

Plasma Modification of Polyolefin Blends and Composites



H. Akhina, Arunima Reghunadhan, Jiji Abraham, P. S. Sari,
and N. S. Baneesh

Abstract Polyolefins are very important commercial polymers. They represent a broad class of materials which include different grades of polyethylene(PE), poly(propylene), polystyrene, polybutylene, and so on. This chapter is discussing about the blends and composites of different types of polyolefins. They are the class of thermoplastics from which a large percentage of blends and composites are made. The polyolefin-polyolefin blends and composites are itself a large category. In addition to that they have been added to other thermoplastics like PVC, PTT, PC, etc. and elastomers such as natural rubber, SBR, NBR, EPDM, etc. and thermosets like epoxies. Generally they hold a degree of immiscibility with most of the other polymers and in order to enhance miscibility and decrease the interfacial tension, fillers and compatibilizers are preferred. Other than these, the surface functionalization is preferred in most of the cases. Plasma modification is one such method to introduce surface functionalities in an otherwise non-polar material. High voltage electric current will be applied to gases such as oxygen, argon, ozone to make them ionized. The resultant state contains a large number of different species such as ions, atoms, molecules, electrons, neutral species, etc. These plasma are effective in modifying the surface of polyethylenes. The blend components are either pre-treated or post treated with plasma to enhance the interfacial adhesion.

Keywords Polyolefin · Blends · Compatibilization · Interface · Plasma

H. Akhina · A. Reghunadhan
School of Energy Materials, Mahatma Gandhi University, Kottayam, Kerala 686560, India

Postgraduate Department of Chemistry, Milad-E-Sherif Memorial College, Kayamkulam,
Alappuzha, Kerala, India

J. Abraham
Postgraduate Department of Chemistry, Vimala College, Ramavarmapuram, Thrissur, Kerala,
India

P. S. Sari (✉) · N. S. Baneesh
Department of Polymer Science and Rubber Technology, CUSAT, Kochi, Kerala, India

1 Introduction

Poly olefin plays a significant role in modern industry and it constitutes the most widely used plastics today, especially polyethylene and poly propylene. Polyolefin can be regarded as the as the most widely produced commodity plastics also and its production exceeds several million tonnes. The usage as well as researches on polyolefin based blends and composites have increased drastically because of their new applications in medical, packaging, automobile, electronic and industrial fields [1–5].

The blending of polyolefin with other polymers leads to the improvement of its native properties as well as leads to the cost effect products having high end use. Polyolefin based blends possess many advantages such as low density, low cost ease of processing and improved chemical, physical and mechanical properties. Polyolefin blending requires the knowledge of miscibility, crystallinity and other features components. Polyolefin can be studied under two distinct headings such as polyolefin-polyolefin blends and polyolefin-non polyolefin blends. Polyolefin blends are usually prepared by in- reactor blending or non reactor blending [6]. The former method involves the blending of polyolefin different polyolefin in the polymerization reactor and the latter involves the mechanical blending of the premade polyolefins with other polyolefin or non poly olefins in compounding extruders. The hydrophobic nature of the polyolefin usually leads to the poor miscibility which in turn results in phase separation and that can be solved by the use of suitable compatibilizer. The compatibilizer reduces the interfacial tension between the polymers and strengthen the interface.

Polyolefin composites are the polyolefin materials containing at least one non polymeric reinforcement of organic or inorganic origin. The reinforcement may be micro or nano in size, natural or synthetic, which includes glass fibers, natural fibers, carbon based nanomaterials, clay minerals, magnesium hydroxide, aluminium hydroxide, calcium carbonate, titanium dioxide, silica [7–11] etc. In the next section, we have discussed briefly about the fiber reinforced polyolefin blends and composites.

2 Fibre Reinforced Polyolefin Blends and Composites

Fiber reinforced polyolefin blends and composites are on of the most popular type of materials in which the continuous thin fibers are embedded in the polymer matrix. Fiber-reinforced polyolefin blends and composites offer not only high strength to weight ratio, but also provides exceptional properties such as high durability; stiffness; damping property; flexural strength; and resistance to corrosion, wear, impact, and fire. A great number of research and developments has been done with different

fibers on the effects in the origin, type, surface modification, loading and orientation [12–15]. In the recent years natural fibers attains more attraction among the researchers owing to the availability, cost effectiveness, environmental friendliness etc.

Recently, polypropylene-high density polyethylene-coir coconut fiber (PP-HDPE-CCF) biocomposites were prepared as alternative materials for the design and manufacturing of sustainable products. The addition of CCF generates an increase of the tensile and flexural modulus up to 78% and 99% compared to PP-HDPE blend. This stiffening effect is attributed to the decrease in the polymeric chain mobility due to CCF and the higher mechanical properties of the CCF compared to the polymeric matrix [16]. Old Newspaper Recycled Fibers-Reinforced Polypropylene Composites were prepared by adding Maleic anhydride as a coupling agent in order to increase the strength of the interface between the matrix and the reinforcements. The prepared composites exhibit increased the impact strength of the composites and decreased the water uptake. Impact strengths of 21.3 kJ/m³ were obtained for a coupled composite with 30 wt % reinforcement contents, which is a value higher than that obtained for glass fiber-based materials [17, 18]. Even though the natural fibers have many advantages, they suffer from lower modulus, lower strength and relatively poor moisture resistance when compared the synthetic fibers. Glass fibers (GF) are also used as reinforcement agent used in polyolefin based blends and composites. The effect of fiber content on the stress relaxation of polypropylene/glass fiber composites was conducted with and without coupling agents was studied [19]. Another interesting study demonstrates the preparation and properties of glass fiber-reinforced polypropylene composites using different fiber loading and different compatibilizers. Toughness, crystallization ability and heat resistance were all enhanced when compared to the pure polymer matrix [20]. It has been reported that the strength and toughness increases three times and the interfacial strength duplicates in PP/GF composites prepared with *in-situ* polymerized fibers [21].

Intermixing of natural fiber with stronger and more corrosion resistant synthetic fibers such as glass fiber can lead to the synergetic effect. Literature review reveals that the addition of a small amount of glass fiber enhance the durability of bamboo-fiber reinforced polypropylene [22]. Recycled low density polyethylene composite materials having hybrid coconut/glass fiber as reinforcement were fabricated to enhance the desired mechanical properties for car bumper as automotive structural components [23].

3 Interfacial Adhesion in Polyolefin Blend System

Polymer blending is a cost effective and easier way to develop materials for high performance applications. Generally, blends are of three types-miscible, immiscible and partly miscible. The miscibility has a direct connection with the morphology and properties. Miscibility is also dependent on the interfacial tension, viscosity and

process conditions and technologies. A huge percentage of the reported works in blends contain polyolefins.

Polymer blending is a cost effective and easier way to develop materials for high performance applications. Generally, blends are of three types-miscible, immiscible and partly miscible. The miscibility has a direct connection with the morphology and properties. Miscibility is also dependent on the interfacial tension, viscosity and process conditions and technologies. A huge percentage of the reported works in blends contain polyolefins. On analyzing the miscibility of the liquid mixtures, it was noted that at the interface between low molecular weight liquid in an immiscible liquid mixture, there exists a tension-the interfacial tension. When polymer blends are mixed, shear or elongation processes distort the minor phase into long fibrils or thin films, which are then broken down into minute particles. Lesser interfacial adhesion prevents shear stress from moving from one phase to the next, hence higher interfacial tension implies lower interfacial adhesion [24].

Intermolecular forces, chain entanglements, or both are used to establish adhesion through interfaces between phases or materials is considered as interfacial adhesion. When two separate materials are fused, merged, or mixed, interfacial adhesion occurs. Typically, to improve interfacial adhesion, a mixture of materials with similar properties, such as hydrophilic fillers and hydrophilic matrices or hydrophobic and hydrophobic materials, must be used, resulting in a close bond between the two. Instead, when hydrophobic and hydrophilic materials are combined, there must occur some problems. Interfacial adhesion is an important parameter to define the dimensional stability of materials. The schematic representation of the above statement is given in Fig. 1. It is clearly indicated that when A and B are of different nature a distinct interface exist between them.

Interfacial interactions are generally characterized using microscopic techniques and poor interfacial adhesion results in poor mechanical properties. In the case of blends and composites, the demand is always to enhance the miscibility. Generally miscible and partially miscible blends make the processing easier. When it comes to the immiscible blend system, different methods have been employed to enhance the interfacial adhesion. These methods are generalized by the term compatibilization and the materials which enhance the interaction are called compatibilizers. A variety of materials are being incorporated in different immiscible systems as compatibilizers—fibers, metal oxides, clays, nanoparticles, biopolymers, etc. The mechanism of compatibilization is very simple, the material added for this will have affinity towards both the phases and thus forms bond between the two. Even though they are immiscible, due to the common dissolved materials, they tend to interact with each other through the new added phase/material. There are different ways to implement compatibilization. Other than compatibilizers, introducing functionalities which can react with the immiscible phases are efficient in improving the adhesion.

Normally the polyolefin- polyolefin blends appear to be miscible, but a huge number of reports are available on the miscibility of these blends. Polyolefin based blends and composites are very important in the application point of view. Among the polyolefins, polyethylene and polypropylene are used more widely. The adhesion in polyolefin blends is enhanced by means of fillers. The following discussion will

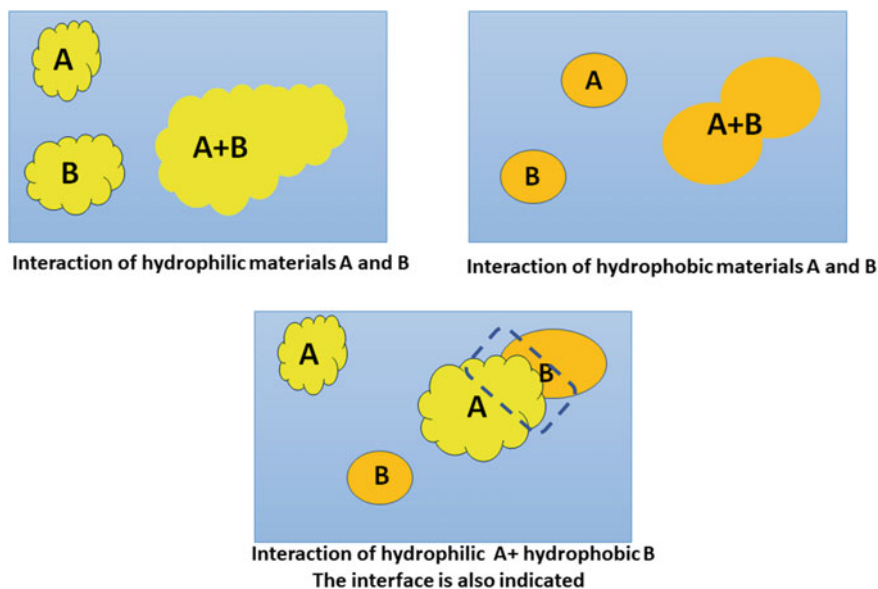


Fig. 1 Schematic representation of the interfacial interaction of like and unlike materials

be about the different types of modifications implemented so far in the case of most common polyolefins. Polyethylene, the common plastic material in applications worldwide, can be blended with polystyrene. The polymers interacted through graft polymerization. The high molecular weight polymer serves as a compatibilizing agent. Even with a catalytic amount of the polymers better interfacial adhesion and reduced particle size were resulted [25]. Even with the addition of compatibilizing agents, the processing conditions will change the adhesion and morphology (Fig. 2). One such example is the study done with PE/PS and PP/PS blends with and without compatibilizing agents and with different mixing strategies such as single-screw, twin-screw and an internal mixer. The studies on morphology revealed that the single-screw extruded materials gave better adhesion [26].

With the change in interfacial interactions, the morphology also changes. By examining the morphology, the miscibility and reduction in interfaces can be predicted. Also the effect and interaction of the compatibilizer can also be analyzed [28]. When compared to the other polyolefins, the polycarbonate shows more adhesion towards the PE phase. The improvement in adhesion resulted in the enhancement of mechanical properties and this was owed to the debonding mechanism of the blend system. The debonding relieves the triaxial tension in front of the crack tip, followed by shear banding of the PC matrix. The fact was a surprise as there were no visible reactive functionalities in PE and PC but an assumption can be made that the mixing was done in the brabender and this will cause the breakdown of PE polymer(oxidation) into finer PE particles and these particles can penetrate into the

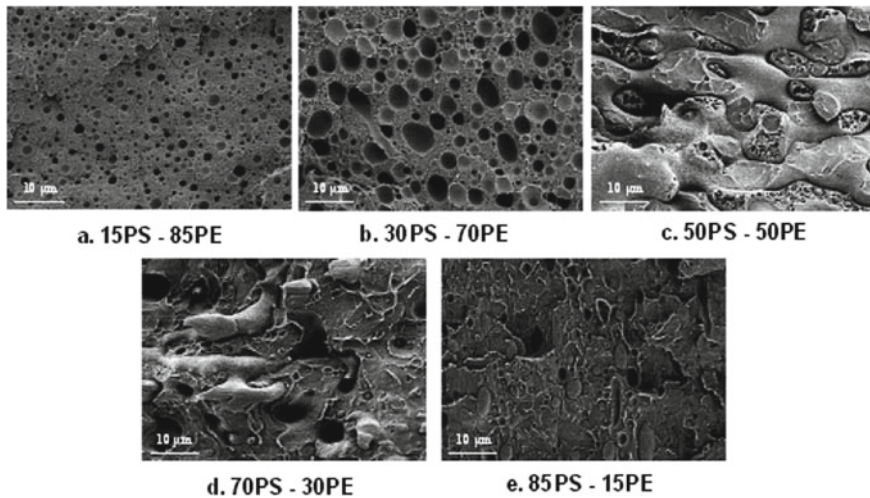


Fig. 2 Morphology of different composition blends of polyethylene and polystyrene (Reproduced with permission from [27])

polycarbonate chains by making available suitable reaction sites [29]. The compatibilization can also be done by certain chemicals like dicumyl peroxide [30]. The interfacial adhesion can also be enhanced via the addition of copolymers with both polar and nonpolar functionalities. The otherwise immiscible NBR and polyolefins can be made compatibilized by the aforementioned way. The added copolymer along with the melt mixing enhances the compatibilization action.

Another common procedure is the filler addition. With the inclusion of different fillers, the blends which are immiscible or in compatibilized can be made compatible. In their study, Pracella et al., investigated the effect of different types of natural fibers in polyolefin systems. In the report, they have included the composites of isotactic polypropylene (PP), polystyrene (PS), poly (ethylene–vinyl acetate) (EVA) as matrices and cellulose fibers, hemp or oat as natural fillers. Bi-functional monomers (glycidyl methacrylate, GMA; maleic anhydride, capable of inducing chemical interactions between the components during melt mixing) were used to modify both polymers and fibers. As compatibilizers, reactive polyolefin copolymers (PP-g-GMA, SEBS-g-MA, PS-co-MA, etc.) were utilized [31]. The addition of fibers could not improve the morphology, but the reactive functionalities could. The improved interfacial adhesion is revealed from the SEM micrographs of the composites given in the Fig. 3.

Effect of addition of ethylene-based compatibilizers in the immiscible polybutylene terephthalate (PBT) with very low-density polyethylene (VLDPE) was studied and results suggest significant improvements in the mechanical properties through modification of phase morphology and interfacial adhesion [32]. Surface functionalization can also be suggested as a route to improve interfacial adhesion. Chlorinated polyethylene can act as a compatibilizer for the poly-(vinylchloride)/polyolefin

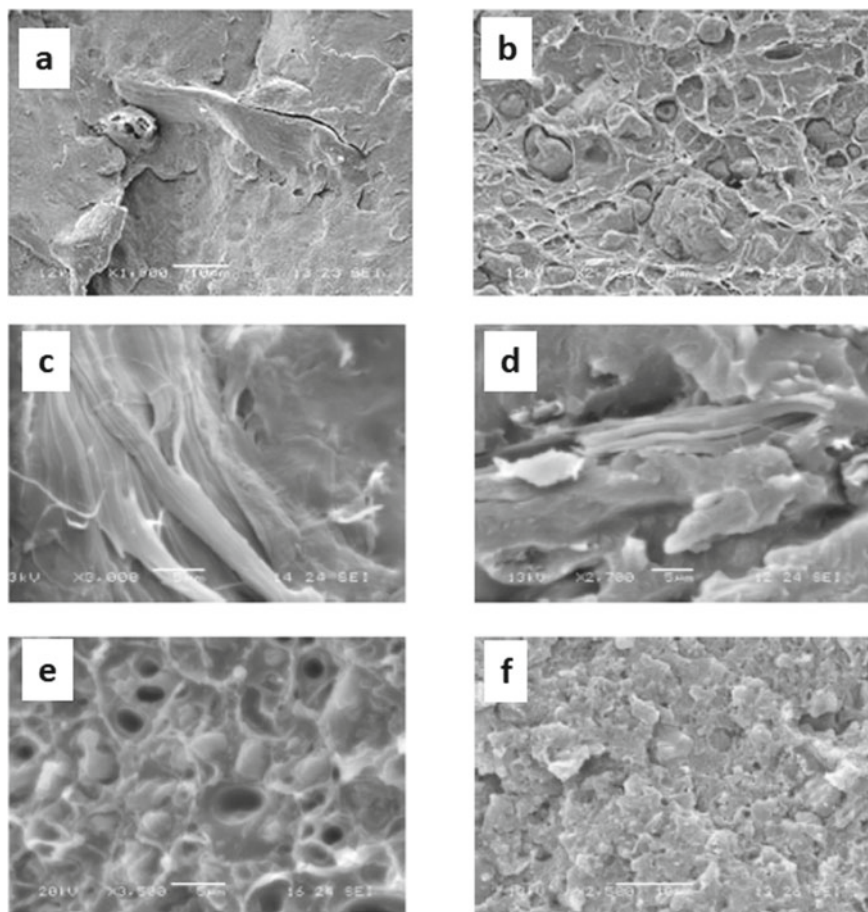


Fig. 3 SEM micrographs of polyolefin composites. **a** PS/Cellulose **b** PS/oat **c** cellulose modified with grafted polymer **d** PS-co-MA/cellulose **e** PS/oat/PEG **f** PS/Calcium carbonate/graft polymer (Reproduced with permission from [31])

elastomer blend system. According to the findings, the improvement in interfacial adhesion between the PVC and the POE is significantly greater with the blocky chlorinated PEs than with the randomly chlorinated PEs [33]. The studies on the composites and blends of polyolefins with and without functionalization and fillers are still a hot topic of research. The publications are beyond the limit and above the scope of this chapter. The interfacial properties can also be enhanced by an advanced technology called plasma modification.

4 Plasma Modification in Polyolefin Blends

The surface modification of polyolefins becomes necessary when cases arise where the mixed polymers are incompatible or the processing become difficult. The plasma modification is a superior technique where surface functionalities are introduced by the irradiation with suitable source. Plasma is created when enough energy is applied to a gas, causing the electronic structure of the atoms or molecules to reorganize, resulting in the generation of excited species and ions. The theory and other details are already mentioned in previous chapters. Corona discharge, which is produced by electrifying gases inside a chamber, is one of the favorite methods to introduce oxygen or other ions. It has been widely employed in the pretreatment of polyolefins [34]. But the reports on the plasma modification of blends and composites seems to be very less compared to the other modification methods (Fig. 4).

It has been shown that oxygen plasma can create a variety of oxygen functional groups at the surface of olefins, including C=O, C-O, OCO, COO⁻ and CO₃⁻. In a reported work, the polymer substrates made up of a polypropylene-polyethylene were investigated copolymer with a high percentage of PP and a mixture of ethylene-propylene rubber in the range of 15 to 60 mol%. For graft polymerization, plasma pretreatment was utilized to create reactive radicals and oxygenated groups on the polymer surfaces. It was concluded that plasma pretreatment endorsed the ethylene-propylene rubber component of the substrate, and that the ethylene-propylene rubber concentration was related to graft yield [35]. Low density polyethylene(PDPE)-casted polypropylene(CPP) films were modified by

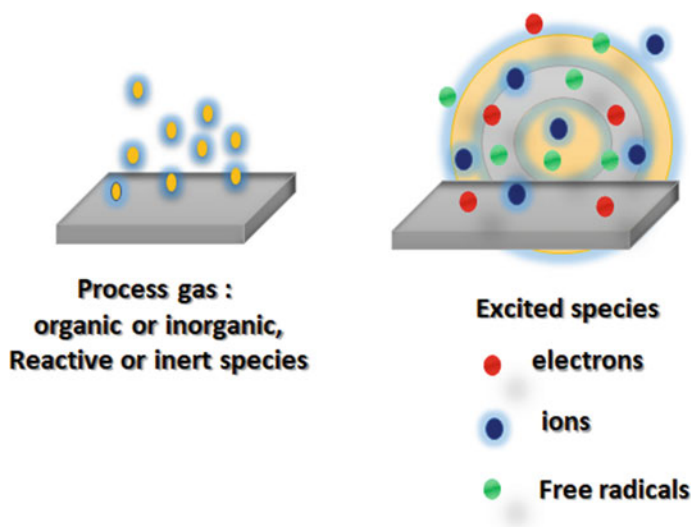


Fig. 4 Schematic representation of the effect of plasma irradiation on surface of a material

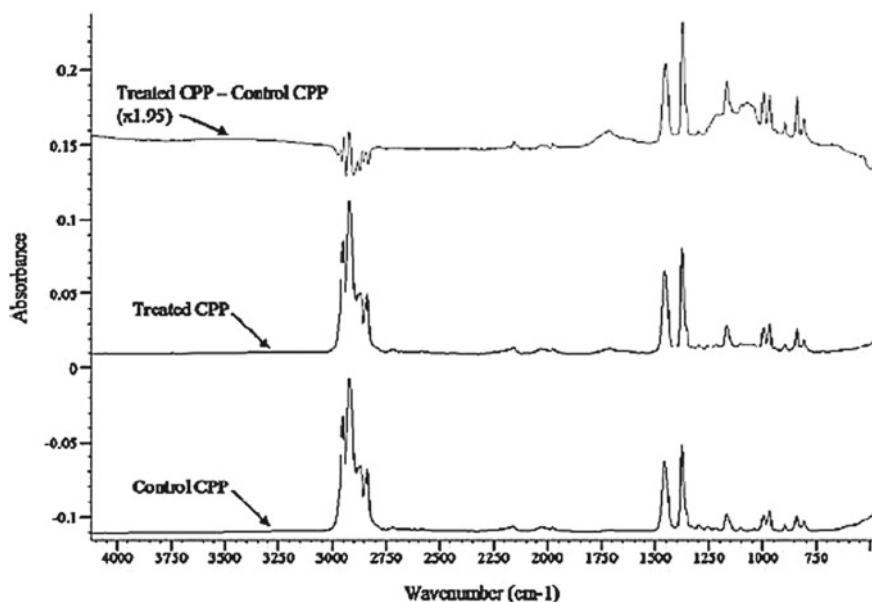


Fig. 5 ATR-FTIR results to confirm the introduction of surface functionalities (Reproduced with permission from [36])

capacitively-coupled radio-frequency oxygen plasma of field strength 13.56 MHz, essentially, to raise the quantity of active molecules attached to them [36] (Fig. 5).

In another report, to enhance the dispersion of the filler in the polymer matrix and decrease space charge buildup by modifying the charge trapping capabilities of these silica/PP/POE blends composites, the compatibility of silica with the PP/POE blends matrix must be increased.

A polypropylene (PP) blend used for automotive bumper fascia was subjected to surface modifications using a radio frequency Ar-plasma treatment. According to surface characterization, the Ar-plasma treatment on a PP blend surface turns the wholly annular surface into a locally dimpled surface, resulting in improved wettability. The increased wettability and interfacial adhesion between the PP blend substrate and bumper coating layers can be attributed to the observed surface characterization and morphologies [37]. The ambient pressure air discharge is observed to change the morphology and structure of the PP base, as shown by the following results: the spherulitic characteristics of the pristine PP film's layer transform into arbitrarily shaped surface appendages as the processing time is increased; highly oxidized carbon species are present on the plasma-processed surface, and the contact angle is significantly decreased from 93.7° for the untreated surface to 53.8° post-treatment [38].

Plasma modification can be done to enhance the interaction between fillers and blend system in composites. The aim of one such modification on polypropylene/polyolefin elastomer blend was to optimize the compatibility of silica filler

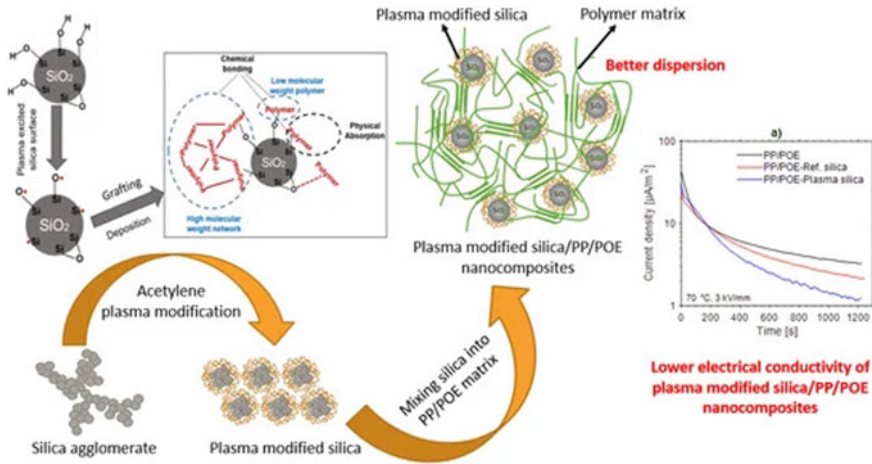


Fig. 6 Schematic representation of the process of plasma modification of silica particles to enhance the interaction with the PP/POE blend matrix (Reproduced with permission from [39])

with the PP/POE blends mixture in terms of improving filler dispersion in the polymer matrix and to inhibit space charge deposition by changing the charge sealing properties of such silica/PP/POE blends composites [39] (Fig. 6).

Wood fiber was modified using argon and air-plasma to enhance the compatibility with polypropylene (PP) and the surface characterization suggested enhanced oxygen/carbon ratio after the treatment [40]. PP/PS interface was modified by surface modification of polypropylene (PP) film is induced by CO₂ plasma [41]. The hexamethyldisiloxane (HMDSO)-radiofrequency plasma was employed on PP fabric to get the inorganic surface [42]. By analyzing a sample made of polypropylene (PP) decorative paper, the substrate, treated with low temperature plasma PP surface treatment, and coated with waterborne primer coating and topcoat material, to investigate the effects of plasma treatment on waterborne painting film adhesion. According to the findings, plasma treatment reduced the water touch angle on the surface of a PP decorative board material and increased the surface free energy and roughness. Besides that, plasma alteration can provide a large number of oxygen-containing active elements on the surface of the PP decorative material, which aids in the dissemination, adsorption, and adhesion of waterborne paints on the surface [43]. In recent years, the cold atmospheric pressure plasma jet (CAPPJ) has gotten a lot of attention for materials processing applications including surface alteration and biomedical applications. The surface properties of polypropylene were modified using a cold atmospheric pressure plasma jet maintained in pure argon [44]. Thus the plasma modification on blends can be used to enhance filler-matrix interaction, wettability, as coating on surface and for introducing functionalities.

Plasma modification has been successfully employed to improve the interfacial adhesion between nonpolar PE powder and polar polyamide prepared via rotational molding [45]. PE powders first treated with plasma [46] to impart functional groups

such as hydrauxyl, which interact with CONH groups present in the polyamide. Multilayer rotomolded treated PE and polyamide blends have been produced and compared their properties with untreated PE polyamide blends prepared in same manner. They found that improved joint strength is a result of chemical bonding and mechanical anchoring. In another work, plasma modified PE powder has been incorporated as filler in natural rubber matrix and compared the properties with samples with unmodified PE [47].

5 Plasma Modification in Polyolefin Composites

Being nonpolar in nature, polyolefine find difficulty to prepare composite with important fillers like cellulosic fibers, glass fibers etc. which are highly polar because of the lack in interfacial adhesion. Plasma modification of polyolefin surface found to be innovative method to enhance the reactivity of the polymer surface by introducing several functional groups on it. Consequently these polar fuctional groups allow possible interaction with OH groups present in cellulosic fibers and glass fibers.

Adhesion between glass fibers and plasma treated PE has been analysed by Novacek and also compared it with that of industrially using chemical bonding agents [46]. Previously, research is focused mostly on the modification of inorganic fillers and fibers by themselves or combined with chemical agents to enhance the interfacial strength. But this work measure the adhesion properties of the low temperature plasma-modified PE powder onto glass sheet surfaces in comparison with the commonly used chemical modifiers MAH and silane, and the examination of the dependence of the adhesion to the glass on the plasma treatment time of PE. Adhesion and mechanical properties were studied by Universal testing machine and the interface was closely examined using SEM. It was found that the maximum mechanical properties has been shown by the sample in which good interfacial adhesion has been observed.

As a continuation of the previous work, glass fibers composites based on unmodified and plasma modified polyethylene matrixes were successfully manufactured via rotational moulding [48]. Plasma treatment of PE powder improves the mechanical properties of the composites produced using treated powder comparing to the composites produced using untreated powder. Tensile strength increased by 10% as the fiber content increased up to 10 wt.%, Tensile modulus, increased as the fibers contents increased for all composites, composite prepared with treated powder showed even higher modulus.

The natural fibre composites gained major attention in this era because of the environmental concerns and their specific advantages over synthetic fibre composites. natural fibre composites there is usually limited interfacial bonding between the hydrophilic fibres and matrices which are commonly hydrophobic leading to limited mechanical performance. The used methods to enhance compatibility and interfacial adhesion in natural fibre composites are the use of compatibilizer and modifications of fibres or polymers. Plasma modified polyethylene (PE) was used as the matrix

for coir fibre reinforced composites [49]. The use of compatibilizers, and chemical modification of fibre or polymer is a usual practice to improve the interfacial adhesion and to make the fibre and polymer matrix compatible [50–52]. Here, plasma modification of PE was introduced as a new method to improve the compatibility between hydrophobic PE and hydrophilic natural fiber. Plasma modified PE (PPE) and coir fibre composites have been manufactured using different preparation methods. The mechanical properties of the composites obtained from UTM were compared with unmodified PE/coir fibre composites. The newly prepared thermoplastic composites based on PPE and modified coir fibre showed lower water absorption due to better fiber/matrix interaction. We could observe different kinds of interfaces in the composites. In the plasma modified one, a good wetting of fibre by the matrix eliminated the possible microvoids. Finally, it is important to add that plasma modification of the polymer was found to be an effective technique to improve the compatibility between polyethylene and natural fibre.

Rotomoulding is an important pressureless processing method in the polymer industry which can produce stress free products. Use of composite material in rotomoulding is facing a lot of issues because of the filler aggregation and lack of good adhesion with polymer matrix. We successfully prepared plasma modified PE/natural fibre composites with improved properties [53]. We have created four different types of interfaces these include PE/natural fibre, PE/bleached natural fibre PPE/natural fibre, PPE/bleached natural fibre. Among all, PPE/bleached natural fibre showed the best balance of properties. SEM images given in Fig. 7, showed that a strong interfacial interaction between natural fibre and polymer matrix is possible with plasma modification of PE matrix. Plasma treatment modifies the surface of powder polymer to become more hydrophilic by imparting functional groups on it. This could improve the compatibility between the polymer matrix and natural fibre. Finally, it is important to add that plasma modification of PE coupled with mild bleaching of natural fibre is an excellent cost effect technique for the manufacture of rotomoulded natural fibre composites of PE having good mechanical properties and moisture resistance.

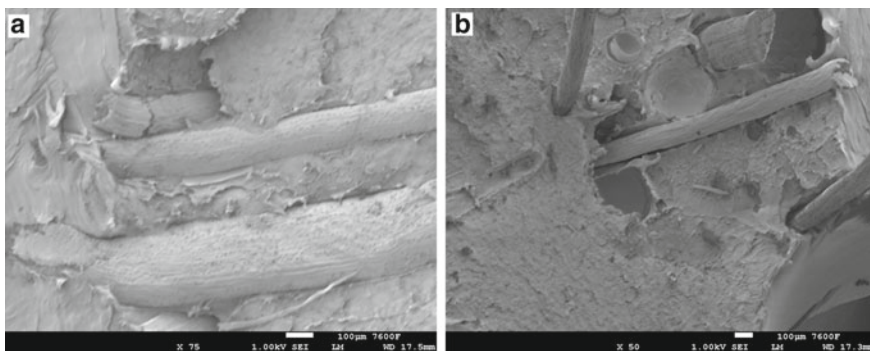


Fig. 7 SEM image of **a** PPE coir fiber composite and **b** untreated PE coir fiber composites

6 Applications of Plasma Modified Polyolefine Blends and Composites

The surface treated polyolefins and their blends and composites can be used in many fields such as biomedical, electrical, electronics, coatings, and so on. Environmental applications such as antifouling is important in water treatment. Plasma treatment can be utilized for introducing antifouling coatings on low density polyethylenes (LDPEs). Pandiyaraj and colleagues explained how they used atmospheric pressure non-thermal plasma (APNTP) assisted copolymerization with a mixture of acrylic acid and polyethylene to produce antifouling functional coatings on the surface of low density polyethylene (LDPE) films (ethylene glycol) [54]. Polyethylene is an important material in the fabrication of separators in lithium-ion based batteries. Many research works applied different types of plasmas to modify the surface of the films. Plasma modification is also meant to enhance the electrolyte retention and wettability, ionic conductivity and adhesion [55–60]. Similarly polypropylene membranes are also employed [61–63].

Plasma modified polyolefine blends have been employed in biomedical applications such as in tissue engineering [64] Ultra-High-Molecular-Weight-Polyethylene (UHMWPE) is a promising material in the biomedical field [65]. Another important application of plasma modified polyolefin composites are in the field of antibacterials. PET/PP films were treated with ambient pressure plasma before being assembled with chitosan and various preservatives and used for antimicrobial food packaging [66]. For food packaging applications the barrier properties should be improved. This can also be done with plasma modification [67]. Most of the reported application of plasma modified polyolefins are for polyethylenes and polypropylene along with fillers for the above mentioned applications.

7 Conclusion

Polyolefine blend and composites have great importance many application. However the lower surface energy of polyolefin demand the use of chemical compatibilizing agents or chemical modifications to have enough interfacial adhesion, which is necessary for the required performance of blends and composites. The negative impact of using chemicals and solvents can be avoided by plasma modification of polymer, a new method to improve the interfacial adhesion. By this way polyethylene composites of natural fibers and glass fibers have been successfully manufactured which possess improved properties. Plasma modified polyolefin exhibited good bonding with other polymeric materials even with polyamide that are polar in nature.

References

1. Mohite, A.S., Rajpurkar, Y.D., More, A.P.: Bridging the gap between rubbers and plastics: a review on thermoplastic polyolefin elastomers. *Polym. Bull.* (2021). <https://doi.org/10.1007/s00289-020-03522-8>
2. Sadiku, R., Ibrahim, D., Agboola, O., Owonubi, S.J., Fasiku, V.O., Kupolati, W.K., Jamiru, T., Eze, A.A., Adekomaya, O.S., Varaprasad, K., Agwuncha, S.C., Reddy, A.B., Manjula, B., Oboiren, B., Nkuna, C., Dluđu, M., Adeyeye, A., Osholana, T.S., Phiri, G., Durowoju, O., Olubambi, P.A., Biotidara, F., Ramakokovhu, M., Shongwe, B., Ojijo, V.: Automotive components composed of polyolefins. In: *Polyolefin Fibres Struct. Prop. Ind. Appl. Second Ed.*, pp. 449–496 (2017). <https://doi.org/10.1016/B978-0-08-101132-4.00015-1>
3. Sadiku, E.: Automotive components composed of polyolefins. *Ind. Med. Appl.* pp. 81–132 (2009). <https://doi.org/10.1533/9781845695552.1.81>
4. Chirayil, C.J., Joy, J., Maria, H.J., Krupa, I., Thomas, S.: Polyolefins in automotive industry. pp. 265–283 (2016). https://doi.org/10.1007/978-3-319-25982-6_11
5. Jiraroj, D., Tungasmita, S., Tungasmita, D.N.: Zeolite A-polypropylene and silver-zeolite A-polypropylene composite films for antibacterial and breathable applications. *J. Appl. Polym. Sci.* **134** (2017). <https://doi.org/10.1002/app.45450>
6. Kresge, E.N., Lohse, D.J., Datta, S.: Polyolefin blends. *Makromol. Chemie. Macromol. Symp.* **53**, 173–189 (1992). <https://doi.org/10.1002/masy.19920530117>
7. Anzlover, A., Primožic, M., Svab, I., Leitgeb, M., Knez, Z., Zagar, E.: Polyolefin/ZnO composites prepared by melt processing. *Molecules* **24** (2019). <https://doi.org/10.3390/molecules24132432>
8. Hao, W., Wang, M., Zhou, F., Luo, H., Xie, X., Luo, F., Cha, R.: A review on nanocellulose as a lightweight filler of polyolefin composites. *Carbohydr. Polym.* **243** (2020). <https://doi.org/10.1016/j.carbpol.2020.116466>
9. Ghanbari, A., Sadat Jalili, N., Haddadi, S.A., Arjmand, M., Nofar, M.: Mechanical properties of extruded glass fiber reinforced thermoplastic polyolefin composites. *Polym. Compos.* **41**, 3748–3757 (2020). <https://doi.org/10.1002/pc.25672>
10. Sobczak, L., Brüggemann, O., Putz, R.F.: Polyolefin composites with natural fibers and wood-modification of the fiber/filler-matrix interaction. *J. Appl. Polym. Sci.* **127**, 1–17 (2013). <https://doi.org/10.1002/app.36935>
11. Kittinaovararat, S., Suthamnoi, W.: Physical properties of polyolefin/bamboo charcoal composites. *J. Met. Mater. Miner.* **19**, 9–15 (2009)
12. Nair, A.B., Joseph, R.: Eco-friendly bio-composites using natural rubber (NR) matrices and natural fiber reinforcements. In: *Chemistry, manufacture and applications of natural Rubber*, pp. 249–283 (2014). <https://doi.org/10.1533/9780857096913.2.249>
13. Panthapulakkal, S., Raghunanan, L., Sain, M., Kc, B., Tjong, J.: Natural fiber and hybrid fiber thermoplastic composites: advancements in lightweighting applications. In: *Green Composites Waste Nature-Based Mater.* pp. 39–72 (2017). <https://doi.org/10.1016/B978-0-08-100783-9.00003-4>
14. Dong, C.: Review of natural fibre-reinforced hybrid composites. *J. Reinf. Plast. Compos.* **37**, 331–348 (2018). <https://doi.org/10.1177/0731684417745368>
15. Andrzejewski, J., Tutak, N., Szostak, M.: Polypropylene composites obtained from self-reinforced hybrid fiber system. *J. Appl. Polym. Sci.* **133** (2016). <https://doi.org/10.1002/app.43283>
16. Hidalgo-Salazar, M.A., Correa-Aguirre, J.P., García-Navarro, S., Roca-Blay, L.: Injection molding of coir coconut fiber reinforced polyolefin blends: mechanical, viscoelastic, thermal behavior and three-dimensional microscopy study. *Polymers (Basel)*. **12**, 1–20 (2020). <https://doi.org/10.3390/polym12071507>
17. Hernández-Díaz, D., Villar-Ribera, R., Julián, F., Tarrés, Q., Espinach, F.X., Delgado-Aguilar, M.: Topography of the interfacial shear strength and the mean intrinsic tensile strength of hemp fibers as a reinforcement of polypropylene. *Materials (Basel)* **13** (2020). <https://doi.org/10.3390/ma13041012>

18. Serrano, A., Espinach, F.X., Tresserras, J., Pellicer, N., Alcalá, M., Mutje, P.: Study on the technical feasibility of replacing glass fibers by old newspaper recycled fibers as polypropylene reinforcement. *J. Clean. Prod.* **65**, 489–496 (2014). <https://doi.org/10.1016/j.jclepro.2013.10.003>
19. Obaid, N., Kortschot, M.T., Sain, M.: Predicting the stress relaxation behavior of glass-fiber reinforced polypropylene composites. *Compos. Sci. Technol.* **161**, 85–91 (2018). <https://doi.org/10.1016/j.compscitech.2018.04.004>
20. Wang, Y., Cheng, L., Cui, X., Guo, W.: Crystallization behavior and properties of glass fiber reinforced polypropylene composites. *Polymers (Basel)* **11** (2019). <https://doi.org/10.3390/polym11071198>
21. Etcheverry, M., Barbosa, S.E.: Glass fiber reinforced polypropylene mechanical properties enhancement by adhesion improvement. *Materials (Basel)*. **5**, 1084–1113 (2012). <https://doi.org/10.3390/ma5061084>
22. Thwe, M.M., Liao, K.: Effects of environmental aging on the mechanical properties of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Compos. - Part A Appl. Sci. Manuf.* **33**, 43–52 (2002). [https://doi.org/10.1016/S1359-835X\(01\)00071-9](https://doi.org/10.1016/S1359-835X(01)00071-9)
23. David, A.O., Chukwuemeka, I.S., Ooster, E.E., Salihi, G.N.: Development and characterization of hybrid coconut/glass fibers reinforced low density polyethylene composites for bumper application. *Metall. Mater. Eng.* **27**, 89–104 (2020). <https://doi.org/10.30544/453>
24. White, J.L., Yang, J.: Miscibility and characteristics of polyolefin blends. In: *Polyolefin blends*, pp. 27–56 (2007). <https://doi.org/10.1002/9780470199008.ch2>
25. Díaz, M.F., Barbosa, S.E., Capiati, N.J.: Reactive compatibilization of PE/PS blends. Effect of copolymer chain length on interfacial adhesion and mechanical behavior. *Polymer (Guildf)* **48**, 1058–1065 (2007). <https://doi.org/10.1016/j.polymer.2006.12.040>
26. Kallel, T., Massardier-Nageotte, V., Jaziri, M., Gérard, J.F., Elleuch, B.: Compatibilization of PE/PS and PE/PP blends. I. Effect of processing conditions and formulation. *J. Appl. Polym. Sci.* **90**, 2475–2484 (2003). <https://doi.org/10.1002/app.12873>
27. Thirtha, V., Lehman, R., Nosker, T.: Morphological effects on glass transition behavior in selected immiscible blends of amorphous and semicrystalline polymers. *Polymer (Guildf)*. **47**, 5392–5401 (2006). <https://doi.org/10.1016/j.polymer.2006.05.014>
28. Wycisk, R., Trochimczuk, W.M., Matys, J.: Polyethylene-polystyrene blends. *Eur. Polym. J.* **26**, 535–539 (1990). [https://doi.org/10.1016/0014-3057\(90\)90204-H](https://doi.org/10.1016/0014-3057(90)90204-H)
29. Sue, H.J., Huang, J., Yee, A.F.: Interfacial adhesion and toughening mechanisms in an alloy of polycarbonate/polyethylene. *Polymer (Guildf)*. **33**, 4868–4871 (1992). [https://doi.org/10.1016/0032-3861\(92\)90707-4](https://doi.org/10.1016/0032-3861(92)90707-4)
30. Wang, Z., Chan, C.M., Zhu, S.H., Shen, J.: Compatibilization of polystyrene and low density polyethylene blends by a two-step crosslinking process. *Polymer (Guildf)*. **39**, 6801–6806 (1998). [https://doi.org/10.1016/S0032-3861\(98\)00174-8](https://doi.org/10.1016/S0032-3861(98)00174-8)
31. Pracella, M., Haque, M.M.U., Alvarez, V.: Functionalization, compatibilization and properties of polyolefin composites with natural fibers. *Polymers (Basel)*. **2**, 554–574 (2010). <https://doi.org/10.3390/polym2040554>
32. Nabi Saheb, D., Jog, J.P.: Compatibilization of PBT/polyolefin blends: mechanical and dynamic mechanical properties. *Adv. Polym. Technol.* **19**, 41–53 (2000). [https://doi.org/10.1002/\(SICI\)1098-2329\(20000117\)19:1<41::AID-ADV5>3.0.CO;2-C](https://doi.org/10.1002/(SICI)1098-2329(20000117)19:1<41::AID-ADV5>3.0.CO;2-C)
33. Eastwood, E.A., Dadmun, M.D.: Compatibilization of poly(vinyl chloride) and polyolefin elastomer blends with multiblock/blocky chlorinated polyethylenes. *Polymer (Guildf)*. **43**, 6707–6717 (2002). [https://doi.org/10.1016/S0032-3861\(02\)00639-0](https://doi.org/10.1016/S0032-3861(02)00639-0)
34. Popelka, A., Novak, I., Krupa, I.: Polyolefin adhesion modifications. pp. 201–230 (2016). https://doi.org/10.1007/978-3-319-25982-6_8
35. Keen, I., George, G.A., Fredericks, P.M.: Selective plasma-induced grafting of polystyrene onto polyolefin blends. *J. Appl. Polym. Sci.* **88**, 1643–1652 (2003). <https://doi.org/10.1002/app.11789>
36. Lee, K.T., Goddard, J.M., Hotchkiss, J.H.: Plasma modification of polyolefin surfaces. *Packag. Technol. Sci.* **22**, 139–150 (2009). <https://doi.org/10.1002/pts.829>

37. Weon, J.-I., Choi, K.-Y.: Surface Characterization and morphology in Ar-plasma-treated polypropylene blend. *Macromol. Res.* **17**, 886–893 (2009). <https://doi.org/10.1007/BF03218631>
38. Cui, N.Y., Brown, N.M.D.: Modification of the surface properties of a polypropylene (PP) film using an air dielectric barrier discharge plasma. *Appl. Surf. Sci.* **189**, 31–38 (2002). [https://doi.org/10.1016/S0169-4332\(01\)01035-2](https://doi.org/10.1016/S0169-4332(01)01035-2)
39. He, X., Rytöluoto, I., Anyszka, R., Mahtabani, A., Saarimäki, E., Lahti, K., Paaanen, M., Dierkes, W., Blume, A.: Surface modification of fumed silica by plasma polymerization of acetylene for PP/POE blends dielectric nanocomposites. *Polymers (Basel)* **11**, (2019). <https://doi.org/10.3390/polym11121957>
40. Yuan, X., Jayaraman, K., Bhattacharyya, D.: Effects of plasma treatment in enhancing the performance of woodfibre-polypropylene composites. *Compos. Part A Appl. Sci. Manuf.* **35**, 1363–1374 (2004). <https://doi.org/10.1016/j.compositesa.2004.06.023>
41. Ma, G., Liu, X., Huang, D., Yuan, X., Sheng, J.: Surface modification of polypropylene and compatibilization of interfaces in incompatible blends of polypropylene with polystyrene by plasma of CO₂. *Appl. Surf. Sci.* **255**, 7483–7494 (2009). <https://doi.org/10.1016/j.apsusc.2009.03.066>
42. Sarmadi, A.M., Ying, T.H., Denes, F.: HMDSO-plasma modification of polypropylene fabrics. *Eur. Polym. J.* **31**, 847–857 (1995). [https://doi.org/10.1016/0014-3057\(95\)00016-X](https://doi.org/10.1016/0014-3057(95)00016-X)
43. Peng, X., Zhang, Z.: Research of polypropylene (PP) decorative board surface painting used for wood product decoration and the paint film adhesion improvement by plasma. *J. Adhes. Sci. Technol.* **34**, 246–262 (2020). <https://doi.org/10.1080/01694243.2019.1667139>
44. Baniya, H.B., Guragain, R.P., Baniya, B., Subedi, D.P.: Experimental study of cold atmospheric pressure plasma jet and its application in the surface modification of polypropylene. *Rev. Adhes. Adhes.* **8**, 1–14 (2020). <https://doi.org/10.7569/RAA.2020.097304>
45. Sezemský, J., Špatenka, P.: Adhesion improvement between PE and PA in multilayer rotational molding. *Polymers (Basel)* **13**, 387–453 (2021). <https://doi.org/10.3390/polym13030331>
46. Novacek, V., Špatenka, P.: Application of low temperature plasma treatment for thermoplastic composites, 650 (n.d.) 1027–1032
47. Sasidharan, S.P., Špatenka, P., Anisimov, E., Thomas, S.: Plasma modified and unmodified polyethylene as filler in natural rubber compounds: morphology. Cure behavior, and vulcanization kinetics **1800135**, 1–9 (2018). <https://doi.org/10.1002/masy.201800135>
48. Ghanem, Z., Sasidharan, S.P., Jenikova, Z., Špatenka, P.: Rotational molding of plasma treated polyethylene/short glass fiber composites. *Int. J. Eng. Manag. Sci.* **4**, 103–108 (2019). <https://doi.org/10.21791/ijems.2019.4.11>
49. Sari, P.S., Špatenka, P., Jenikova, Z., Thomas, S.: RSC advances new type of thermoplastic bio composite: nature of the interface on the ultimate properties and water absorption. *RSC Adv.* **5**, 97536–97546 (2015). <https://doi.org/10.1039/C5RA16311K>
50. Musanif, I.S., Thomas, A.: Effect of alkali treatments of physical and mechanical properties of coir fiber. **3** 23–28 (2015). <https://doi.org/10.13189/cme.2015.030202>
51. Mir, S.S., Hasan, M., Hasan, S.M.N., Hossain, J., Nafsin, N.: Effect of chemical treatment on the properties of coir fiber reinforced polypropylene and polyethylene composites. 1–7 (2015). <https://doi.org/10.1002/pc>
52. Geethamma, V.G., Thomas Mathew, K., Lakshminarayanan, R., Thomas, S.: Composite of short coir fibres and natural rubber: effect of chemical modification, loading and orientation of fibre. *Polymer (Guildf)* **39**, 1483–1491 (1998). [https://doi.org/10.1016/S0032-3861\(97\)00422-9](https://doi.org/10.1016/S0032-3861(97)00422-9)
53. Sasidharan, P., Thomas, S., Špatenka, P., Ghanam, Z.: Effect of plasma modification of polyethylene on natural fibre composites prepared via rotational moulding. *Compos. Part B.* **177**, (2019). <https://doi.org/10.1016/j.compositesb.2019.107344>
54. Pandiyaraj, K.N., Ramkumar, M.C., Arun Kumar, A., Padmanabhan, P.V.A., Pichumani, M., Bendavid, A., Cools, P., De Geyter, N., Morent, R., Kumar, V., Gopinath, P., Su, P.-G., Deshmukh, R.R.: Evaluation of surface properties of low density polyethylene (LDPE) films tailored

- by atmospheric pressure non-thermal plasma (APNTP) assisted co-polymerization and immobilization of chitosan for improvement of antifouling properties. *Mater. Sci. Eng. C*. **94**, 150–160 (2019). <https://doi.org/10.1016/j.msec.2018.08.062>
55. Yin, M., Huang, J., Yu, J., Chen, G., Qu, S., Wang, X., Li, C.: The polypropylene membrane modified by an atmospheric pressure plasma jet as a separator for lithium-ion button battery. *Electrochim. Acta* **260**, 489–497 (2018). <https://doi.org/10.1016/j.electacta.2017.12.119>
 56. Kim, J.Y., Lee, Y., Lim, D.Y.: Plasma-modified polyethylene membrane as a separator for lithium-ion polymer battery. *Electrochim. Acta*. **54**, 3714–3719 (2009). <https://doi.org/10.1016/j.electacta.2009.01.055>
 57. Kim, J.Y., Lim, D.Y.: Surface-modified membrane as a separator for lithium-ion polymer battery. *Energies* **3**, 866–885 (2010). <https://doi.org/10.3390/en3040866>
 58. Jin, S.Y., Manuel, J., Zhao, X., Park, W.H., Ahn, J.H.: Surface-modified polyethylene separator via oxygen plasma treatment for lithium ion battery. *J. Ind. Eng. Chem.* **45**, 15–21 (2017). <https://doi.org/10.1016/j.jiec.2016.08.021>
 59. Young, J., Young, D.: Plasma-Modified Polyethylene Separator Membrane for Lithium-ion Polymer Battery. *Lithium-Ion Batter.* (2010). <https://doi.org/10.5772/9118>
 60. An, G.H., Kim, J.Y., Lim, D.Y.: Plasma modification of polyethylene separator for lithium-ion battery. In: *ACS Natl. Meet. B. Abstr.*, (2010)
 61. Li, X., He, J., Wu, D., Zhang, M., Meng, J., Ni, P.: Development of plasma-treated polypropylene nonwoven-based composites for high-performance lithium-ion battery separators. *Electrochim. Acta* **167**, 396–403 (2015). <https://doi.org/10.1016/j.electacta.2015.03.188>
 62. Wang, Z., Zhu, H., Yang, L., Wang, X., Liu, Z., Chen, Q.: Plasma modified polypropylene membranes as the Lithium-Ion battery separators. *Plasma Sci. Technol.* **18**, 424–429 (2016). <https://doi.org/10.1088/1009-0630/18/4/16>
 63. Heidari, A.A., Mahdavi, H.: Recent development of polyolefin-based microporous separators for Li–Ion batteries: a review. *Chem. Rec.* **20**, 570–595 (2020). <https://doi.org/10.1002/tcr.201900054>
 64. Joshy, K.S., Snigdha, S., Thomas, S.: Plasma modified polymeric materials for scaffolding of bone tissue engineering. In: *Non-Thermal Plasma Technol. Polym. Mater.*, pp. 439–458. (2019). <https://doi.org/10.1016/b978-0-12-813152-7.00016-0>
 65. Hussain, M., Naqvi, R.A., Abbas, N., Khan, S.M., Nawaz, S., Hussain, A., Zahra, N., Khalid, M.W.: Ultra-high-molecular-weight-polyethylene (UHMWPE) as a promising polymer material for biomedical applications: a concise review. *Polymers (Basel)*. **12** (2020). <https://doi.org/10.3390/polym12020323>
 66. Lei, J., Yang, L., Zhan, Y., Wang, Y., Ye, T., Li, Y., Deng, H., Li, B.: Plasma treated polyethylene terephthalate/polypropylene films assembled with chitosan and various preservatives for antimicrobial food packaging. *Colloids Surf. B. Biointerfaces*. **114**, 60–66 (2014). <https://doi.org/10.1016/j.colsurfb.2013.09.052>
 67. Vishnuvarthanan, M., Rajeswari, N.: Preparation and characterization of carrageenan/silver nanoparticles/Laponite nanocomposite coating on oxygen plasma surface modified polypropylene for food packaging. *J. Food Sci. Technol.* **56**, 2545–2552 (2019). <https://doi.org/10.1007/s13197-019-03735-4>