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INSIGHTS

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Grafted Polymers as Compatibilizer to Modify Properties of Recycled Plastics

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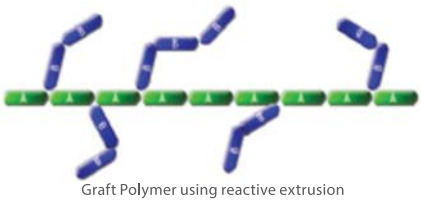
Functionally Modified polymers are specialty polymers that have pendant functional groups attached to the backbone polymer chains. Exceptional properties like polarity or specific reactivity can be imparted to the base polymer, while the fictionally modified (grafted) polymer retains the same processability as the parent polymer.



Graft Polymer using reactive extrusion

Polarity and specific reactivity can also be imparted in high polymers through copolymerization of monomers in a polymerization reactor. Graft modified polymers differ from reactor made copolymers, however, in terms of better production flexibility and variety of grades of grafted products that can be produced in smaller volumes. Tailoring products to suit different processes or equipment is better possible in grafted polymers made from the reactive extrusion route. Major use of functionalized polymers is as additives in polymer compounding sector. But they can also be used on their own in some applications such as extrudable and co-extrudable coatings and adhesive layers.

The need for Functionally Modified Polymers

Plastics have well-known widely useful properties and ease of processing. These characteristics over the years have made plastics the material of choice in all spheres of our life. Each application needs specific properties to give the desired performance. To meet all these processing and performance requirements the basic polymers need to be modified by use of additives, and property enhancers. High performance fillers and reinforcements may have compatibility issues with the polymer matrix. Graft modified polymers serve as flow promoters, chain extenders, dispersing agents, coupling agents, compatibilisers, impact modifiers in different polymer systems. In comparison with the low molecular weight solid or liquid additives, high molecular weight of grafted polymers blend well with other ingredients of the composition at compounding stage, without posing any processing problems like feeding and dispersion and exudation in the compound or end product.

Polymer alloys and blends combine the best of properties of the constituent polymers to produce a unique material with unique properties. Grafted polymers play a very important role of compatibilizer here. The incompatible polymers are physically and / or chemically bound together via grafted polymer based compatibilizer interphase layer. By a similar mechanism, reinforcements like glass fibres are coupled to the polymer matrix through an interphase of grafted polymers. Improvement in mechanical properties due to such reinforcements depends also on the integrity of this interphase layer through which stress applied on the component is transmitted to the reinforcement.

How are Grafted polymers produced?

Literature is replete with lot of work done on grafting of different monomers on different backbone polymers. Common polymers like polyethylene, polypropylene and their copolymers, PVC and Styrenic polymers are the most commonly used polymer backbones used in grafting. Bifunctional monomers are generally used for grafting, with one functional group being used for effecting the grafting reaction on the polymer backbone and the other remaining intact to be useful in application of the grafted polymeric additive. Some examples of the molecules used for grafting are: Acrylics, Esters, Epoxides, acids & anhydrides. Grafting reaction generally follows free radical mechanism, with heat, peroxides or electron beam as catalysts for free radical generation.

Grafting on Polyolefins via Reactive Extrusion

Composed of non-polar hydrocarbon molecules, polyolefins are the most abundant of the polymers commercially used in various applications including packaging, wire & cable compounds automotive, and household goods. In addition to relative low raw material cost and ease of processing, polyolefins also possess some wonderful properties like chemical inertness and moisture barrier. Imparting a little polarity expands usage of these polyolefins further, in combination with minerals and some polar polymers. This makes polyolefins a good contender for grafting with polar molecules.

Grafting is carried out via reactive extrusion of polymer and reactants in a specially designed extruder. The graft modified polymer, in the form of granules or pellets, appear, behave and process almost like the base polyolefin polymer,

but have enhanced affinity and compatibility towards polar fillers polymers and substrates. The grafting reaction can be shown as in Fig. 2.

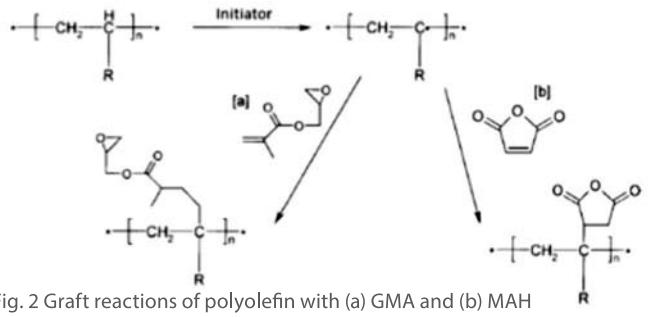


Fig. 2 Graft reactions of polyolefin with (a) GMA and (b) MAH

Function & Applications

Incorporating polar functional groups like maleic anhydride on the main backbone chain of non-polar polymers opens up huge possibility of applications like coupling agents for filled compounds, compatibilizers for polymer blends and alloys, tie or adhesive resins in multilayer barrier films and containers, chain extenders for recycling of engineering plastics and many more. Each of these applications in packaging, compounding and recycling needs specific set of properties that are possible to obtain in grafted products.

Grafted polymer comprises of polar side groups and non-polar backbone of the base polyolefin. Due to this chemical nature, they have affinity towards minerals and some polar polymers like Nylon and EVOH, as well as non-polar polyolefins. Fig.3 shows the reaction mechanism between the maleic anhydride grafted polyethylene and Nylon.

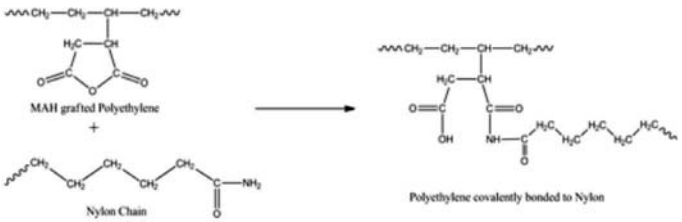


Fig. 3 Reaction between MAH-g-PE and Nylon

Global Market Scenario

Overall global demand for grafted polymers is estimated to be 900KTA across different applications. Introduced in 1970s, initially it was only the polyolefin raw material manufacturers who started manufacturing grafted polymers. Specific property requirements led to numerous grades to be produced, at times in smaller quantities than would be attractive to the large polymer manufacturers. Over a period of time, they have been yielding the market place to non-polymer manufacturers, like Pluss in India & a few others in US , Europe & Asia.

Domestic consumption of grafted polymers in India is estimated at 10KTA catering to the key segments such as Compounding (PP,PA,PC,PBT, Wire & Cables, ACP, WPC), Recycling (PP, PA, PC, & PBT) and Flexible packaging (Metallized films, Multi-layer barrier films & Lamitubes). Pluss Advanced Technologies is the only major graft modified speciality polymers manufacturer in India. A broad overview of segments catered to in domestic market include:

- **Coupling agents in HFFR compounds,** for cables and PE core in Aluminium Composite Panels used in building & construction applications. For eg: OPTIM® E series coupling agents from Pluss allow high filler loading for effective flame retardance, good extrudability and mechanical strength.
- **Coupling agent for glass & mineral filled compounds,** for moulding and extrusion applications. Depending on base polymer for the compound, PP and PE grafted products are used to provide desired tensile, flexural and impact strength required in polymer compounds for components in automobile and white goods segments.
- **Compatibilizers for polymer compounds,** such as PA-PE, PA-PP, PC-ABS for improvement in moisture sensitivity, dimensional stability, toughness and processability, using OPTIM® P-, E- & R-series speciality polymers.
- **Impact modifier for recycled engineering plastics.** Recycled nylon, PBT & PC undergo reduction in impact strength due to thermal degradation. Pluss in India is the only company manufacturing GMA grafted polymers make up that loss and prevent brittleness in recycled PC and PBT. Small amount of contaminants also get compatibilised in the process.
- **Value addition in PP Film recycling:** Factory waste of oriented or non-oriented PP film can be recycled into moulding of load bearing core plugs for fresh film rolls. OPTIM® R- series additive has made it possible to replace virgin PP by recycled in-house generated waste.
- **Tie layer resin for multilayer barrier films, bottles & lamitubes:** BindEX™ grades of Coextrudable resins are used as tie layers between polymers of different chemistries needed for combination of barrier and bulk properties. Graft modified tie layer resins provide the required interlayer adhesion to give a composite structure. Grades suitable for both, blown and cast barrier films are available. Such films have wide range of applications in food and non-food packaging. The latest trend is to make plastics fuel tanks by Coextrusion. This also needs the right type of tie layer.
- **Extrudable adhesive** in extrusion coating / lamination applications. BindEX™ resins are used for bonding PP & HDPE woven cloth to BOPP or paper for bulk packaging applications.
- **Adhesive layer** in films for Aluminium Composite Panels used in wall cladding, partitioning, decoration, advertising and furniture manufacturing.

Future of grafted polymers

Despite lobbying against use of plastics, its use is not going to decrease. Sustainability issues and the general awareness about Reduce, Recycle & Reuse is likely to cause the much needed lowering of consumption of virgin plastics. Grafted polymers have an important role to play for sustainable use of plastics. The development of new polyolefin polymers and new processing equipment has increased the opportunities for production of different range of grafted polymers like elastomer based grafted polymers, EPR based grafted polymers, and others. Also, the global demand of recycling of plastics waste opens up a huge opportunity for grafted polymers. There is no solution available at present to recycle mixed plastic waste into usable products with value addition. Grafted polymers can provide value addition to mixed recycle stream in terms of mechanical strength, compatibility and flow characteristics. Pluss has been actively working on such solutions that are aimed at extending the value chain of plastics materials through its reCouppTM brand of grafted polymers. One such product is already in the market that makes film-to- film recycling of multilayer nylon film possible.