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Functionalised Polyolefins: Compatibilisers & Coupling Agents for Alloys, Blends & Composites

Compatibilisation is referred to any physical or chemical method that results in stabilisation (prevention to separate) of polymer blends morphology and properties.

Functionalized polyolefins (polyolefins grafted with maleic anhydride/glycidyl methacrylate or other monomers) have been known to act as cou-

pling agent for filled polymer compounds and as compatibiliser for dissimilar polymers.

Such graft polymers are result of post reactor grafting reactions. One re-

cent estimate put the worldwide consumption of these materials at 18,000 tonnes per annum (Special Chem). They are used in small quantities but as additives they give substantial improvement in properties of the base compound.

The basic steps in the production of functionalised polyolefins are:

- Use a polymer such as LDPE, LLDPE, HDPE, EVA, EPDM or others
- Choose a monomer to be grafted, e.g. Maleic Anhydride, Glycidyl Methacrylate, Acrylic Acid etc.
- Use a peroxide to generate free radicals on the polymer backbone
- Use appropriate extrusion conditions such as residence time, temperature, mixing, de-volatilisation of unreacted constituents
- Inject any additives desired before extrusion into pellets

The equations in Fig. 1 give the chemistry of the reactions taking place in the extruder. Free radicals extract hydrogen from polymer chains, thus forming radicals on polymers which add to maleic anhydride and initiate grafting process, under melt mixing conditions applied for grafting inside the extruder.

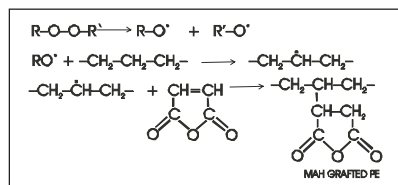


Fig. 1: Reactions in the Extruder.

However, due to the technological aspects associated with the handling of maleic anhydride, the need for specialized extruders to achieve good dispersion of incompatible materials and small tonnage global market, there are very few manufacturers of such products worldwide. Some major suppliers with their trade names within the

brackets are:

Atofina	(Orevac)
Dupont	(Fusabond)
Exxon	(Excelor)
Eastman	(Epolene)
Mitsui	(Admer)
Polyram	(Bondyram)
Dow	(Primacor, Amplify)
Pluss Polymers	(Optim)

The base polymers like LDPE, LLDPE, HDPE, PP, EVA and EPDM are grafted predominantly with maleic anhydride glycidyl methacrylate, acrylic acid and other functional groups that impart a degree of polarity to the otherwise non-polar base polymers. The additional chemical groups provide exceptional compatibility, reactivity and adhesion properties to these resins and cause good affinity towards other polar materials leading to their use in alloying blending, compounding, co-extrusion, printing, and lamination.

Applications

Some of the established applications for these are:

Coupling Agent in Filled and Reinforced PP Compounds

Maleic anhydride grafted polypropylene act by improving interfacial adhesion between the filler and polymer matrix. Thus, the polar functional groups in these materials, bind with the surface of fillers like calcium carbonate, talc, mica and glass fibres, while the PP backbone mixes well with the matrix polymer. This results in a better dispersion of the filler and enhances the mechanical properties of the compound. Maleated EPDM is an excellent impact modifier for filled PP compositions.

Higher filler loadings also become possible. In such cases Maleated prod-

ucts replace the conventionally used low molecular weight additives like waxes, which have a tendency to plateout and form undesirable die deposits during processing.

Nylon Alloys

Maleic anhydride grafted polyethylene is used for reactive blending with nylon to improve its overall toughness, particularly in the dry state. Polyethylene on its own is not known to blend with nylon. But the anhydride groups in maleated products readily react with the amine end groups in nylon and thus compatibilise polyethylene moiety. These products are suitable for unfilled as well as mineral and glass filled nylons.

Such nylon alloys have a wide range of applications, like safety helmets, luggage frames, handles and other components, automobile accessories such as motor cycle side boxes, brake and clutch levers, castor wheels, hand tool bodies, equipment housing, fan blades, rifle butts and industrial components.

In-situ Nylon Alloying

Maleated polyethylenes are being successfully used by hopper blending with nylon and moulding into small or large components using screw type injection moulding machines which allow adequate mixing. At the nylon processing temperatures, an alloy having good impact properties is formed during the injection moulding process itself.

Upgradation of Nylon Waste

Value can be added to nylon scrap, be it in the form of fibre, film or moulding waste, by using the compatibilising action of maleated polyethylene. The modified product is suitable for injection moulding applications.

Compatibilisers for PET/PE Waste Recycling

Recycling of commingled PET/PE film waste, such as generated in plenty by the packaging industry, is not possible due to the widely different nature of the two polymers. Maleic anhydride grafted EVA may be used for compatibilising the two polymers in such a mixture. Presence of fillers, inks and other additives in the mixture does not affect the process.

When a maleated polymer is used as a coupling agent, the fine particulate mineral no longer remains a filler but it reinforces the polymer matrix.

Co-extruded Films

Packaging demands high barrier films and sheets for long shelf life. Commodity polymers do not provide adequate barrier but have all the other characteristics like low cost, adequate mechanicals, etc. Barrier properties are obtained by co-extruding a middle layer of polymers such as nylon, EVOH, PVDC. Functionalised polyolefins are co-extruded as bonding layers between the commodity and barrier polymers. This is a special topic and needs detailed treatment on its own and hence not included here. Products available from the manufacturers are listed earlier.

Wood Composites

Wood Flour/Rice Husk – Polymer composites have all the advantages of polymer and have no disadvantages of wood. The compatibilisation action between the filler and the polymer is imparted by the use of maleic anhydride grafted polyolefins.

From the above applications, the following applications are established in India:

- Blends and Alloys
- PP Composites (Mineral & Glass Filled)
- Co-extruded Films

Blends & Alloys

Blending of two or more polymers offers an interesting route to modify the properties of thermoplastics. It is a cost effective way to produce new materials with desired property combination. But, even within the same family of plastics, materials are so different in properties and processing behaviour that as a mix-

ture they cannot be ordinarily converted into a composite material. Materials from the same family viz. polyolefins like LDPE & PP, do not mix together homogeneously to give a molecular dispersion necessary to obtain acceptable properties. Due to poor compatibility of the components, most of these systems are characterised by high interfacial tension, low degree of dispersion and poor mechanical properties. Therefore, it is of uttermost importance to use a compatibiliser to make the blend a compatible one with desired properties.

A compatible blend is mixture of polymers with low repulsive forces between phases. Compatibilisation is referred to any physical or chemical method that results in stabilisation (prevention to separate) of polymer blends morphology and properties. Polymer blends are used to change impact or flex properties, chemical resistance, thermoformability and printability, for example. Some properties of the compatibilised blend exceed that of either component alone.

A few simple examples of compatibilisers that may be used are given in the table 1.

Mechanism of Compatibilisation

Compatibilisers act through a chemical reaction (Reactive Compatibilisation) or through intermolecular forces of attraction such as Van der Waals, hydrogen bonding, based on polarity of the materials (Non Reactive Compatibilisation). In addition, a compatibiliser may function by more or less the same mechanism as a surfactant does to stabilize oil/

water mixture, i.e., by being soluble in one or both major components of the blend. One such mechanism is by attaching itself to one of the blend components through chemical grafting and leaving a polymeric “tail” that is soluble in the other component (See Fig. 2).

Stabilised, more uniformly dispersed domains result because of reduced interfacial energy between phases. In addition, the interfacial adhesion is improved because the compatibiliser segments, which reside in separate phases, are linked covalently.

Maleic anhydride (MA) grafted polyolefins are typically used as reactive compatibilisers for blends of polyolefins with polymers such as nylon. MA-grafted polyethylene (PE) or PP can be used to allow nylon-PP blends in applications where the high-temperature properties of nylon are required but PP is needed to reduce moisture absorption that can degrade nylon.

Production of Super Tough Nylon Alloys

Nylon, an excellent engineering plastic, suffers from a disadvantage that it is brittle under dry and low temperature conditions. The solution lies in blending it with a suitable impact modifier. This task is generally performed by the nylon resin manufacturers themselves or by some custom compounders, who then supply these modified nylons to moulders.

As a matter of fact, conversion of nylon to super tough nylon is nothing new and has been practiced for more than 20 years. The chemistry behind this alloy formation is represented in Fig. 3.

POLYMER 1	POLYMER 2	COMPATIBILISER
LDPE	PS	POLYSTYRENE ETHYLENE DIBLOCK
LDPE	PVC	CPE
LDPE	NYLON	MAH Grafted PE
PP	NYLON	MAH Grafted PE
PET	PE	MAH Grafted PE

Table 1: Examples of some Compatibilisers.

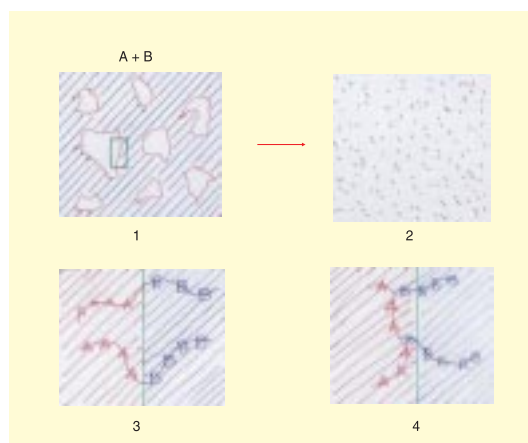


Fig. 2: Mechanism of Compatibilisation.

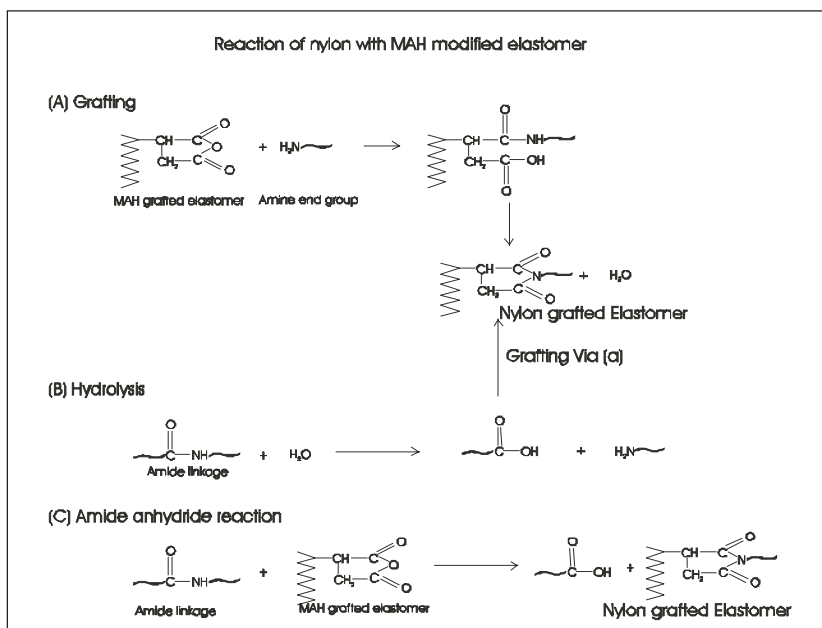


Fig. 3: Alloy Formation Chemistry.

Presence of anhydride or acid group serves two purposes:

1. During melt processing, acid or anhydride groups react with nylon via amine end group or through route that involve amide linkage to produce nylon graft on elastomer. Thus grafting reduces interfacial tension and retards coalescence of particles through steric stabilization both of which aid development of stable, fine dispersion of rubber phase in nylon matrix.

2. Graft structures also increase interfacial adhesion and aid stress transfer between phases

Table 2 gives indication of improvement in notched impact strength brought about by hopper blending 5 to 30% of OPTIM MAH grafted Poly ethylene (E-142) with nylon 6 and injection moulding into test specimen.

The impact strength improvement is more pronounced in annealed samples but it is more significant in unannealed condition (as moulded) since it implies

Material	Impact Strength J/m	
	Unannealed	Annealed in Hot Water
Nylon 6	21	35
Nylon 6 + 5% OPTIM E-142	200	
Nylon 6 + 20% OPTIM E-142	800	No break
Nylon 6 + 30% OPTIM E-142	1000	No break

Table 2: Improvement in Notched Impact Strength.

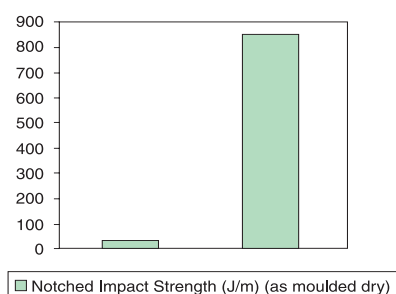


Fig. 4: Improvement in Properties.

that a nylon component can go through the assembling process directly, without necessarily going through the annealing step. This means lesser hold up time with the moulder and quicker deliveries to the customer. Suitable compatibilisers are available for both nylon 6 and 66 and others.

In Situ blending (Hopper blending during Injection Moulding)

The greatest advantage this in-situ alloying gives to the moulder is that he can choose different proportions of OPTIM to be used for each component depending upon the improvement desired and not be restricted by the specific grades that a manufacturer or a compounder offers.

Components of Supertough Nylon Alloy can be moulded directly in a screw type injection moulding machine without going through a separate compounding step. There would be an upper limit to the additive proportion that can be thus incorporated, thereby limiting the improvement in impact properties.

Mineral and Glass Filled PP

Polypropylene is frequently compounded with fillers such as clay, calcium carbonate and talc. These fillers reduce shrinkage in moulding, impart a considerable degree of toughness, increase the heat distortion temperature and simultaneously reduce cost.

The filler level is generally in the range of 20 to 40%; but lately compounds with filler content up to 80% have been produced and used in moulding and extrusion applications. These materials find use in the production of automotive parts such as air conditioner and heater housing, exterior light housing, interior side panels and air filter housings. The filled compounds are also used in the manufacture of appliance bodies, moulded furniture and electronics components. Moulders either use the compound as such or employ a compound of higher filler content and dilute it with virgin PP before moulding. Such carefully mixed formulations become the moulder's in-house know-how.

MAH grafted Polypropylene is used for talc/calcium carbonate filled polypropylene where it acts as a coupling agent between mineral filler and PP matrix and this coupling action is responsible for enhancing the mechanical properties and overall processability of the compound. When a maleated polymer is used as a coupling agent, the fine particulate mineral no longer remains a filler but it reinforces the polymer matrix. Besides talc and calcium carbonate, maleated PPs are known to act equally well with wollastonite and particularly with mica. The

NYLON ALLOYS

Applications demanding:



- High Impact Strength
- Low Moisture Absorption
- No Annealing
- Good Paintability
- To be used in low temperatures

e.g.: Suitcases, Sports Equipment, Cables, Furniture Parts



most sought after application in this case is glass filled PP which is the first choice material for allocations requiring high impact strength as in case of an automobile.

The latest product emerging out of the ongoing process of application development has been the extruded V-profile used as water baffles in cooling towers. Such profiles have hitherto been produced with PVC. For obvious advantages, there was a need to switch over to PP. For application in such a product, stiffness and impact strength were the important properties required. In addition, holes of 6mm dia were required to be punched all over the V-profile surface in a post extrusion operation. The punching requirement turned out to be the most critical and difficult-to-achieve development work. Unfilled PP could be used but its stiffness was low. The section had to be made thicker so that it would not sag under its own load when installed. Increased thickness offsets the cost advantage. Besides, punching the holes was almost impossible, as the resistance was too high.

Any of the standard PP compounds used for injection moulding failed for these-profiles due to low tear strength in MD. This low strength also meant that the section fibrillated on punching. High filler content was also necessary to get clean punching with 100% release of punched discs from the holes.

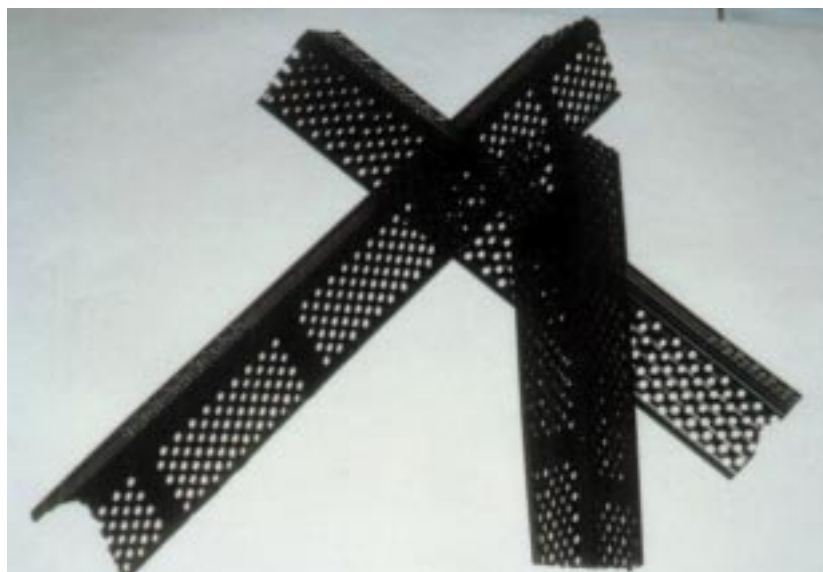
Addition of 3% OPTIM Maleated PP (P-415) in the PP compound with 30% mineral filler, brought the desired results. The presence of maleic anhydride grafted PP OPTIM P-415 offered the necessary coupling action between the mineral filler and PP matrix thus

providing mechanical properties required during extrusion, finishing operation and end use. The high MFI of OPTIM P-415 (50g/10 min at 230°C, 2.16Kg) improves filler dispersion and overall MFI and processability of the PP compound. This ensures smooth extrusion and good surface finish. OPTIM P-415 (being polymeric and of a much higher molecular weight than the conventional wax additives used as processing aids in highly filled compounds) does not migrate or leach out of the component during extrusion and service in cooling towers.

OPTIM MAH grafted PP is available in various grades having different melt flows. The high MFI grade also acts as a flow-aid by increasing the overall flow of the compound and thus ease processing. By lubricating the metal-polymer interface OPTIM further improves flow (higher productivity) and reduces melt imperfections.

The other notable improvement in finished products by using maleated polyolefins are:

- Gloss on the moulding is enhanced. In the case of coloured components,



Wood plastic composites are a relatively new application and are likely to grow to large volumes although not yet established in India.

an improvement in the hue is obtained.

- In filled PP extrusions (films, sheets and other profiles), it reduces die plate out due to its solvating effect on the other additives normally added to these compositions. It also makes extrusion of highly filled materials smoother and distribution along the width of the die better.
- It allows increased filler content in HDPE and PP based synthetic paper, thus improving writability

The same efficacy of MAH grafted PP is reported in jute and wood flour filled PP compounds commercially known as Wood – Plastic Composite materials.

Wood Plastic Composites

These composites are a relatively new application and are likely to grow to large volumes and hence discussed in some details, although not yet established in India. Wood Plastic Composite uses a fine wood waste (cellulose based fiber fillers such as hardwood, softwood, plywood, peanut hulls, bamboo, straw, etc.) mixed with various plastics (PP, PE, PVC). The powder is extruded to dough like consistency and then extruded to the desired shape. Additives such as colorants, coupling agents, stabilisers, blowing agents, reinforcing agents, foaming agents, lubricants help tailor the end product to the target area of application. Of these, maleic anhydride grafted polyolefin coupling agents play a vital role in increasing the level mechanical properties of the composite. Products based on PP



and HDPE are available. With up to 70 per cent cellulose content, wood-plastic composites behave like wood using conventional woodworking tools. At the same time, they are extremely moisture-resistant. There is little or no water present, thus increasing resistance to rot.

The properties are enhanced substantially by addition of MAH grafted polyolefin as illustrated in the table below for rice husk.

Products in wood plastics composites
Lumber, decking and railing, window profiles, wall studs, door frames, furniture, pallets, fencing, docks, siding, architectural profiles, louvers, automotive component are some of the established applications abroad.

Characteristics

- Dimensional stability
- Resistance to termite and microbial attack

- Stable over a wide temperature range
- Moisture resistant
- High impact resistant
- Low flame spread
- Excellent thermal properties
- Outstanding screw and nail retention
- Compressive-tensile-shear strength
- High slip resistance
- Environmentally friendly
- Recyclable
- Broad range of finishes and appearance
- Use of waste and recycled materials
- Competitively priced
- Easily produced and easily fabricated.

The properties of the composite end product are a function of the matrix, filler and the interfacial bond strength between the two. The factors affecting the interfacial bonding are:

- Component properties of the blend – type, amount, distribution
- Modification of the filler and/or plastic
- Method of incorporating the filler
- Processing conditions – compounding, injection moulding, extrusion

Conclusion

This article provides just a flavour of what is possible using functionalised polyolefins. Commercially each one of the manufacturer will have tens of grades available. The user needs to interact with the supplier to select one appropriate for his application.

Rice Husk %	PP %	OPTIM P-415 %	Den g/ml	U-Izod I.S. J/m	Flex Str. Kg/cm2	Flex mod. Kg/cm2	Water Abs. % (24hr)
40	60	-	1.00	32	329	15,400	0.50
50	50	-	1.06	21	289	25,800	0.56
60	40	-	1.07	21	261	26,000	0.89
40	50	10	1.02	43	444	22,900	0.10
50	40	10	1.05	51	427	28,900	0.49
60	30	10	1.09	47	422	30,300	0.47

Table 3: Enhancement in Rice Husk Properties by addition of MAH Grafted Polyolefin.