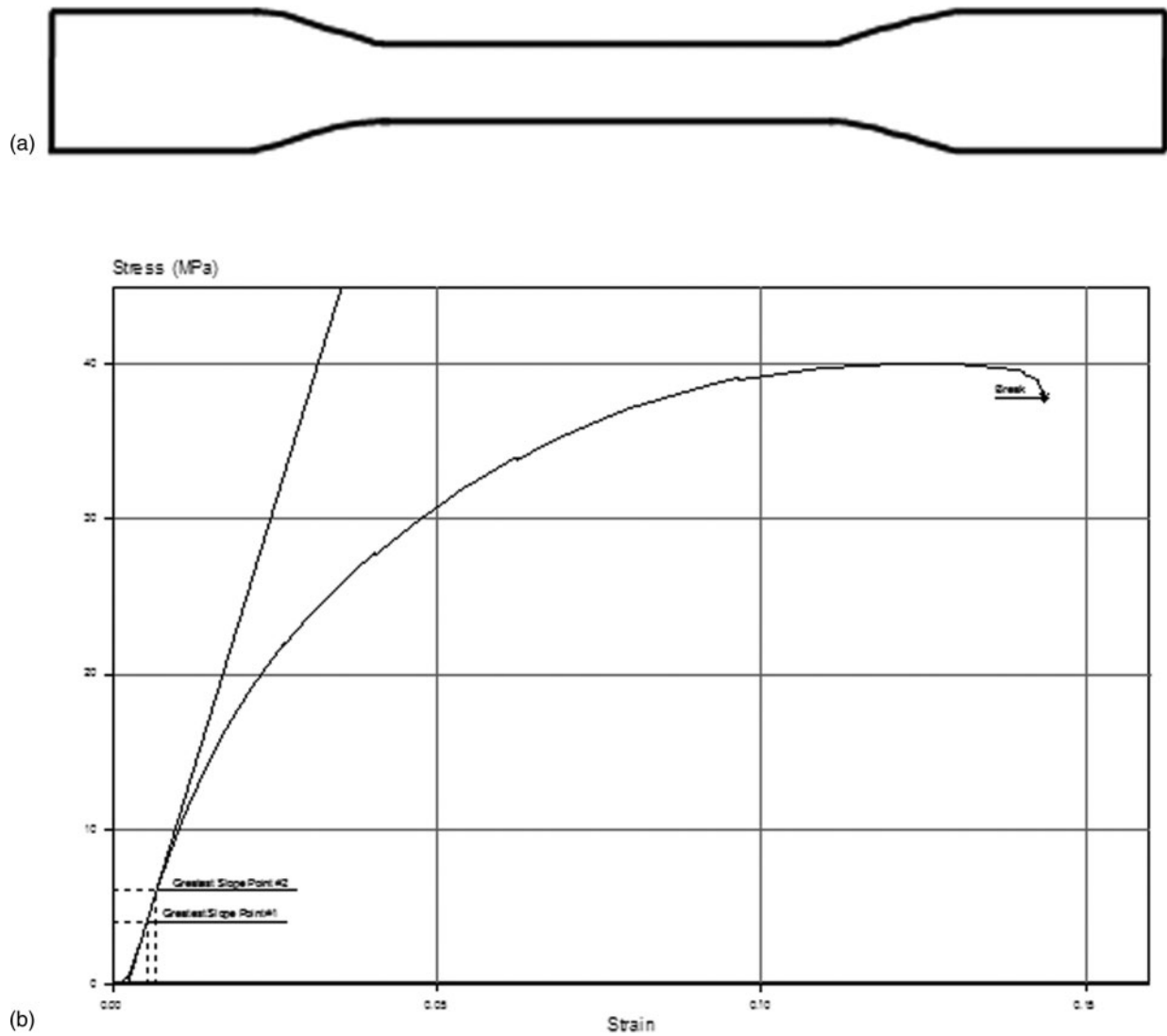
(a)

(b)

Figure 3 *a* Dog bone shape of tensile samples; *b* stress−strain curve of high-density polyethylene (HDPE)/glass fiber (GF) composite

Figure 4 Tensile fracture sample of polyethylene (PE) composite made with recycled low-density polyethylene (LDPE) and wood as a filler

over and adhere to the fiber, thus creating a strong adhesive bond. Cellulosic fibers have hydrophilic surfaces that make them incompatible with hydrophobic polymers. Therefore, chemical modification is required for cellulosic fibers to increase fiber/polymer interactions. The chemical modifications are done by a variety of chemicals such as coupling agents. These coupling agents act as bridge between fiber and the matrix. This bridge must adhere or bond to the fiber and strongly interact with the polymer. In GFs, the coupling agents react with the surface of the glass forming covalent bonds. Without the coupling agent, there is simply adhesion of the polymer to the glass through weak bonding, i.e. Van der Waals or induction interactions.[38]

Organic fibers may offer the possibility to arrange covalent bonds to the matrix polymer either directly or through a similar type of chemical bridge.[39] Covalent bonds are much stronger than induction or Van der Waals interactions. So, covalently bonded interface would be more beneficial for a better composite. Coupling agent, such as silane can be used for treating the fiber, especially organic silane coupling agents to the cellulosic fibers.

The interface region can be cross-linked and has an improved bonding by using coupling agents. Silane is known to be one of the best coupling agents for natural fibers in a polymer matrix. Silane coupling agents improve the mechanical properties of

the PE composites such as tensile, flexural, and hardness and also improve the adhesion between the fiber and matrix.

Vinyl-based silanes are used for PE composites with different concentrations such as 1 and 3% silane-treated wood/PE composites show higher tensile, flexural strength and also shows good fiber–matrix adhesion.[40] 3 wt-% of η-methacryloxypropyltrimethoxy (MPS) and γ-mercaptoproyltrimethoxy (MRPS) improved the tensile strength and tensile modulus of natural fiber-reinforced PE composites.[41] Gamma-aminopropyltriethoxysilane (GS) and dichlorodi-ethyl silane (DCS) were employed for surface modification of radiate pine (Pinus radiata) wood fiber. Obtained results showed that an increase in strength was at fiber contents of 5 wt-% for silane treatments compared to composites with untreated fiber, this is because of the increased compatibility of the fiber surface to PE.[41]

A 20% v/v fiber content of HDPE–henequen fiber composite was prepared to determine the effect of the surface treatments on its tensile properties. In this research, the henequen fibers were treated with 0.033% w/w vinyltris(2-methoxy-ethoxy) silane.[42] Silane treatments improved the tensile strength of HDPE composites.

Grafted coupling agents are also used to develop the mechanical properties of polymer composites. These coupling agents (especially maleated coupling agents) improve the mechanical properties of the polymer composites. Maleic anhydride is one of the most commonly used coupling agents. In general, enhancements in tensile strength and elongation at break when maleic anhydride-grafted matrices are used as a coupling agent is reported.[43] Maleic anhydride-grafted coupling agents improved the bonding between the fiber and the matrix.

Optimum level of fiber content, fiber length and fiber aspect ratio play an important role in tensile properties of PE composites. Because tensile properties improved at certain optimum level of fiber volume%, fiber length and fiber aspect ratio. Optimum fiber loading differ according to the type of fiber and type of PE. The fiber can be damaged during the process, which is normally occur in the melt mixing method and can be avoided by adopting solution mixing process.

One of the reports indicate that 6 mm sisal fiber improved the tensile properties of the LDPE composites and this is the maximum length for improvement for LDPE matrix.[44] The introduction of 40 wt-% distillers grains (DG) in the LDPE matrix increased the tensile modulus by three times compared to the pure LDPE, which is attributed to the higher modulus of the DG compared with LDPE. Whereas tensile strength and elongation at break of the composites decreased with the increasing of DG content.[45] The tensile strengths of the recycled PE composite increased with increasing percentage of the bagasse fiber to a maximum of 20 wt-% UBp (un carbonized) and 30 wt-% CBp (carbonized). The developed composites have the best properties in the ranges of 30 wt-% bagasse particle additions and for optimum service condition, carbonized bagasse particles addition should not exceed 30 wt-%.[46] Date palm wood powder reinforced LDPE composites were prepared with different concentrations of fillers ranging from 10 to 70 wt-%. The Young's modulus of the composites significantly increased with the increase in the filler content in the entire concentration range. The maximum value of 1933 MPa for the composite filled with 70 wt-% of the filler is approximately 13 times higher than that for the neat LDPE.[47]

Extrusion process, such as screw speed can affect the mechanical properties. The study by Siaotong *et al.*[48] determines the optimum values for fiber content by mass (0, 12.5 and 25%), extrusion barrel zone temperatures (75–110–120–130–140°C and 75–120–130–140–150°C) and extrusion screw speed (110 and 150 rpm) for the production of flax fiber-reinforced PE (HDPE and LLDPE) composites.[48,49] According to their statistical analysis, the optimum values were with fiber content of 6.25%, barrel zone temperatures of 75–116–126–136–146°C and screw speed of 118 rpm for LLDPE composites, and fiber content of 5%, barrel zone temperatures of 75–118–128–138–148°C and screw speed of 128 rpm for HDPE composites. The optimum values of temperatures (T) were closer to the higher levels (75–120–130–140–150°C) because lower temperatures result in inconsistent melt of resin that can lead to non-uniform dispersion of the fibers in the composites and eventually lower the tensile strength. The optimum values of screw speed were closer to the lower level (110 rpm). This was because the higher screw speed led to shorter residence time, non-uniform dispersion of fibers, high porosity, and consequently, lowers tensile strength.[48,49] In case of hybrid composites of natural fibers with synthetic fiber, addition of small amount of synthetic fiber to natural fiber increased the tensile strength of the natural fiber PE composites.[50,51] Tensile properties of rotational molding prepared GF-reinforced PE composites were increased under the optimum molding conditions, and the tensile strength of virgin PE could be increased by 54% for a glass loading of 25% by weight.[52]

Flexural tests

Flexural strength is defined as the ability of materials to resist deformation under load. This is used to measure the rigidity of the PE composites. The short beam shear (SBS) test is a flexural test that is performed on the samples of composites to evaluate the value of inter-laminar shear strength (ILSS). It is a three-point bend test, which generally promotes failure by inter-laminar shear. The flexural strength of any composite material is determined using the following equation

$$\sigma = \frac{3FL^2}{2bt^2}. \tag{4}$$

where F is the maximum load (in newtons), L is the distance between the supports (in millimeters), b is the width of the specimen (in millimeters) and t is the thickness (in millimeters).

Flexural modulus is calculated by using following formula

$$E = \frac{FL^3}{4bt^3d}. \tag{5}$$

where F is the maximum load, L is the distance between the supports, b is the width of the specimen, t is the thickness of the specimen, and d is the deflection (in millimeters) corresponding to load F.

A UTM is used to measure the flexural test. This machine is a similar machine that is used in tensile testing, only grips are changed with flexural setup. By using UTM, flexural strength and flexural modulus can be measured for PE composites. Generally, the strength of fiber-reinforced composites depends

on the properties of the constituents and interface interactions. It is well known that for fiber-reinforced composites, the interfacial zone plays a leading role in transferring the load between fiber and matrix, which consequently affects the mechanical properties such as strength. Flexural failure depends mainly on the fiber and matrix adhesion, the increased value of flexural strength in case of treated composite may be because of the increase in effective surface area available for contact with the matrix.[42] Incorporation of synthetic fiber with natural fiber also improves the flexural strength and modulus of the PE composites.[51]

It is observed that interfacial shear strength (IFSS) is related with the treated surface of the natural fibers. The treatment improved the IFSS by double factor, because of the change of the interaction between fiber and matrix, which improves the interface. Flexural strength also improved with chemical treatment of natural fiber (short henequen fiber) with HDPE.[42]

Flexural strength of PE composites improved by adding some bonding agents. Incorporation of natural fiber increases the flexural strength of maleic anhydride-grafted PE (MAPE) matrix.[53] The flexural strength of HDPE/wood flake increases rapidly with an increase in flake content to a maximum at 40%, beyond this percentage the strength decreases. This can be explained by flake distribution, flake wetting and PE penetration.[54] Flexural modulus of the HDPE/wood flakes composites increases with an increase in wood flake content. The increase in modulus is primarily influenced by the amount of flake loading, although the maximum value depends on the processing methods and flow behavior of the matrix.[55]

The presence of the date palm wood powder filler improved the flexural strength of LDPE, which was represented by the flexural stress at peak. The flexural strength of 17.8 MPa for the composite filled with 70 wt-% of the filler was two-times greater than that for the neat LDPE.[47]

The effect of jute content on the bending strength of LDPE/jute composites was studied by Miah *et al.*[55] Their results showed that bending strength of the composites increases with jute content, but it reached maximum value at 20% of jute in the composites. After that, the values decreased with further increase of jute content.

Flexural strength of wood fiber/LDPE composites can be increased with the silane cross-linking. Flexural strength of silane cross-linked composites increased by a double factor compared to the uncross-linked composites.[56]

Flexural strength and modulus of wood/HDPE composites was increased by using different anhydride treatments like maleic, propionic and succinic anhydride.[57] Flexural strength for silver grass fiber -reinforced high-density PE composites increased with the treatment of sodium hydroxide (NaOH) and polymer methylene dipheylisocyanate (PDMI).[58] Maleic anhydride-grafted polyethylene improves the flexural properties of the injection molded wood/HDPE composites and flexural properties increased with the increase of fiber length.[59]

Flexural modulus of GF-reinforced PE composites, which is prepared by rotational molding increased by 40% for a GF loading of 25% by weight.[52]

Impact tests

Impact test can be used to evaluate the fracture characteristics of PE composites, by using two standard techniques, Charpy and Izod impact testing. These methods are used to measure the impact energy of polymers. In this test, pendulum with a massive striking edge is allowed to hit the specimen. The mass and the drop height determine the potential energy of the hammer. Breaking the sample is a two-step process: Energy is needed to create a crack, and more energy is needed to enlarge the crack to failure. The specimen is often notched to improve the reproducibility of the mode of failure. Impact test can be used to determine whether polymer composites have brittle-ductile transition with decreasing temperature. The impact test can be carried out by using ASTM D-256 method.

The incorporation of $CaCO_3$ in the PE increases the impact strength for the entire temperature range of Izod impact tests. This behavior is observed for 5 and 10% $CaCO_3$–PE composite systems.[60] The addition of calcium carbonate to PE increases impact strength in the investigated temperature range of −40 to 70°C and alters the primary micromechanism of plastic deformation from crazing–tearing and brittle behavior in neat PE to particle-induced cavitation and fibrillation in the composite.[60] The impact strength of the composites with compatibilizer is higher than those without the compatibilizer.[61] The impact strength of the wood fiber/PE composites with compatibilizer (MAPE) is 60% higher than those without compatibilizing agent, i.e. MAPE.[62] The addition of MAPE as a compatibilizer, improves the level of adhesion between the wood fiber and the HDPE matrix, which improves the impact strength of the composites. Impact properties of natural fiber composites (from MAPE and hemp fibers) were calculated. Incorporation of hemp fiber decreased the impact strength with increasing hemp content, but GTR (ground tire rubber) addition led to a noticeable increase in impact strength (up to 50% at 10% GTR).[53]

Izod impact strength of the LDPE-rice husk flour (RHF) and LDPE-wood flour (WF) shows a decrease in impact strength with filler loading, because of the increase in the size of the poor bonding between the hydrophilic filler and the hydrophobic polymer matrix. Low-density polyethylene is a flexible polymer matrix, which causes the composites made with this material to have a high-impact strength among unfilled samples, however, as the filler loading increases the brittleness of the composite increases.[63]

Impact strength of polypropylene (PP)/hydroxyapatite (HA) and LLDPE ternary biocomposites shows increase in impact strength with the increase of LLDPE content and impact resistance increases with temperature.[64]

For the composites produced by two-step blending, by adding modified LLDPE, the impact strength is 90% more than that of pure PP/HA composites. Some of the natural fiber lower the impact strength of PE composites. Treated by chemicals or by grafting, impact strength of PE composites can be improved, because of the improved interfacial adhesion.

The effects of electron radiation and compatibilizers on the Charpy impact strength (σ_c) composites made of blends of the recycled polymers: LDPE, HDPE, PP, polystyrene (PS) and poly(ethylene terephthalate) (PET) studied by

Żenkiewicz and Dzwonkowski.[65] They applied high-energy electron radiation with doses up to 300 kGy and adding a compatibilizer of styrene–ethylene/butylene–styrene elastomer grafted with maleic anhydride (SEBS-*g*-MA) and trimethylolpropane trimethacrylate (TMPTA) at 10 and 1 wt-%, respectively. It was found that the addition of SEBS-g-MA (compatibilizer) enabled the increase in the impact strength of composites, and radiation reduced the impact strength of the composites because of the degradation.[65] The compatibilizer increased the impact strength of the polymer but irradiation did not improve the impact properties.

Impact strength of HDPE/rice husk and wood fiber composites was decreased by increase in the fiber loading in HDPE.[66] Irradiation of HDPE with gamma rays reinforced with silane-treated filler (sericite–tridymite–cristobalite) improved the impact strength of PE composites.[67] The chemical modification of the fiber surface improved its adhesion with the matrix. Impact tests demonstrated that surface treatment of PE/rice husk composites improved mechanical performance comparative to the pure polymer matrix.[68] Addition of 5 vol.-% Fe reduced Izod impact strength of HDPE because of large particle size of Fe.[69]

Hardness properties

Hardness is a mechanical property of the material, and it can be described as the resistance of the material to localized deformation. For polymer materials, several types of hardness tests that involve different shaped indenters are commonly used. Usually, hardness for PE composite property is a combination of resistance to penetration, scratching, marring and so on. Mostly, tests are based on resistance to penetration by an indenter pressed into the plastic under a constant load. The Rockwell hardness test uses a spherical steel indenter and the hardness is determined from the penetration depth. For Rockwell hardness, there are two conditions, which are used for polymers. The shore hardness test uses pin-shaped indenters, whereas Barcol indenter is used in Barcol hardness testing. For this test, ASTM D785-08 (2008) and ASTM E 18-11 (2011) methods can be applied for measuring the hardness.

For Rockwell hardness test in samples of PE composites, a total of 10 indentation points can be measured on the samples' surface. Generally, mechanical properties of composites depend on the properties of the matrix and the reinforcements, the interaction between the matrix and reinforcement amount type, arrangement type of the fiber with the composite and fabrication process.

Generally fillers improve the hardness of the PE composites.[70,71] Mechanical properties of HDPE and HDPE containing 5, 10 and 15 vol.-% Fe polymer composites were investigated experimentally. Composite materials were prepared with a twin-screw extruder and injection molding, hardness (Shore D) was determined for each sample. It was found that iron particles had significant impact on the mechanical properties of HDPE. Compared to the mechanical properties of unfilled HDPE, Fe-filled polymer composites showed higher hardness of the composites than those of HDPE.[69]

The hybrid composites of UHMWPE exhibited good hardness than UHMWPE, which is prepared by using bioactive HA, bioinert aluminium oxide (Al₂O₃), and carbon nanotubes (CNTs).[72] The interfacial effect of reinforcement phases has showed the effectiveness of Al₂O₃ over HA and CNT reinforcements, showing synergistic enhancement in hardness and elastic modulus. Weak interfacial bonding of polymer matrix with HA and CNT requires utilization of coupling agents to achieve enhanced mechanical properties without deteriorating cytocompatible properties.[72] Hardness of carbon fiber UHMWPE composites increased with the increase of carbon fiber content.[73]

Hardness can be enhanced by the improved adhesion of the fiber to the polymer matrix. The hardness improved by adding treated fiber to the PE. This is because of better interfacial adhesion, and this adhesion increases the hardness of PE.[74] Addition of 1.0 wt-% of GO (graphene oxide) increased the hardness of the pure UHMWPE.[75] The density and hardness of HDPE/zinc composites were also higher than that for the unfilled polymer.[70]

Valente *et al.*[76] reported that hardness of polymer matrix is found to slightly increase with increasing wood fiber content for both LDPE and PP. The glass ficon causes further improvement of the hardness at high temperatures. The more the basalt content (natural fiber) in the basalt-filled low-density PE composites resulted in higher hardness.[76] The addition of BHA (bovine bone hydroxyapatite) powder enhanced the hardness of UHMWPE matrix.[77,78]

Radiation also improves the hardness of PE composites, because radiation works as a cross-linking agent, which improves the strength and hardness.[79] The bagasse fiber particles added to the RLDPE polymer improved its rigidity and the hardness values of the composites.[80]

Thermal properties

Thermal properties of polymer composites are important especially in selecting processing conditions and applications field. Differential scanning calorimetry and TGA are the techniques that will be described in this review.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry equipment can be used to study the oxidative degradation of PE composites. A standard test involves heating a sample in nitrogen atmosphere to 200°C. The time of the onset of exothermic oxidation is recorded. Alternatively, the polymer samples can be heated in oxygen and the temperature at which the onset of oxidation occurs is reported.

The glass transition temperature (T_g) of the PE composites can be detected by using DSC, as an endothermic shift from the base line is observed in the case of crystallizable polymers.

Figure 5*a* shows the DSC curve for a polymer composite of MDPE. Crystallization temperature (T_c) and melting temperature (T_m) can be seen in this curve.

Generally, for PE composites, DSC measurements are done under nitrogen atmosphere at heating and cooling rates of 10°C min^{-1}. The following procedures can be followed: (i) heating from 30 to 200°C, (ii) cooling from 200 to 30°C and (iii) heating from 30 to 200°C. The percentage of crystallinity (X_c%) of a sample is calculated as follows

$$X_c\% = \frac{(\Delta H_f / W\%)}{\Delta H_0} \times 100 \tag{6}$$
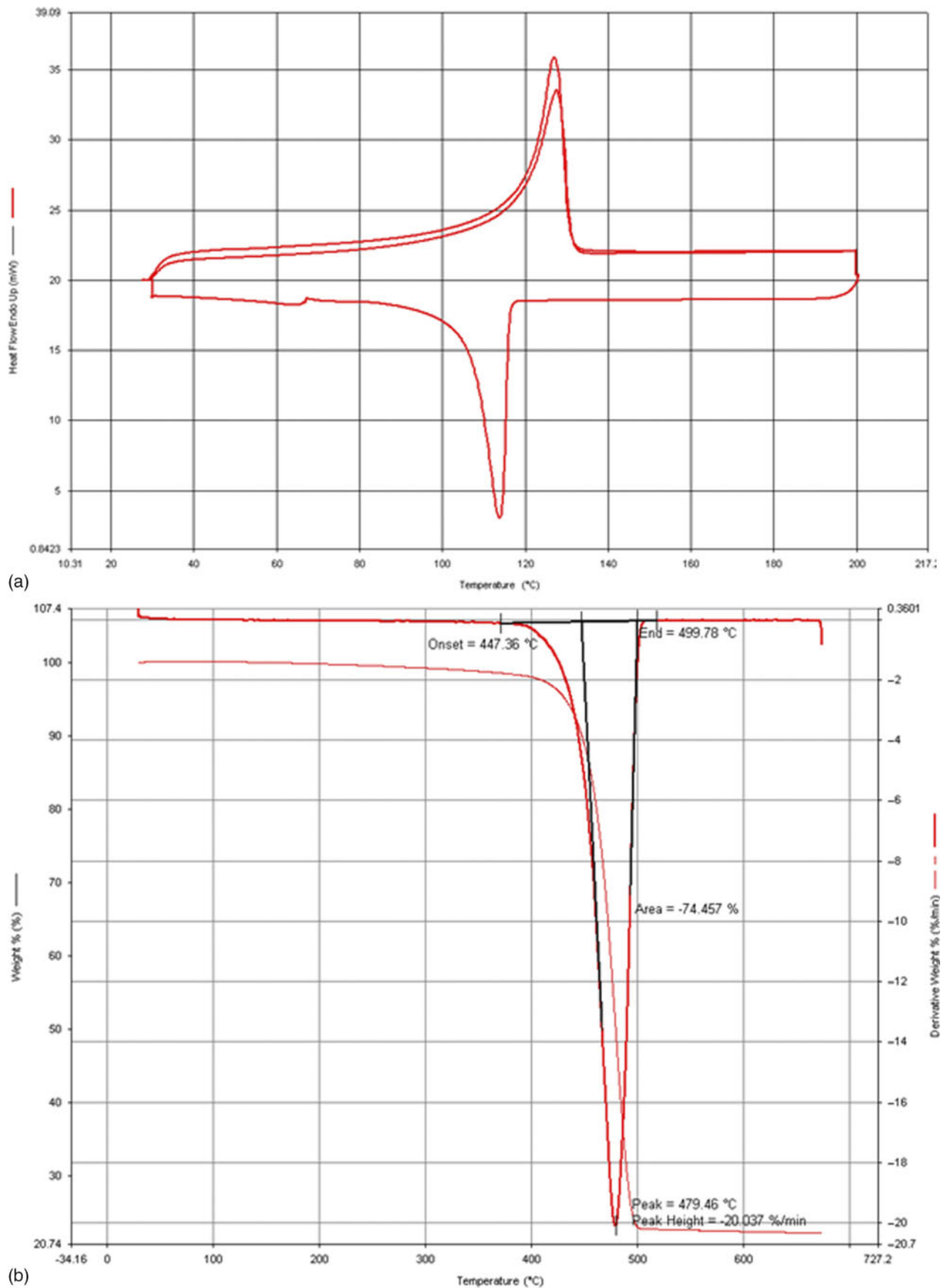
(a)

(b)

Figure 5 *a* Differential scanning calorimetry (DSC) curve of glass fiber (GF)-reinforced medium-density polyethylene (MDPE) composite; *b* thermogravimetric analysis (TGA) curve for GF-reinforced HDPE composites

where ΔH_f is the heat of fusion of PE in a composite determined from the DSC thermogram, ΔH_o is the heat of fusion of 100% crystalline PE and $W\%$ is the weight percentage of PE in the composite.

Crystallization occurs in several stages in PE composites. Nucleation is the first stage, where new small particles (nuclei) can be formed with new phase, which is capable of growing. For polymers, this involves the ordering of chains in parallel arrays. The second stage involves the growth of the crystalline region nucleus.

Incorporation of some fiber/fillers to the pure PE can change the melting and crystallization temperature and the percentage of crystallization because of the change in the nucleating agents.[20,81] The reinforcement effect increases the bulk crystallinity, while the nucleating effect decreases the spherulite size in case of calcium carbonate-reinforced PE micrometric composite.[60] Changes in T_g and increase in crystallinity were observed with hydroxyapatite (HA)-filled HDPE composites.[82] Thermal analysis results of banana fiber (BaF)-filled composites based on HDPE/nylon-6 blends showed that fractionated crystallization of the nylon-6 component in the composites was induced by the addition of both SEBS-g-MA and PE-g-MA.[83] Melting peak becomes broad when LDPE is filled with 5 wt-% of doum fibers.[84] This indicates that, in comparison to LDPE, there were more crystallites formed in LDPE/5 wt-% fiber composites because of the role of natural fibers as nucleating agent.[84] The DSC results of hydroxyapatite (HA) nanoparticles/HDPE composites indicated that the melting temperature and crystallinity were affected by the addition of HA nanoparticles into the matrix.[71]

Aging of HDPE increases the degree of crystallinity compared to non-aged material. The chain scission produces an overall decrease in tie molecules, allowing for lamellar reordering that results in an increase of the crystallinity of HA/HDPE composites. Glass fiber increases the percentage of crystallinity of LDPE, HDPE and MDPE composites.[20] But other kind of fillers (glass, carbon black, carbon nanotube) also increase the percentage of crystallinity and increases the melting temperature and crystallization temperature of PE composites.[20,28] In this case, fibers act as nucleating agents and these produce crystals that increase the percentage of crystallinity of PE composites. The addition of the filler to the PE leads to a decrease in mobility of the crystalline regions and reduces the size of crystallites. The composite in this case will have less perfect crystals.

The mechanical and thermal behaviors of LLDPE pipe with variation in thermal exposure time were studied. The prolongation of thermal exposure time lead to a progressive increase (until 6000 h) in crystallinity, followed by the increase of cross-linking density and the decrease in chain mobility because of thermal oxidation as the exposure time increases.[85]

Lamellar thickness (L_c) values for the PE composites can be evaluated from their T_m values using Hoffman and Weeks's equation

$$T_m = T_{m0}\left(\frac{1 - 2\delta}{L_c \rho_c \Delta H_0 m}\right) \qquad (7)$$

where T_m is the melting temperature (the maximum of the endothermic melting peak); T_{m0} is the equilibrium melting point of a perfect crystalline PE = 145.8°C; ρ_c is the crystalline phase density = 1.005 g cm^{-3}; δ is the fold surface energy = 93×10^{-7} J cm^{-2} and $\Delta H_0 m$ is the enthalpy of melting of a perfect crystalline PE = 288.84 J g^{-1}.[86]

Rectangular-shape UHMWPE samples that was irradiated by gamma rays at room temperature to total doses of 5, 25, 50, 100, 200, and 400 kGy in two different environments, air and nitrogen[86] were studied. Increasing irradiation in a nitrogen environment caused an increase of lamellar thicknesses in first heating, while increasing the irradiation in air caused the formation of two or more new lamellae with higher thicknesses and consequently higher melting points. In the second heating and cooling in air and in nitrogen, UHMWPE exhibited approximately the tendency to slightly decrease the lamellar thickness because of exceeding the melting point and breaking down and dissolution of the big crystals into smaller ones.[86]

The decrease in lamellar thickness in the composites does not affect the crystallinity. There are other factors such as the distribution, length and type of curvature that changes the lamellar thickness of the composites.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a thermal method that measures the weight loss as a function of temperature or time. Thermogravimetric analysis can be used to quantify the mass change in PE composites associated with transitions or degradation processes. Thermogravimetric analysis data show a characteristic curve for PE composite because each composite has a unique pattern reaction at specific temperatures. Thermogravimetric analysis curve can be plotted as the sample weight loss with temperature or alternatively in a different form where the change in sample mass with time is plotted as a function of temperature. Figure 5b shows the TGA of GF-reinforced HDPE composite from room temperature to 750°C.

Usually polymers exhibit a wide range of degradation processes. For example, PTFE decomposes at much higher temperature than PE because of the fluorine substitution. In comparison, PP decomposes at a lower temperature than PE because of the substitution of a methyl group. Fillers increase the thermal stability of PE composites that is needed in many applications.[20,66,77] Carbon nanotubes and some other synthetic fibers increase the degradation temperature of PE.[20,70,81,87]

For natural fiber PE composites, degradation shows two steps because of the addition of cellulose fiber.[88] Thermal stability of cellulosic fiber composites decrease with the increase in fiber loading. NaOH-treated composites had higher thermal stability in comparison to untreated hemp/HDPE composites.[89]

Thermogravimetric analysis thermograms of unirradiated GF-reinforced composites of waste polyethylene (WPE)/recycled waste rubber powder (RWRP) and maleic anhydride as compatibilizing agent revealed enhanced thermal stability than that reported for the blend, whereas comparatively slight improvement has been demonstrated by irradiation.[79]

The incorporation of zinc powder in HDPE can increase the thermal diffusivity and conductivity and decreases the specific heat.[70] The addition of GFs also improved thermal

stability of various PE type samples.[20] By adding different weight percentages of maleated coupling agents, the thermal stability of the PE is improved.[90,91] Thermal stability of LDPE/DG composites decreased slightly by adding DG as the percentage of mass loss at DG's decomposition peak temperature increased monotonically from 4.51 to 15.13% for 10 to 40 wt-% addition of DG.[45]

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis is a thermal analysis technique that measures the properties of materials as they are deformed under periodic stress. Dynamic mechanical properties refer to the response of a material as it is subjected to periodic force. This test is useful for evaluating the stress relaxation and the creep behavior of polymers. This analysis is an important method, which determines the elastic modulus of the material, and its mechanical damping or energy dissipation characteristics as a function of frequency and temperature. Dynamic mechanical analysis instruments have the same design as thermal mechanical analysis instruments, which can be operated in various modes, including flexure (measures the dynamic modulus), tension (measures the glass transition temperature T_g), torsion (measures the melting temperature T_m) shear (examines the relaxation behavior) or compression (investigates the cross-link density).

Dynamic analysis of HDPE/carbon nanocomposites was studied in literature, and the results showed that the storage modulus increased with increasing the carbon nanoparticles ratio and with increasing the testing frequency.[28] The dynamic mechanical properties of LLDPE/nano-SiO$_2$ composites have been investigated in literature.[92]

The results showed that with the increase of nano-SiO$_2$ content, the storage modulus E′ and loss modulus E″ of LLDPE composites filled with untreated SiO$_2$ and amine-triethoxysilane-treated SiO$_2$ increased and the α transition peaks of the composites shifted to lower temperature. The storage modulus E′ of LLDPE composites filled with aminetriethoxysilane-treated SiO$_2$ was lower than the corresponding value for LLDPE/untreated SiO$_2$ composites at lower temperatures, and this trend was reversed as the temperature increased to room temperature.

When SiO$_2$ was treated with vinyl trimethoxy silane, E′ and E″ of the resulting composites were both higher than for LLDPE composites with aminetriethoxysilane-treated SiO$_2$. The interaction between the matrix and the fillers had a remarkable effect on the dynamic mechanical properties of the composites.[92]

Compatibilizers improve the dynamic mechanical properties of HDPE/WF composites.[93] Dynamic mechanical thermal measurements showed that MAPE coupling agent improved the storage modulus of jute fiber/HDPE composites.[91] An increase in the storage modulus of the treated jute fiber/HDPE composites was observed. The tan δ spectra presented a strong influence of fiber content and coupling agent on the α and the η relaxation processes of HDPE. This can be attributed to the segmental immobilization of the matrix chain at the fiber surface.[91]

Storage modulus of hemp fiber-reinforced HDPE composites revealed an increase in the storage modulus of the treated composites compared to untreated samples. The increase in storage modulus was observed up to 40% fiber

volume fraction, but at 50%, it dropped drastically. Silane-treated hemp composites exhibited higher storage modulus compared to NaOH-treated ones suggesting a better fiber–matrix interface.[89]

Dynamic thermomechanical analysis technique has been used to investigate the effect of preheat treatments on the viscoelastic properties of UHMWPE as a function of frequency and temperature. These properties include storage modulus (E′) and loss modulus (E″). The UHMWPE specimens were preheated at 50, 80 and 100°C for periods of 2 and 4 h, respectively. The degree of crystallinity of the UHMWPE has been measured as a function of preheat treatment time and temperature. The results showed a strong dependence of most of these properties on the degree of crystallinity, which is a function of preheat treatment temperature and duration.[94]

In the case of hydroxyapatite (HA)-filled HDPE composites, DMA revealed an increase in storage and loss component indicating enhanced recoverable and non-recoverable energy dissipation with HA content.[82] The dynamic mechanical properties of oil palm fiber (OPF) LLDPE composites is available in literature[94] in terms of storage modulus (E′), loss modulus (E″) and damping parameter (tan δ) in a temperature range of −150°C to 100°C with the effect of fiber content, fiber size and fiber surface treatment on the dynamic mechanical properties. The storage modulus and loss modulus increased with the increase in fiber content and also upon alkali treatment of fibers. The glass transition temperature of pure LLDPE was −145°C, which increased to −128°C for composites with 40% fiber content. Fiber loading in composite and alkali treatment of fiber increased the loss modulus peak. The tan δ peak values decreased upon fiber addition, whereas alkali treatment increased the tan δ peak at all frequencies indicating better impact properties after alkali treatment. The interfacial strength indicator values (B) decreased upon alkali treatment and higher B values were observed for composites containing fiber size range of 75–177 μm followed by 425–840 μm and 177–425 μm indicating decreased order of bond strength. Activation energy was found to be high for composites with 425–840 μm size fraction (80.7 kJ mol⁻¹) followed by 177–425 μm size fraction (72.6 kJ mol⁻¹) and 75–177 μm size fraction (68.1 kJ mol⁻¹). Storage modulus (E′) and damping parameters predicted using different equations were in agreement with the experimental values.[95]

Study of the viscoelastic, rheological and hardness behavior of bioinert HDPE with the addition of HA nanoparticles was studied by Fouad *et al.*[71] They also studied the effects of accelerated thermal aging on the composite properties. Their results showed that complex viscosity increased as the percentage of HA increased because of the restriction of the molecular mobility. The DMA results revealed that higher storage modulus (8.3×10^{11} Pa) could be obtained in the developed HDPE/HA in 30 wt-% compared to neat HDPE (5.1×10^{11} Pa). The changes in the HDPE and its nanocomposite properties because of aging showed that HDPE and its nanocomposites crystallinity increased while the fracture toughness, hardness, wear resistance, storage and loss modulus decreased.[71]

For LDPE with glass bead, the relative storage modulus and the relative loss modulus increased non-linearly at 25°C,

Khanam and AlMaadeed Processing and characterization of PE-based composites · *Adv. Manuf.: Polym. Compos. Sci.*, 2015, 1, 63-79

but the damping reaction decreased. The effects of the glass bead size on the dynamic modulus are insignificant except for individual data points. When the weight fraction of the glass beads is 10%, the values of the glass transition temperature for the composites greatly reduced. The dynamic moduli of the filled system, for which the surface of the glass beads was pretreated with a silane coupling agent, are greater than that of the one in which the glass beads are untreated in the composites.[96]

Researchers developed the HDPE/carbon nanofiber composites and studied their dynamic mechanical properties. The results showed dual increase of storage modulus and loss modulus at different speeds. It was found that the composites showed a higher damping than pure PE, because of the viscoelastic energy dissipated as a result of fiber–fiber friction and fiber–PE interaction. The composites showed higher viscosity than pure PE and the complex viscosity increases along with the speed. The complex viscosities of nanofiber composite samples converged to that of pure PE at high temperature, which indicated that at high temperatures, the viscous behavior was dominated by the semi-crystalline matrix.[7]

Morphological properties

Transmission electron microscopy, SEM and AFM are common techniques for analyzing morphological properties of composites, and they will be described in this review.

Transmission electron microscopy (TEM)

Transmission electron microscope is similar to the light microscope but it is illuminated by an electron beam instead of light. The instrument works under vacuum to restrict the scattering of electron beam by air. The resolving power of TEM approaches 0.1 nm by adjusting the power of an intermediate lense. Transmission electron microscope has a high resolution with rich information of the structure details. Transmission electron microscopy is a very effective technique to study the morphology of polymer samples. Transmission electron microscopy also identifies the crystalline regions of polymer and the spherulitic structure of PE composites.

Transmission electron microscopy can be used to study the dispersion of different clays in PE (see an example in Fig. 6).

One important limitation of the TEM is the need to use thin layers in order to allow the electrons to penetrate the sample without losing energy. Composite samples can be microtomed as very thin slices below 200 nm by a cryomicrotome with a knife in liquid nitrogen.

Transmission electron microscopy images can be used to calculate the average thickness of a stack of additives. Exfoliated structure of the composite can be identified as well as the intercalated tactoids. Even at highly exfoliated regions, 2–3 clay layers can exist in LLDPE.[97,98] Aspect ratio can also be calculated by using TEM.

Agglomeration and dispersion of additives can be examined by TEM as the TEM picture can show the dispersion of the particles in the PE.[99] Mohan and Kanny [99] investigated the dispersion of the clay particles in HDPE matrix and showed that gMA addition acts as a compatibilizer between clay and matrix phase and gives the better dispersion. This improvement of the dispersion can be seen also in LLDPE
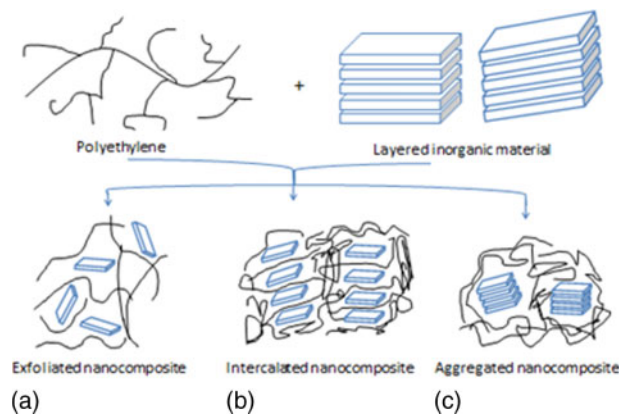

Figure 6 Diagram of clay morphologies of polyethylene (PE) composites *a* exfoliated; *b* intercalated; *c* aggregated

with HNT nanotubes when the polymer is grafted, which was observed by Jia *et al.*[100]

Various morphologies and level of aggregation of the CNT in PE can be identified through TEM photos, and it is possible to distinguish individual multi-walled carbon nanotubes (MWCNTs) and the crystallinity of the tubes.[101]

The relation between the nanostructure and properties can be studied by TEM as done by McNally *et al.*[18] who studied the aspect ratio of MWCNT in a PE/MWCNT composite, which is prepared by twin-screw melt compounding.

The distribution of graphene layers in the LLDPE matrix polymer was examined by TEM.[102] Transmission electron microscopy image showed that the graphene nanosheets were dispersed homogeneously in the LLDPE matrix. The good dispersion of graphene sheets should be because of the good interfacial interaction between the modified graphene and polymer matrix.[102] The exfoliation of the silicate layers and also its thickness in PE were observed using TEM.

Scanning electron microscope (SEM)

The SEM shows the surface of the polymer composites. In the "scanning" process, the electron beam interacts with the surface region and generates secondary electrons from the composite. Backscattering of the incident electrons is also available. The intensity of the secondary or back-scattered electrons is measured and compared to the scanned electron beam. A contrast picture relates to the surface of the composite as appeared on the screen.

Scanning electron microscope has been used in a broad range of polymers and composites studies and applications, including surface roughness, adhesive failure, fractured surfaces, networks and phase boundaries in blends.

Scanning electron microscope can be used to reveal the interfacial region and identify the fractured surface after tensile testing. Scanning electron microscope of hydroxyapatite (HA)-reinforced HDPE composites showed that HA particles are well dispersed in PE.[71] Scanning electron microscope has been used to study the morphological properties of glass beads-filled LDPE composites, and the results showed good interfacial adhesion between the additives and the matrix as well as good particle distribution in the matrix.[96] For individual nanotubes in HDPE, SEM showed that some were scattered in the matrix

and most of them were clumped together in aggregates in HDPE/MWCNT composites.[103] Scanning electron microscope was employed to demonstrate the electrostatic adsorption of graphene on the surface of UHMWPE powders in UHMWPE/graphene nanosheet composites.[104]

Scanning electron microscope photos can be used to show the fiber pull out and also it measures the particle size of the fillers. The pulled out fibers in the SEM photos detect a poor adhesion between the fiber and the matrix. The crystallinity of the PE matrix can affect the bonding between the fiber and the matrix.[20] The LDPE has lower tensile strength as the network formed between the fiber and the chains with long chain branching (LCB) is destroyed at high loads and more pull outs is noticed. Figure 7 shows the adhesion/ pull out of the GF in LDPE matrix.

Fiber pull out observed in SEM of HDPE–GF fracture surface.[99] The SEM of the matrix fracture surface shows brittle and smooth fracture features. In HDPE–GF–nanoclay composites SEM, matrix shows branched cracks and fracture surface, the branched crack surface have bright regions. Matrix fracture surface shows smooth crack surface in HDPE–GF–microclay composite system.[99]

The high branching improves the strength and strain values of the composites. The presence of interfacial interaction between filler and polymer indicated stronger mechanical properties.

Agglomeration and non-homogeneous dispersion can be detected by SEM. Rice husk ash distribution in HDPE with and without compatibilizer have been studied.[13] The compatibilizer with its polar groups improved the properties, 18% increase in tensile strength compared to virgin HDPE was noticed. Rotationally molding process can increase the adhesion between the filler and the matrix in talc and mica with maleic anhydride-modified PE.[52]

Atomic force microscopy (AFM)

In this type of microscopy, a cantilever with a sharp force sensing tip interacts with the surface. The interaction force induce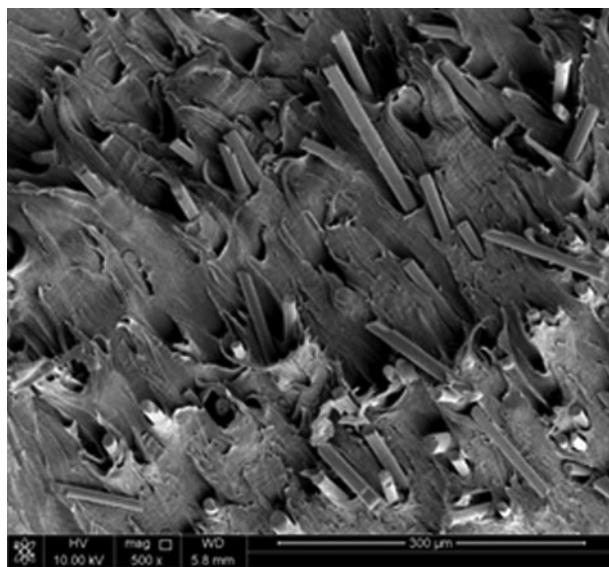s a deflection in the cantilever and a topographic image surface can be arranged through the variation of the surface. Surface roughness and morphology can be seen and analyzed. This equipment consists of a very fine tipped probe, which is positioned above the surface of the sample.

Measurements can be taken in two different modes, i.e. contact mode and tapping mode.

1. Contact-mode AFM: In this case, the feedback signal is received because of the deflection of the cantilever.
2. Tapping mode AFM: In this case, the cantilever vibrates at a large oscillation amplitude near a resonant frequency and upon the approach of the surface, the oscillation amplitude decreases. An example of an AFM photo of LLDPE mixed with wax is shown in Fig. 8.

Plasma treatment of wood/PE composites[105] showed that increasing the discharge power increases the number of the sharp peaks to be grooves at 800 W, which is very important for adhesion properties. After plasma treatment, the content of carbon decreased and an increase in oxygen element was observed.

Atomic force microscope images can show the spherulites texture as seen in LDPE/Al nanocomposites. Atomic force microscope showed that lamellar bundles are arranged in disordered way, and it is difficult to resolve the individual spherulites.[106] This is because of the hindering effect of the nanoparticles for the movement of the PE chains.

A large number of non-spherulitic objects observed in single-walled CNT/HDPE nanocomposites were observed using AFM, which gives the supermolecular structure that is built from crystalline sheaf-like lamellae that mostly originated at the walls of the nanotubes and spread three-dimensionally from those centers.[107] Alignment of the fibers can be seen in the AFM photos as seen by McNally *et al.*[18] The extruder die induced the alignment of MWCNTs, which reduce the entanglements in the PE.

Atomic force microscope can be used also to measure the thickness of the reduced graphene sheets that added to PE.[102]

Rheological measurements

The rheological behavior of polymers involves several widely different parameters, which can be related to some extent to different molecular mechanisms, which are viscous flow, rubberlike elasticity, viscoelasticity and Hooken elasticity.

Many parameters affected the viscoelastic properties of polymer including temperature, pressure, and time.

By adding fillers to the neat polymer melt, the rheology of the polymer is changed as a result of the effect of the melt processes and the properties of the tailored product. The following properties of the fillers can affect the rheological properties: shape, weight percentage, size and adhesion properties.

Particle interactions increase the non-Newtonian range, and it causes a lower shear rate than the unfilled polymer melt. Filled polymer composites have a higher viscosity at low shear rates.

Dynamic viscosity of LDPE, MDPE and HDPE showed similar trends in the effect of adding GF on polymer viscosity.[20] The incorporation of GF at 20% level (high level and high stress) disturbs the mobility of the polymer chains

Figure 7   Glass fiber (GF)/low-density polyethylene (LDPE) surface image after tensile testing
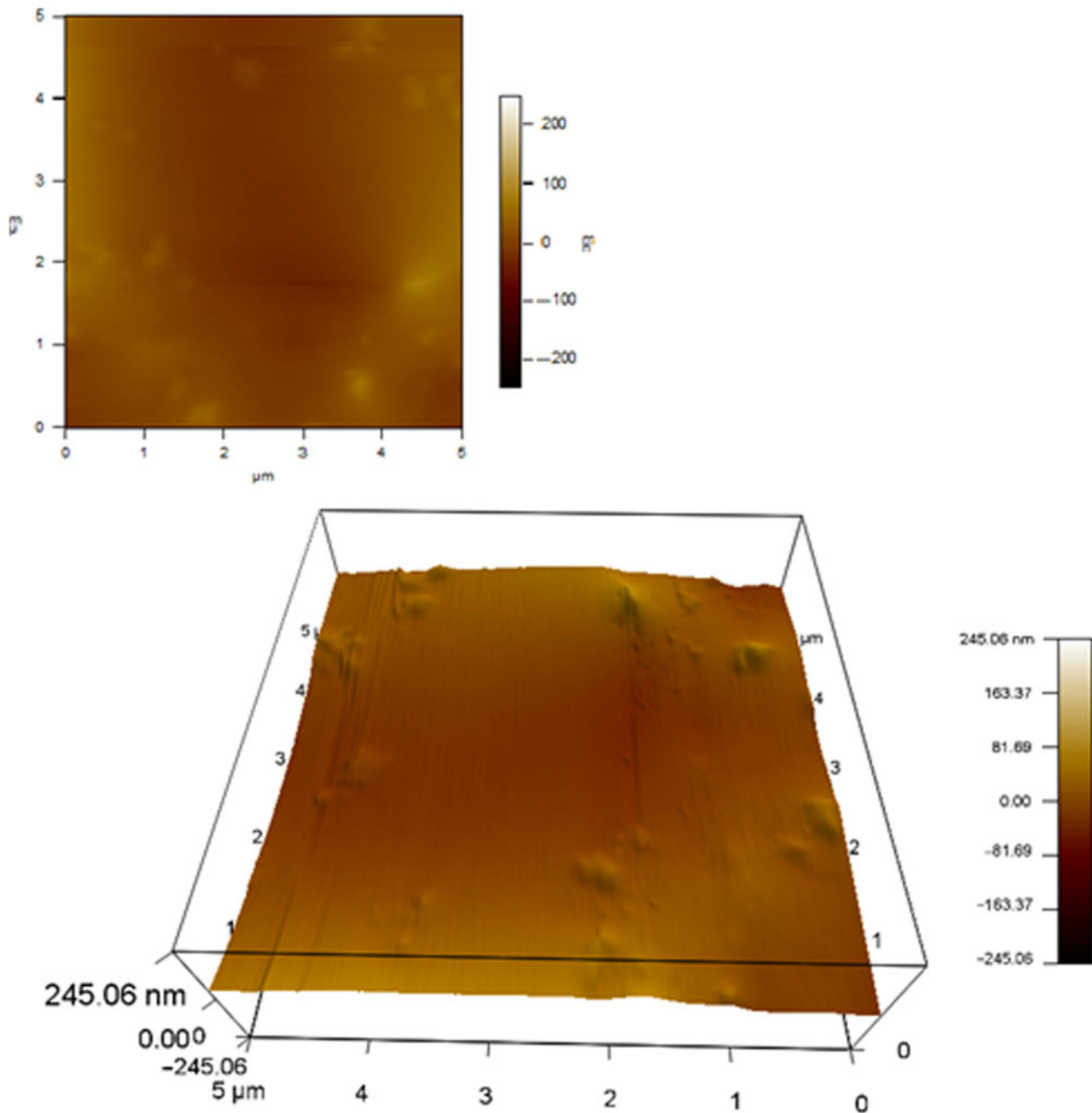
Figure 8   Atomic force microscopy (AFM) of linear low-density polyethylene (LLDPE) mixed with wax

in the melt and hence increases the complex viscosity.[20] LDPE, which has LCB, has lower storage modulus values, but with the addition of 20 wt-% of GF, the storage modulus at low frequencies increases to higher values compared to the less-branched polymers. Low-density polyethylene composite, which had higher storage modulus at low frequencies, falls behind at high frequencies because of the disentanglement of the LCB as the sample is stressed. Owing to the disentanglement of the LCB, the gap between LDPE composites and the others is larger when samples are subjected to more shear (higher frequencies). This is because the disentanglement causes a steep drop in viscosity in what is called "shear thinning."[20]

Wood particle/HDPE composites melt-blended by a twin-screw extruder were characterized by a Haake micro compounder, torque rheometer, capillary rheometer, and rotational rheometer.[108] Results showed that removal of lignin and/or

hemicelluloses changed the crystallinity and microstructure of cell walls. These changes in cell wall composition and morphology altered the melt torque, shear stress, viscosity, and storage and loss moduli. Specifically, the melts viscosity decreased in this order αC/HDPE > HR/HDPE > WF/HDPE > HC/HDPE. This demonstrates that the composition of cell walls substantially affect the rheological behavior of wood particle/HDPE composites.[108]

Low-density polyethylene (LDPE)/DG composites prepared by melt extrusion[45] were investigated by dynamic rheological measurements. Dynamic rheological analysis showed that the storage modulus increased for all composites compared to LDPE, indicating that the addition of DG fillers to LDPE is beneficial to improve stiffness.[45]

Mechanical and rheological properties of CNT/PE composites were studied by Xiao *et al.*[109] At a higher MWNT content, the plateau vanishes and the composites show a strong

shear thinning effect. The viscosity almost decreases linearly with increasing the frequency, but the reduction gradient becomes greater when the MWNT content increases. As a result, viscosity difference of the composites and the pure LDPE at the high frequency region becomes small. Tan δ, where δ is the phase angle, is very sensitive to the structural change of the materials and decreases with increasing CNT content, viscoelastic peak occurs at the frequency of about 1 rad s^{-1} and disappears with increasing the CNT content, showing that the material becomes more elastic. This is also a characteristic when a viscoelastic fluid experiences a fluid–solid transition.[109] The curving and coiling of MWNTs plays an important role in the enhancement of the composite modulus. It was also found that the materials experience a fluid–solid transition at the composition of 4.8 wt-%, beyond which a continuous MWNT network forms throughout the matrix and in turn promotes the reinforcement of the MWNTs.[109]

The rheological data provide a further understanding of the polymer–fiber interaction, in the melt state. The addition of GFs by 20% disturbs the mobility of polymer chains in the melt and hence increases the initial complex viscosity. This type of behavior for non-Newtonian fluids is in agreement with the literature for fiber-reinforced polyolefins such as HDPE and LDPE. A high loading of GF increases the storage modulus of all types of PE translating the reinforcement effect of GF.[20]

X-ray diffraction

X-ray diffraction technique is used to identify the following: preferred orientation, crystalline areas, and grain size of crystalline materials.

If the structures are arranged in an orderly array or lattice, the interferences of the electromagnetic radiation of the X-ray with the structure are sharped so that the radiation is scattered or diffracted only under specific experimental conditions.

X-ray diffraction techniques are useful for semicrystalline polymers and reorganization of crystalline phases (polymorphism) of polymers. X-ray diffraction is a primary technique to determine the degree of crystallinity in polymers because polymers are not 100% crystalline in nature. The size of the crystallites can be determined by using the Scherrer equation. X-ray diffraction is preliminary tool for the determination of crystalline orientation through the Hermans orientation function. Chain confirmation is given by XRD. For example, the repeat distance of 2.55 A in the crystals of PE is readily identified with a single repeat unit in the planar zigzag conformation.

Deformation behavior of PE/silicate nanocomposites was studied by real-time wide-angle X-ray scattering (WAXS).[110] The results confirmed the exfoliation of the silicate layers of organically modified montmorillonite clay throughout the maleated PE (PEMA) matrix, but the SiO$_2$ particles were not well dispersed in the matrix. The long axes of exfoliated silicates were aligned along the tensile axis during deformation and showed no sign of cavity formation in the matrix. During the tensile deformation, the crystallographic changes of pure PEMA and composites containing organically modified montmorillonite clay, and SiO$_2$ were investigated using the real-time X-ray scattering. The organically modified

montmorillonite clay and SiO$_2$ particles in composites caused little effects on the initiation of martensitic transformation, but they effectively inhibited the orientation of PE lamellae in the tensile direction. The lamellar fragmentation was higher in PEMA/organically modified montmorillonite clay than in PEMA/SiO$_2$, while the former was less effective in inhibiting lamellar orientation.[110]

Genetti *et al.*[111] studied the WAXS and crystalline orientation in reticulate-doped polymer composites. Polyethylene was doped with the CTC tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) to prepare the composite. Wide-angle X-ray scattering measurements were done on samples that were uniaxially stretched at 80°C and cooled to room temperature. These experiments showed a smaller incremental increase in crystalline orientation with increasing TTF–TCNQ. In the unoriented composites, increasing TTF–TCNQ loading had no effect on PE crystallinity; however, the increase in crystallinity caused by uniaxial stretching was decreased by the presence of TTF–TCNQ.[111]

Small-angle X-ray scattering techniques were used for carbon black reinforced PE composites.[112] The experimental results indicate that the CB has no significant effect on the crystallinity and the long spacing of crystalline domains of LDPE.

Wide-angle X-ray diffraction (WAXD) of MWCNT-reinforced PE composites showed that the MWCNTs are very well distributed and dispersed in the PE matrix.[18] There is a broadening and reduction in intensity of the 110 and 200 PE reflections with increasing MWCNT concentration, indicative of altered amorphous and crystalline phases.

X-ray diffraction results of calcium carbonate and PE composites were studied, and the results showed that the adoption of calcium carbonate in PE has two primary effects: the reinforcement and the nucleating effect. The reinforcement effect increases the bulk crystallinity and modulus, while the nucleating effect decreases the spherulite size.[60]

X-ray diffraction of composite panels using virgin and recycled high-density polyethylene (VHDPE and RHDPE) and five types of natural fibers including four rice straw components (i.e. rice husk, rice straw leaf, rice straw stem, and whole rice straw) and wood fiber as control were studied.[62] The particular recycled HDPE resin and its composites had significantly better moduli and strength properties compared to the virgin HDPE systems because of additives used during initial processing. X-ray diffraction experiments showed that introducing fiber to HDPE matrix did not change the characteristic peak position, but the fiber increased crystalline thickness of HDPE system.[66]

Crystal size of HDPE, hydroxyapatite and hydroxyapatite-filled HDPE composites is measured by using WAXD.[82] Wide-angle X-ray diffraction also identifies the crystallinity of the hydroxyapatite-filled HDPE composites, which shows that hydroxyapatite content increase the crystallinity of the PE.[82]

Conclusions

Polyethylene is one of the most popular thermoplastics in the world. Polyethylene is generally known in the following types HDPE, LDPE, and LLDPE. This review describes the processing and characterization of PE composites by different methods.

Many procedures can be used to prepare new composites of PE as a matrix and fiber/filler additive. This includes, but not limited to extruding, hot press and injection molding. Mechanical properties such as hardness and tensile strength can be improved by the addition of the fiber/filler. To better obtain fiber/matrix interface, coupling agents are advised to improve the properties of the PE composites. By applying optimum fiber loading, fiber length, aspect ratio, good mechanical properties of PE composites can be achieved. Additives have also effect on dynamic mechanical properties of the PE composites. Thermal analysis especially the DSC can be used to study the change in the melting and crystallization temperature of the PE because of the addition of the fiber or filler. Fiber/filler can change the thermal decomposition temperature of PE, which is confirmed by TGA.

Fiber–matrix bonding, dispersion, agglomeration, fiber pull out, and filler size can be observed by using SEM. Transmission electron microscope is useful for the smaller scale up to nano-levels and shows the spherulitic structure, agglomeration, thickness of a stack of additives and also shows the exfoliated structure. Atomic force microscope can be used to study the surface morphology of the PE composites and shows the alignment of fibers and spherulite structure.

Fiber influence on rheological properties of PE, percentage of crystallinity and lamellas thickness can be calculated by using both DSC and XRD for PE composites. Effect of fiber on crystallization and lamella thickness was measured by using XRD.

Conflicts of Interest

The authors declare no conflicts of interest.

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