

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Polymer blends

Each polymer has both advantage and disadvantage in particular properties, no polymers has complete properties. So, learning each polymer to select its advantage for using such as learning about polymer blends in order to get the best properties to meet requirement has investigated.

Polymer blends is a mixture of at least two polymers or copolymer, which may be miscible or immiscible. The general relation between blends and alloys is shown in Figure 2.1. Polymer blends is different from copolymer but similar to polymers that bring together the properties of different polymers. The main reason for blending is economy. If a material can be generated at a lower cost with properties that meet the required specification, the manufacturer will use it to remain competitive and other reasons could be listed as follows (5):

1. Extending engineering resin performance by diluting it with a low cost polymers.
2. Developing raw materials with a full set of desired properties.
3. Forming a high performance blend from synergistically interacting polymers.

4. Adjusting the composition of the blend to customer specifications.
5. Recycling industrial and/or municipal plastic scrap.
6. Environmental

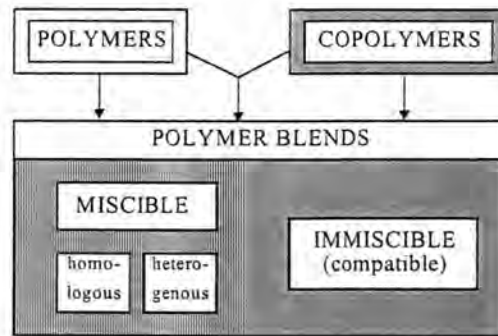


Figure 2.1 Interrelation in polymer blends

The total of all polymer blends is estimated at 3% of the total polymer production that is approximately 2 million pounds per year in the United States. There is considerable activity in this area since “new” products can be obtained and markets expanded by the physical mixing together with existing products (6).

2.2 PP/EPDM blends

PP/EPDM blends is a group of elastomeric block copolymers referred as thermoplastic olefin (TPO) which is one kind of polymer blends. PP/EPDM blends comprise of polypropylene (PP) and ethylene propylene diene monomer (EPDM), where the EPDM is the minor component and exist as the disperse phase into matrix phase of PP. The two phases in these systems have remarkably different

properties. The first phase is disperse phase, it contains a component which is above its glass transition temperature (T_g) and melting temperature (T_m), so that chain is very mobile. Another phase is matrix phase, it contains segments which are rigidity locked in place, because the service temperature is below both T_m and T_g (7).

The primary advantage of PP/EPDM blends is the ease of processing, good impact resistance, the variety of properties and it can be reused. Besides the obvious environmental benefit of recyclable raw material, scrap can be reprocessed rather than throw away. In addition, there are many factors that define PP/EPDM blends properties such as components, processing technique and morphology, which showed as follows:

2.2.1 Main components of PP/EPDM blends

Each component such as PP, EPDM, reinforced additives and minor components has been effected to physical and mechanical properties of PP/EPDM blends.

2.2.1.1 Polypropylene (PP)

PP is one kind of thermoplastic, which can be melted upon the application of heat, can be molded and remolded into virtually any shape by using processing techniques. PP is the most recently introduced of the major plastic manufacturers.

Although PP are excellent material when considered generally, their impact strength and rigidity are relatively poor and this often narrows the range of application of PP. So, the normal method for improving the impact strength of PP is to blend with a polymer having rubbery properties. Therefore, adding PP with reinforced additives such as carbon black, talc, clay and glass fiber, the rigidity and other properties will be improved gradually as the amount of additives reach a certain point.

2.2.1.2 Ethylene Propylene Diene Monomer (EPDM)

EPDM rubber is the polyolefin that is the most often used in toughening PP. The general effect of rubber on glassy polymer is to produce a softer, tougher and more ductile polymer. Toughness, as measured by impact strength, increases significantly with increase rubber level. The impact strength of PP results from the absorption of large quantities of energy during the process of craze formation as shown in Figure 2.2. The structure of EPDM and the manufacturing process are shown in Figure 2.3 and 2.4. By acting as initiating sites for new crazes radiating from their surfaces, the rubber particles prevent the formation of macro-cracks, grow rapidly to the point of rupture of the resin. If the new crazes do not absorb enough of the energy imparted by the original stress, they encounter other rubber particles which, in turn, become the focus for sets of crazes.

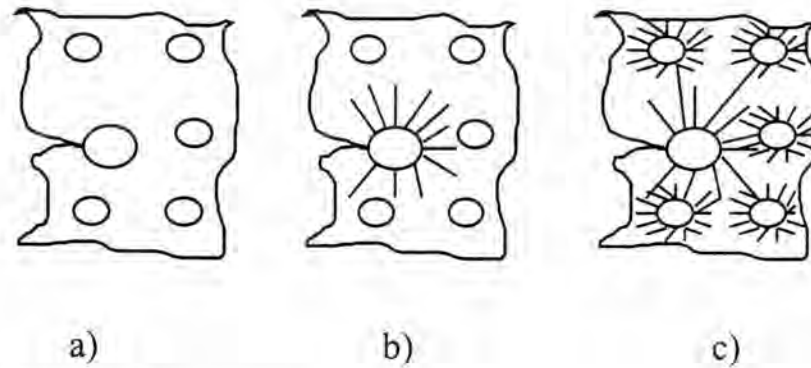


Figure 2.2 Craze formation

- a) Initial crack, b) New crazes formed absorbing energy,
 c) Remaining energy absorbed by formation of crazes at surface of neighbouring particles.

The composition of EPDM elastomers are controlled by using the appropriate monomer feed ratio to obtain the desired composition in a continuous polymerization process.

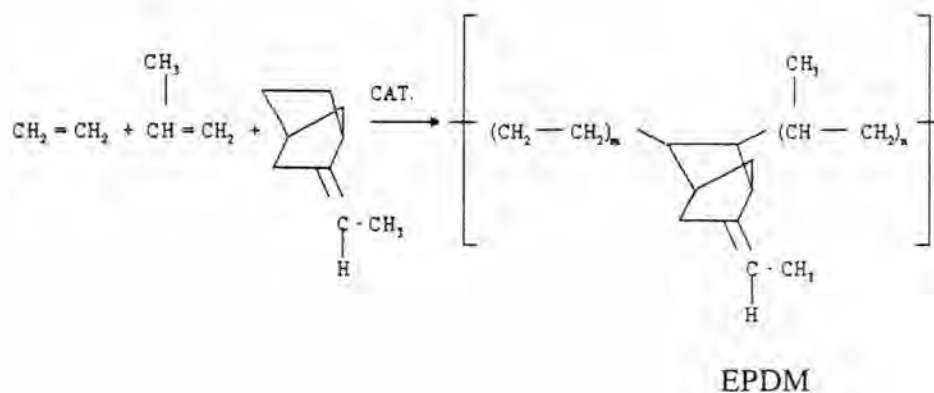


Figure 2.3 The structure of EPDM

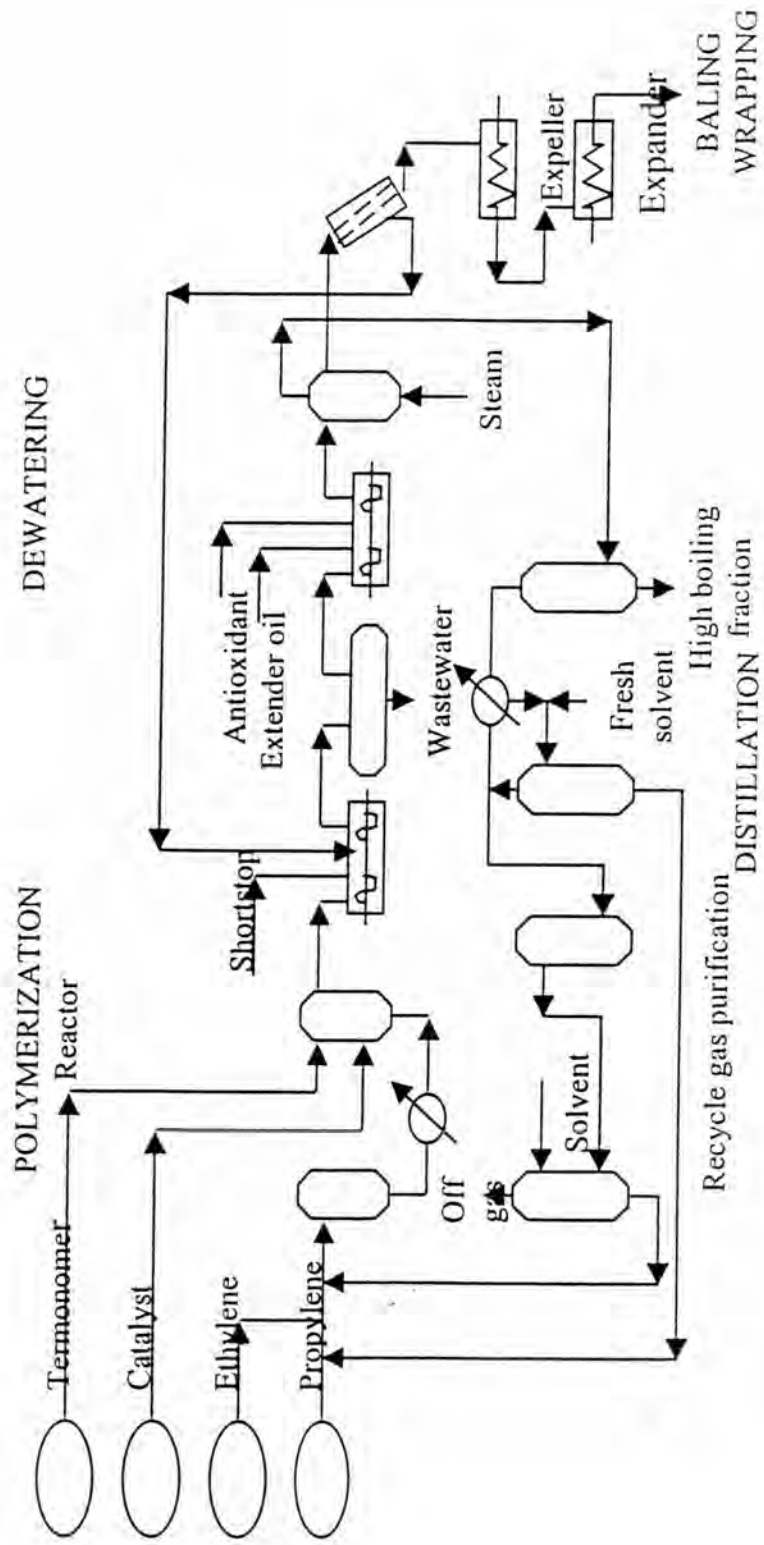


Figure 2.4 EPDM Manufacturing Process

As an adjunct to adding compound ingredients blends parameters may be varied to meet many processing and end-use requirements (8).

Ethylene propylene composition

The contents of ethylene propylene (EP) elastomers are generally reported as weight percent propylene. The monomers are randomly distributed, resulting in amorphous type copolymers. The higher ethylene containing polymers, which contain some crystallinity, are beneficial in that they possess higher green strength (shape retention). The disadvantages of the higher ethylene contains are their poorer mill processing behavior at lower temperatures, inferior low temperature properties, and their difficulty in being mixed. Since crystallinity tends to increase with decrease in temperature, it is appropriate to store high ethylene terpolymers under sufficient warmth to minimize dispersion problems.

Molecular weight

The molecular weight of an elastomer is commonly reported as mooney viscosity (ML). The mooney viscosity equipped with a large disc registers after preheating at 100°C for 1 minute and rotation for 4 minute. The primary reason for this is to melt out any effect that high ethylene content could produce, thus masking the true molecular weight of the polymer.

Molecular weight distribution (MWD)

Molecular weight distribution is normally not reported as a polymer variable but in most applications it is a very important property. A measure of the MWD is now commonly obtained through the use of gel permeation chromatography at elevated temperatures. The reported value is the ratio of the weight-average molecular weight to number-average molecular weight (M_w/M_n). This value can usually vary from 2 to 5. For broad MWD polymers, there is usually a variation in EP composition as well. The end with the higher molecular weight possess a higher ethylene content than the end with the low molecular weight.

Diene content

Ethylidene norbornene (ENB) is the most widely used termonomer employed even though it is the most expensive, the reasons being that it is the most readily incorporated during copolymerization and the double bond introduced has the greatest activity for sulfur vulcanization. Another unique characteristic of this termonomer is that it is possible to prepare linear as well as branched polymers by varying the conditions under which the polymers are synthesized. Branching has an importance role in establishing the rheological properties of a polymer. Under proper control, it can introduce properties to the EPDM that are beneficial in certain application.

EPDM molecule impacts these significant features to product made from it:

- Outstanding resistance to ozone attack
- Excellent weathering ability
- Excellent heat resistance
- Wide range of tensile strength and hardness
- Excellent electrical properties
- Flexibility at low temperatures
- Good chemical resistance, especially to polar media
- Resistance to moisture and steam.

2.2.1.3 Reinforced additives

Reinforced additives have always been importance part of the polymer and rubber industry. The most widely used are glass fiber and some fillers such as the carbon blacks, talc and clay. They are applied to polymer that may serve to reinforce or increase FS and hardness, durability, tensile strength, abrasion resistance and reduce cost. Most reinforced additives are bound to polymer by van der qalls forces and, thus, are better bounded if the surface of the particle is smooth and the surface area and surface to volume ratio are high. Frequently, a combination of reinforcement is used to obtain the required balance of reinforcing properties, processability and economics for the particular application. The important properties are particle size and structure which the effect of structure and particle size is represented as shown in Table 2.1.

Table 2.1 The effect of structure and particle size of reinforced additives

		Particle Size		Structure	
		Fine	Coarse	Low	High
Processing	Improve	→	→	←	←
Reinforcement	Increase	←	←	→	→
Optimum loading (for tensile and tear) at increased oil loadings	Increase	→	→	←	←
Mooney viscosity, modulus and hardness	Increase	←	←	→	→
Compound cost	Increase	←	←	←	←

2.2.1.4 Minor components

Minor components are antioxidant, UV stabilizer, pigment, paraffin oil, wax and so on. Antioxidants and coupling agent are use as the composition in this research.

Antioxidants are particularly important part in polymer and rubber industry. Antioxidants are highly unsaturated and the double bonds are extremely susceptible to attack by oxygen and ozone, resulting in embrittlement, cracking, and general degradation. Since the degradation reaction take place by free-radical mechanisms, antioxidants are compounds that scavenge free radicals (9).

Requirement of antioxidant

- good solubility and compatibility with polymer
- low volatility and resistant to exudation
- resistant to photo-and thermal-degradation
- good color retention

- low toxicity

Silane coupling agent provide a stable bond between two otherwise nonbonding surfaces. In reinforced and filled plastics, the improved bond between fibrous or particulate inorganic components and the organic matrix polymer results in greater composite strength and longer service life (10).

2.2.2 Processing technique

PP and EPDM have similar melt viscosity and both are in particulate form, it may be possible to mix in low shear mixing sections or even directly in the extruder or injection molding machine used to make the final part. However, the most widely used of high shear mixing equipments are internal mixers, two-roll mills, brabender mixers, banbury mixers as well as single and twin screw extruders. For this research, two-roll mills is selected for blending PP, EPDM and other additives.

A two-roll mills is generates high shear rate in a narrow nip between two heated rolls which counter-rotate with slightly different velocities. In commercial mills, the rolls are about 1 ft in diameter by 3 ft long. Once the polymer has banded on one of the rolls, ingredients are added to the bank between the rolls. The band is cut off the roll with a knife, rolled up, fed back to nip at right angles to its former direction. This is done several times to improve mixing (11).

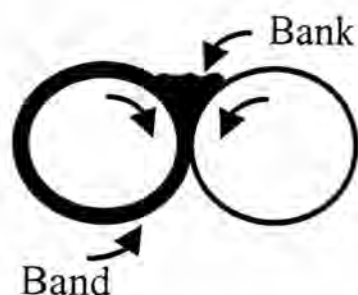


Figure 2.5 Two-roll mills

2.2.3 Morphology

The morphology of a material is its organization on a supermolecular scale, i.e. the form, size, orientation of its crystallites, domains, the structure of group of molecules in the specimen and of their boundaries, and the degree of crystallinity. Most polymer blends are heterogeneous, and the sizes and shapes of the phase domains control mechanical and transport properties. This is especially relevant for elastomeric systems, as many of these are rubber blends, thermoplastic elastomers, thermoplastic olefins such as PP/EPDM blends, and dynamic vulcanizates. The measurement of interfacial tension, which controls phase separation and growth and thus morphology, is also important.

The scanning electron microscopy (SEM) is used to investigate morphology of PP/EPDM blends. SEM is becoming the most popular method of observation of polymer blends. The great advantages of this technique are rapidity, range of readily accessible magnifications, depth of field and almost universal for modern machines.

2.3 Literature reviews

There have been continued interest in the development of thermoplastic olefin especially PP/EPDM blends. The properties of these materials depend on many factors like material properties of polymer matrix, rubber, additives, PP/EPDM ratio, particle size and so on. In this literature survey, the work of fiber reinforced polymer are reviewed.

Sano, H. and Yui, H. (12) studied olefin polymer composition having markedly improved impact strength as a result of including as inorganic filler in a specified form. The compositions comprised a matrix of a thermoplastic olefinic polymer (e.g. high density polyethylene, isotactic polypropylene and maleic anhydride-grafted polypropylene) and a dispersed phase of an impact-absorbing polymer or its composite, which constituting the dispersed phase having filled therein an inorganic filler as calcium carbonate. The reactions were mixed in supermixer, kneaded in twin screw extruder, then cooled to form pellets. In addition, the resulting composition was morphologically examined by scanning electron microscope. It was found that composite having a smaller particle diameter of calcium carbonate than the dispersed phase had higher impact strength than composite having higher particle diameter of calcium carbonate as list in Table 2.2.

Table 2.2 Effect of particle diameter of calcium carbonate in polymer blends

Composition (parts by weight)	Charpy impact strength (kg.cm/cm ²)	
	23 °C	40 °C
1. Ethylene/propylene block copolymer (62) Maleic anhydride-grafted high-density polyethylene (18) Calcium carbonate having an average particle diameter of 0.3 micron (20)	above 50	16.2
2. Ethylene/propylene block copolymer (62) Maleic anhydride-grafted high-density polyethylene (18) Calcium carbonate having an average Particle diameter of 0.3 micron (20)	35.5	10.5
3. Ethylene/propylene block copolymer (62) Maleic anhydride-grafted high-density polyethylene (18) Calcium carbonate having an average Particle diameter of 3 micron (20)	12.0	6.5

Datta, S., Dharmarajan, N. R., Dekoninck, J. M. and White, D. A. (13) disclosed thermoplastic composition which comprised a blends of a polypropylene (PP) with a copolymer of styrene and maleic anhydride (SMA), and elastomeric EPM or EPDM which had been modified with a specified functional group (amine-EP), and an amine-modified maleic anhydride grafted polypropylene (amine-PP). The reactions were carried out in Brabender plasticorder mixer by varying component ratios, order of mixing of the functional EP and PP modifiers and also compared between melt mix and dry blends. It was found that the composition which comprised of four components as PP, SMA and amine-EP/amine-PP (3/1) illustrated good impact

property with optimal properties as shown in Table 2.3. The sequence of addition of amine-EP or amine-PP did not appear to be critical, and both melt mix compounds and dry blends had good impact property .

Table 2.3 Physical property of composites

Composition#	1	2	3	4
PP Impact Copolymer	70	60	67	56
SMA	30	25	28	24
Amine-EP	-	15	-	15
Amine-PP	-	-	5	5
<u>Properties</u>				
Notch Izod Impact (ft-lb/in) 21 °C	0.59	1.1	0.63	6.1
Flexural Modulus (Kpsi)	266	180	280	174
Tensile Strength (psi)	3766	2779	4733	2591
Elongation (%)	6	9	11	91

Thiersault, J. P. and Senez, A. (14) investigated polypropylene compositions with high impact strength which comprised 50 to 97 % by weight of isotactic polypropylene (melt flow index of 3 at 2.16 kg and 230°C), 2 to 49 % by weight of EPDM and 1 to 30% by weight of linear low density polyethylene (LLDP), of a density up to 0.935. The composition are prepared on a twin screw extruder. They found that the level from 80% to 97% by weight of isotactic polypropylene, 2% to 14% by weight of EPDM and 1 to 6% by weight of LLDP, of a density up to 0.935 give high impact strength of polypropylene compositions.

Takimoto, M., Takenchi, J. and Yamazaki, Y. (15) investigated thermoplastic olefin (TPO) of polyblend comprised of 30 to 70 wt% of EPDM, 10 to 30 wt% of EVA, and 20 to 50 wt% of PP which afford

injection molding for automotive exterior, having a good (uniform) matte-finished appearance. The compositions were produced by simple mixing without the process for partial crosslinking, which requires accurate control for temperature and pressure. In addition, the partial crosslinking process required a difficult control in the production. It was found that the amount of EPDM is less than 30 wt% and less than 10wt% for EVA including also less than 20 wt% for PP, the resulting mold items lack a matte-finished appearance. However, the amount of EPDM is greater than 70 wt% and greater than 30 wt% for EVA including greater than 50 wt% for PP, the resulting molded items lack strength required for automotive exterior trim and also lack a uniform matte-finished appearance.

Hazelton, D. R., Puydak, R. C. and Booth, D.A. (16) investigated that thermoplastic compositions of matter useful as gasketing materials as well as flexible boots and seals that were soft have low compression set and high tensile. The compositions comprised a polyolefins resin and at least two different rubbers, one of which was vulcanized to a fully cured state by a cure system which left the other rubbers unvulcanized. The embodiment comprised a blend of polypropylene and ethylene vinylacetate as the polyolefin resin component and ZnO cured halogenated butyl rubber. It was found that compositions having incorporated therein a dynamically cured chlorinated butyl rubber in addition to uncured EPDM demonstrated higher modulus, lower compression set and lower tension set as well

as increased VICAT softening temperature when compared with polyolefin / uncured rubber.

Inoue, T. (17) investigated the effect of selective crosslinking of the unsaturated elastomer particles in polypropylene (PP) matrix. The crosslink system comprised N, N-*m*-phnylene-bis maleimide (PM) and 6-ethoxy-2,2,4-trimety-1-1,2-dihydroquinoline (ETMQ) or polymerized-2,2,2-tri-metyl-1,2-dihydroquinoline (PTMQ). Crosslink the elastomer particles selectively without causing excessive degradation of the PP matrix. The reaction was carried out under a dynamic crosslinking process using a twin extruder on PP/EPDM, PP/SBS, and PP/SIS blends, all of which are obtained by varying the amount of crosslinking system. The result is impact strength of the blends increased especially at 23°C compared to non-crosslinking system. Therefore, the selective crosslinking of the polymer particles in PP/elastomer blends is demonstrated to be an excellent technique to produce a high-impact and high-modulus PP.

Huff, T. (18) disclosed cross-linked, melt-flowable thermoplastic elastomer blends comprised of monoolefin polymer rubber crosslinkable low-density polyethylene which were essentially fully cured in polypropylene resin. It was found that the fully cured blend increased the resiliency, tensile strength and surface hardness without substantially adversely affecting its heat distortion, flexural modulus compared with partially cured or uncured blends, especially at the level of 40 to about 45 wt% monoolefin polymer rubber, 15 to about

20 wt% crosslinkable low density polypropylene and about 30 to 35 wt% polypropylene had excellent balance of mechanical properties.

Peltonen, P., Paakkonen, E.J., Jarvela, P.K. and Tormala, P. (19) investigated the influence of adhesion promoters on the properties of injection mould long-glass-fiber polypropylene. Different grade of coupling agent were added to the polypropylene homopolymer matrix during melt impregnation of continuous glass fibers. All of the ingredients used in the experiments were commercial products, and the amount of coupling agents added to the polypropylene were based on the recommendation of the manufacturer. The addition of coupling agents on the polypropylene matrix did not decrease the degree of impregnation of manufactured prepreg. Melt impregnated PP/GF prepreg was pelletized to the length of 10 mm., injection molded and tested. In addition, two commercial long fiber materials and one commercial short fiber compound were injection molded and tested. All of the components included a glass fiber weight fraction of 40%. The addition to some coupling agents improved tensile and flexural properties remarkably compared to a non-coupled composite. As a typical result, impact strength value of the same specimens were decreased. Low temperature impact strength of long fiber composites was higher compared to impact strength obtained at room temperature. All long fiber composites showed superior impact properties compared to short fiber composites. The melting histories of the matrices were not affected by the addition of different grades of coupling agents, but the cooling run of DSC analysis could cause

differences in the crystallisation of the coupled matrices. Residual fiber lengths were analysed from the mouldings. The morphology of the interface of the composites, studied with SEM indicated a good relation with mechanical testing. The highest tensile and flexural strength of the composites were obtained on the same materials that showed a partially cohesive fracture mechanism, by having matrix polymer on the fiber surface. An optical study of the fracture surfaces revealed a typical fiber pull-out phenomena in the weakest composites.