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Green composites based on coconut pith and recycled PP/reclaimed EPDM

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ABSTRACT

The scientific and commercial progress in the area of polymer blends and composites during the past two decades has been tremendous and blending can be implemented more rapidly and economically than development of new polymers. In the current study Reclaimed EPDM and Recycled PP has been melt blended in a Brabender plasticorder in different ratios and the blend with optimized results was selected, as well as Recycle polypropylene/ Reclaim Ethylene propylene Diene monomer coconut pith composites have been prepared and developed for cost effective foot wear applications. A comparative study of composites in presence and absence of MA -g- EPDM was carried out and the effectiveness of the properties was determined. Coconut pith in different ratios was added into Reclaimed EPDM / Recycled Polypropylene blends along with MA-g-EPDM and other additives. Morphology, thermal and Physico mechanical properties of Recycled polypropylene (RPP) / Reclaimed EPDM coconut pith composites were investigated. Physico mechanical and thermal properties were improved by the addition of maleic anhydride and coir pith. Morphological analysis shows that the compatibility between coconut pith Recycled PP and reclaimed EPDM has been improved by the addition of Maleic anhydride grafted EPDM as a compatibilizer and hence can be used as a low cost filler for foot wear soling application.

KEYWORDS

Recycled polypropylene;
Reclaimed EPDM rubber;
Coconut pith;
Footwear.

INTRODUCTION

Population growth in large urban centers, social and technological developments and changes in consumers' habits have led to greatly increasing amounts of solid wastes. Thus, nowadays, waste management is one of the most significant issues that modern society deals with. The suitability of polymers for a large number of applications and uses is a consequent result of their important properties i.e polymers are lightweight, flexible and versatile, offering many practical benefits to various uses, easy to process in any desirable shape and available with various types of modified properties. The use of plastics and rubbers are growing steadily. Most industrialized have systems for the collection and recycling of plastic and rubber waste, either implemented on a full scale or on trial. An important aspect of polymer recycling is that the types of polymers used for most applications are inexpensive commodity materials. The price of corresponding virgin polymers determines the ceiling for the price at which recycled materials can be sold for reprocessing[1].

Polypropylene (PP) as one of the major commodity polymers has excellent properties such as high stiffness and good mechanical properties. However, its brittle behavior limits the use of PP in many applications. Polypropylene is often blended with elastomers to improve its impact strength[2,3]. Polypropylene can be toughened through incorporating low contents of ethylene during its copolymerization, resulting in random or block copolymers or by the in situ method, inside the reactor, where are formed dispersed elastomeric domains of ethylene-propylene elastomer (EPR) in a polypropylene matrix, called hetero phase polypropylene. Due to similarity in chemical structure to EPDM, with polypropylene, the blends of EPDM / PP has been commercialized for use in various industrial applications. Even though the structure of EPDM is similar to Polypropylene, EPDM is not compatible with PP. EPDM phase exists as a separate phase due to stratification segregation and phase inversions. To improve the compatibility between PP/EPDM phase various compatiblizers were added[4,5].

The incorporation of fillers into thermoplastics' elastomers has been widely practiced in industry to extend the elastomers and to enhance certain properties. The addition of fillers to polymers is a fast and cheap method to modify the properties of the base materials. For this reason, particulate filled polymers have been, and continue to be, the subject of increasing interest in both industry and research. In this way, strength, stiffness, electrical and thermal conductivity, hardness and dimensional stability, among other properties can be tailored to the required values. Natural fillers are the recent trend in the composite preparation because of various reasons like lower cost, light weight, biodegradability, non abrasive nature etc. Now – a - days the materials obtained from non petrochemical industry, and naturally occurring, which are readily available have been used in various industries for reinforcement purposes. Coir pith is one of the most abundant agricultural wastes found in the southern coastal regions of India. Coconut pith, naturally occurring filler obtained from coconut husks has been used to extend the properties of both thermoset and thermoplastic materials[6,7]. Many technologies have been developed successfully for the alternative use of coir pith. However, the application of coir pith as filler in polymers is limited, the major drawback being its low adhesion with the matrix and high water absorption and retention. Moisture absorption is high in lignocelluloses because of their structural compositions, which lead to poor adhesion between filler and matrix[8].

The main problem in preparing coconut pith - thermoplastic elastomeric composites is the incompatibility of hydrophilic coconut pith and hydrophobic PP / EPDM matrix and also the incompatibility of PP / EPDM matrix. However, applying compatibilizer and coupling agents on the surface of the particulate filler can promote filler-polymer interaction, which in turn improves the tensile and impact properties of the composite, as well as its processing capability. In another study Arroyo et al found that the compatibility can be increased by the incorporation of grafted matrix onto the filler matrix system. MA – g – EPDM and MAPP are commonly used as compatibilizers, because it can efficiently improve the filler-matrix bonding due to the formation of covalent linkages and hydrogen bonds between the maleic anhydride and the hydroxyl group of the filler and matrix[9,10]. The elastomeric phase in PP / EPDM blends can be crosslinked by the addition of suitable crosslinking agents such as sulphur, peroxide, resins etc. The vulcanized product obtained is known as Thermoplastic vulcanizates (TPV's). Polypropylene (PP) / ethylene-propylene-diene (EPDM) based TPV receives considerable success since PP and EPDM have the similar chemical structure which is possible to mix PP and EPDM in any ratio. However, they are still thermodynamically immiscible at room temperature, which results in poor interfacial adhesion and a phase- separated morphology, this consequently leads to poor mechanical properties[11]. This article reports the comparative evaluation of with and without the addition of MA – g – EPDM as a compatibilizer on the mechanical, thermal properties and morphology of Recycled PP/ Reclaimed EPDM/coconut pith composites.

EXPERIMENTAL

Materials

Recycled Polypropylene was obtained from

Chethan Plastics Mumbai. Reclaim EPDM with 30% Rubber Hydrocarbon (RHC) for mixing was obtained from Gujarat Reclaim and Rubber Products Limited. Paraffinic oil was procured from Neelam Lubricants. Coconut pith was obtained from Rubber Park; Ernakulam. Dicumyl Peroxide 40 (DCP 40) for dynamic vulcanization was obtained from BP chemicals.

Method to prepare blend and composites

Preparation of the blend

Blends were prepared by using Brabender plasticorder PL 2500 mixer with a temperature of 180°C, rotor speed of 20 rpm for 10 minutes. Blends in variable ratios of recycled PP: reclaimed EPDM – 100:0, 90:10, 80:20, 70:30 and 60:40 were prepared in Brabender. After melt mixing the materials were passed through the two roll mill and sheeted to about 2 mm thick. The sheet was then cut and press molded for 10 minutes in a compression molding machine hydraulic press at 180°C, under specified pressure. Silicone wax paper was placed between the sheet and the press plates to avoid adhesion to mold. The sheet was then cooled down to room temperature still under pressure. The test specimens were die-cut from the compression molded sheet and used for measuring mechanical properties after 24 hours of conditioning at room temperature. On the basis of results obtained by flexing test, impact test and abrasion resistance of different blend ratios an graph was plotted against the blend ratios and the obtained values and optimum value of the blending polymers were determined and 60 : 40 (reclaimed EPDM : recycled PP) was finalized for the preparation of composites.

Preparation of composites

After the optimization study, composite with 60:40 (reclaimed EPDM: recycled PP) were prepared at different coconut pith content (0, 10, 20 and 30). Paraffinic oil was used as processing oil and MA-g-EPDM was used as compatibilizer. DCP40 was used for dynamic vulcanization. Also batches were made by without adding compatibilizer. Compression molding under specified pressure, preparation of test specimen were carried out in a similar manner as described in preparation of blends. TABLE 1 and 2 gives the recipe for the preparation of ternary composites.

TABLE 1 : 60:40 Blend and Composite recipe (Without MA – g – EPDM)

INGREDIENTS	PEC00	PEC0	PEC1	PEC2	PEC3
Recycled PP	60	60	60	60	60
Reclaimed EPDM	40	40	40	40	40
MA-g-EPDM	0	0	0	0	0
Coconut pith	0	0	10	20	30
Paraffinic Oil	10	10	10	10	10
DCP 40	1.2	1.2	1.2	1.2	1.2

TABLE 2 : 60:40 Blend and Composite recipe (With MA – g – EPDM)

INGREDIENTS	PEC0	PECM0	PECM1	PECM2	PECM3
Recycled PP	60	60	60	60	60
Reclaim EPDM	40	40	40	40	40
MA-g-EPDM	0	10	10	10	10
Coconut Pith	0	0	10	20	30
Paraffinic Oil	10	10	10	10	10
DCP 40	1.2	1.2	1.2	1.2	1.2

Characterization

Physico mechanical properties

Tensile strength

Tensile strength properties were done on Instron1185 tensile tester according to ASTM D 638 at a cross head speed of 50mm/min.

Tear strength

Tear strength of the sample was carried out according to ASTM D 624. This test method measures the resistance to tearing action.

Hardness

Hardness testing was carried out by using Shore A durometer according to ASTM D 2240. Specimen should be of 6mm thickness.

Flexing cycles

The no. of flexing cycles for failure was measured using Ross flex tester according to ASTM D 1052. The test specimens shall be 2mm in width, a minimum of 152 mmin length, and 6.35 mm (0.25 6 0.01 in.) in thickness, and shall be cut from a vulcanized sheet of6.35 mm thickness

Impact strength

The impact strength of the sample was carried out using Izod impact strength tester according to ASTM

D 256.

Weight loss

Weight loss of the sample was carried out using Taber Abraser according to ASTM D 4060. The specimen consists of 100mm diameter disc with both side's plane and parallel, also a 1/2in. diameter hole is drilled in the center.

Wear index

1000 times the loss in weight in milligrams per cycle. The sample used is same as for weight loss.

$$\text{Wear Index (I)} = \frac{(A - B)1000}{C}$$

A= Weight of test specimen before abrasion, mg; B = Weight of test specimen after abrasion, mg; C = Number of cycles of abrasion recorded

Thermal analysis (TGA)

Thermo gravimetric analyses of the composites were carried out using TGA Q50 of TA instrument, USA. The samples were tested in N2 atmosphere from 25^{0}C to 600^{0}C at a heating rate of 20^{0}C/min.

Morphological analysis

Phase morphology of the various blends was investigated by a JEOL JSM 5800 Digital Scanning Electron Microscope (SEM). The images were obtained at a tilt angle of 0^o with an operating voltage of 20 kV.

RESULTS AND DISCUSSION

Mechanical properties

Hardness

Hardness is the property that is defined as the resistance to indentation, the hardness of the Recycled PP/Reclaimed EPDM coconut pith composites increases as the coconut pith content increases as compared to the blend ratio. After adding maleic anhydride there is an increase in hardness values, the increase in hardness is due to the interaction of coconut pith with the matrix, i.e the incorporation of coconut pith filler in the blend is proper and hence there is an increase in hardness due to the addition of filler, on contrary if grafted EPDM rubber is used there is also an increase in the hardness, as quantity of rubber required for incorporating more filler is available. With the addition of

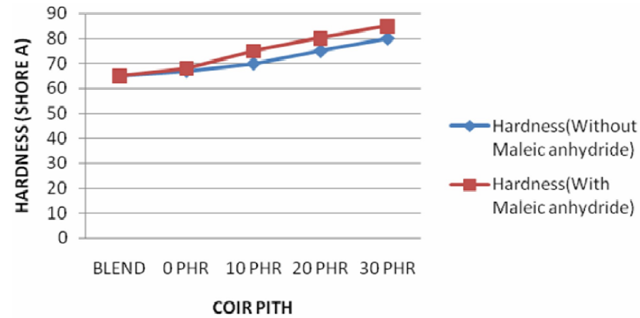


Figure 1: Comparative chart of hardness

coconut pith the hardness values are increased by 3 units and with the addition of MA-g-EPDM and coconut pith the hardness values are increased by 8 units

Tensile strength

The tensile strength values are decreasing in both the cases. The tensile strength properties of composites with maleic anhydride show an increasing trend as compared with and without compatibilizer. The decrease in tensile strength are because of the reason that large inter phase voids exists between the blending polymers, the large voids are due to the filler in the reclaimed rubber, and herein we are again adding coconut pith as a cheap filler between the blending polymers and therein increasing the voids to a large dimensions, and hence addition of coconut pith decreased the tensile strength values. The decrease in tensile strength values may be also due to the increased material stiffness from the interaction of coconut pith into the Recycled PP/Reclaimed EPDM matrix.

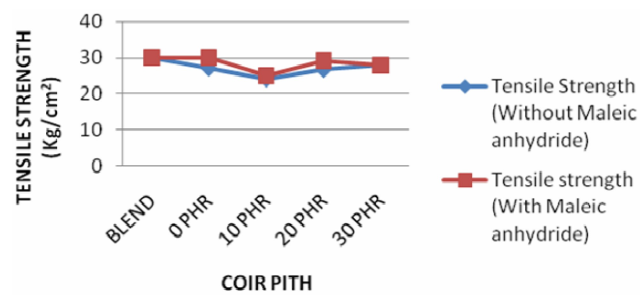


Figure 2 : Comparative chart of tensile strength

Tear strength

Tear strength values are increasing with the addition of coconut pith which is advantageous for footwear applications, and it is decreasing after 20 phr. The surface area of coconut pith is increasing while the concentration increases due to this an increase in tear strength is observed. The composite with maleic anhy-

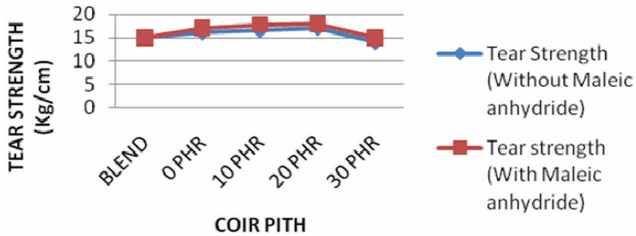


Figure 3 : Comparative chart of tear strength values

dride shows a slight improvement in tear properties as compared to the composites without maleic anhydride. This is because the grafted EPDM improves the interaction of coconut pith with the matrix. The increases in tear strength properties are beneficial to the footwear applications. After 20 phr it shows a decreasing trend because of the poor dispersion of coconut pith in the matrix.

Ross flexing

Flexing cycles for the failure of Recycled PP/Reclaimed EPDM composites increased as the coconut pith content increases. After the addition of maleic anhydride there is an increase in flexing properties as compared with composites without the addition of maleic anhydride. The failures of samples were occurring either by crack initiation or by crack propagation. Addition of filler helps in interfering with the propagation step. A crack front approaches filler particles which have good adhesion to the matrix. The front of the crack is slowed by filler particles because of their interaction with the tip stress field. Cavitation and coalescence of voids is followed by the matrix breaking away from particles and the crack front progressing to the next obstacle, due to this mechanism crack propagation slows and flexing cycles increases. At 30 phr coconut pith concentration there is a decrease in flexing property because at this point the coconut pith dispersion is poor hence instead of reinforcement it acts as a diluent. The improvement in flexing cycles for failure is beneficial for footwear application.

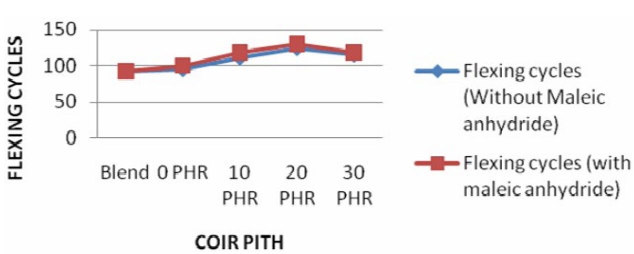


Figure 4 : Comparative chart for counts of flexing cycles

Weight loss

As the coconut pith content increases weight loss increases hence the abrasion resistance decreases. After the addition maleic anhydride as a compatibilizer there is an increment in weight loss so the abrasion resistance decreases. The weight loss increase because of the poor interaction of coconut pith with the matrix, the rubber phase in the blend wears away more rather than the plastic phase. As compared to the blend properties the weight loss is negligible. We can take 20 phr as an optimum filler loading.

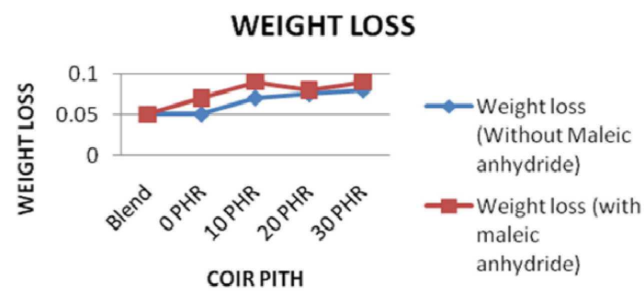


Figure 5 : Comparative chart for weight loss during abrasion

Wear index

Wear Index values are also important with the abrasion resistance. So increase in wear index with the addition of coconut pith leads to decrease in abrasion resistance. It is mainly because in reclaimed rubber and recycled plastics the filler content is more and if we add

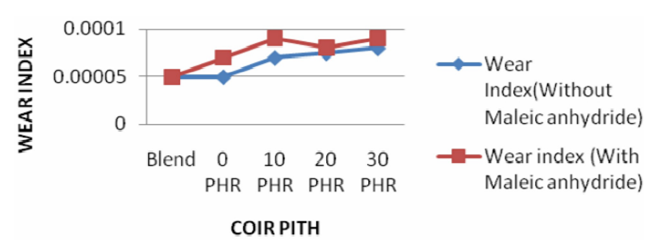


Figure 6 : Comparative chart for wear index during abrasion

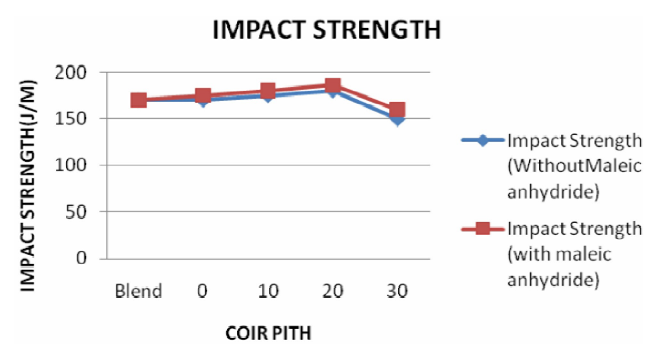
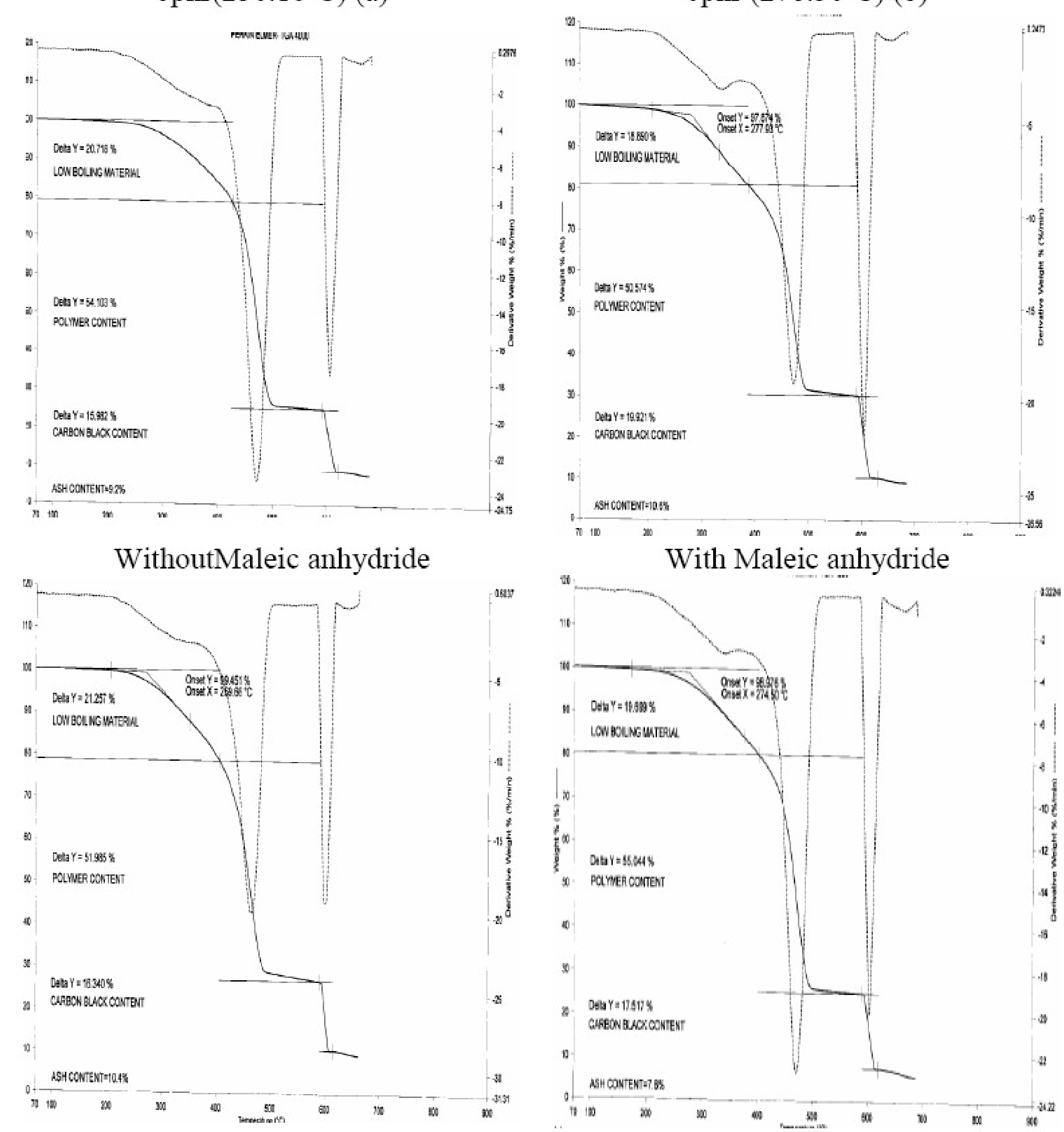


Figure 7: Comparative chart for impact values of coir composites

again, coconut pith - fillers cannot incorporate into the matrix. But as comparing to the wear index of the blends, the wear index values are neglible so we can make use of these composites in footwear applications. After 20 phr there is an increase in values of wear index. So we can conclude that 20 phr of coconut pith is optimum loading.

Impact strength

The impact properties were increasing after the addition of coconut pith. After 20 phr of coconut pith the impact values are decreased because of the dilution effect of coconut pith. The maleic anhydride grafted EPDM acts as a compatibilizer between coconut pith and Reclaimed EPDM / Recycled PP so the impact property increases. There is a decrease in properties after 20 phr due to the dilution effect of coconut pith. So we can conclude 20 phr of coconut pith is the optimum loading for getting good impact properties. The increase in impact strength is due to the nucleation ef-



0phr(250.10°C) (a) WithoutMaleic anhydride

0phr (276.50°C) (b) With Maleic anhydride

10phr (269.66°C) (c) WithoutMaleic anhydride

10phr (277.90°C) (d) With Maleic anhydride

Figure 8 : Graphical representation of 0 and 10 phr coconut pith for with and without MA systems (a, b, c, d)

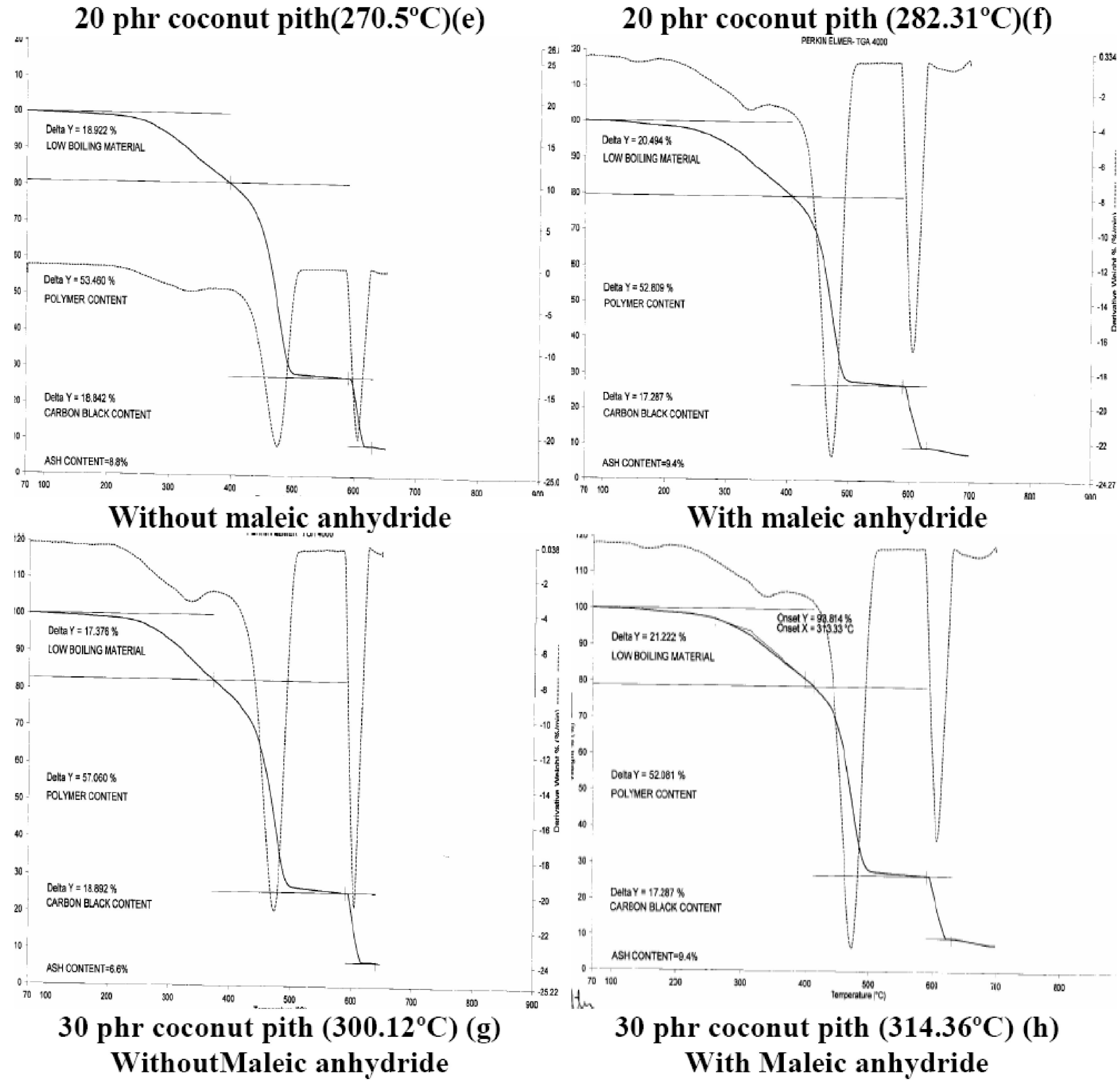


Figure 9 : Graphical representation of 20 and 30 phr coconut pith for with and without MA systems (e, f, g, h)

fect of coconut pith in the matrix. The size of the coconut pith particles is fine, being fine particle sized there is proper dispersion although incorporation is difficult, and this proper dispersion also improves the impact strength of the composites.

Thermal properties

In order to investigate the influence on thermal stability of reclaimed EPDM / recycled Polypropylene / coconut pith composites, TGA study was carried out. Figure below shows the TGA thermographs of reclaimed EPDM / recycled Polypropylene / coconut pith composites with variable dosage of coconut pith. Thermographs reveal that the onset of degradation of the composites shifts towards a higher temperature on increasing coconut pith concentration in the blend indicating higher thermal stability.

The increase in thermal stability is due to the addition of coconut pith because coconut pith itself is having higher thermal stability. So it imparts thermal stability to the Recycled PP / Reclaimed EPDM coconut pith composites. After the addition of maleic anhydride grafted EPDM as a compatibilizer to the Reclaimed EPDM / Recycled PP the degradation temperature shifts to higher as compared with Reclaimed EPDM / Recycled PP / coconut pith composites

Morphological analysis

Morphological analysis was carried out in order to study the matrix after the addition of coconut pith and effect of compatibilizer in the dispersion of coconut pith into the matrix. Phase morphology of the various blends

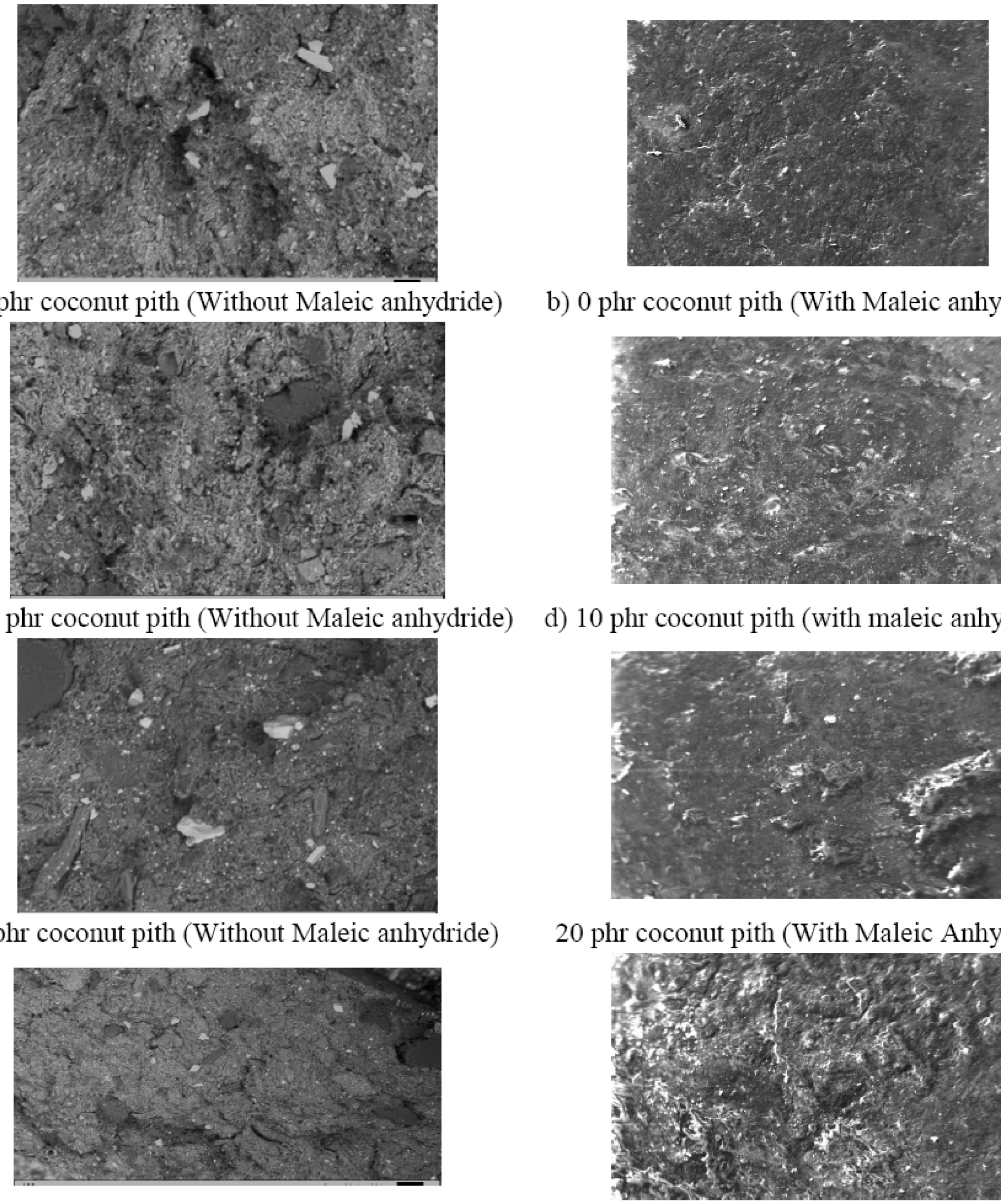


Figure 10 : Micrographs of SEM for coir composites with and without Maleic Anhydride at 0,10,20,30 loading of coconut pith

was investigated by a Digital Scanning Electron Microscope (SEM). The images were obtained at a tilt angle of 0° with an operating voltage of 20 kV.

We can see from the Figure that the rubber particles are dispersed throughout the polypropylene matrix in the form of aggregates and the size of rubber particles is less than 2 μm in the unfilled thermoplastic elastomer sample. It should be noted that after addition of coconut pith the size of rubber particles increases and the voids increases. Initially the coconut pith cannot penetrate into the rubber phase but after adding curing agent DCP40, the rubber phase become more polar. Therefore, it is possible that some coconut pith goes to reclaimed EPDM phase before the curing cycle ends. Hence there is change in the viscosity ratio between the two phases, and consequently, the size of the rubber phase increases. The interaction between coconut pith and Recycled PP / Reclaimed EPDM are poor when there is no compatibilizer addition. After the compatibilizer addition the interaction between the coconut pith and Recycled PP increases due to these properties were increasing. At 30 phr concentration the dispersion of coconut pith is less so the properties were decreasing.

CONCLUSIONS

The study was conducted to determine the Recycled PP/Reclaimed EPDM Coconut pith Composites for low cost sole in footwear and low cost mat application. The preliminary studies on blends showed that 60:40 ratio of Recycled PP / Reclaimed EPDM gives optimum properties based on mechanical properties like tensile, abrasion, flexing and impact so the blends 60:40 (RPP: REPDM) was optimized and selected. Later on the effect of coconut pith loading on 60/40 blend ratio was then determined. The hardness, flexing cycles, impact strength increases up to 20 phr of coconut pith loading and are considered to be optimum for the targeted application but thereafter at 30phr mechanical properties shows decreases in the properties due to formation of large voids due to agglomeration of coconut pith in the matrix. Abrasion resistance decreases as coconut pith loading increases but the values are comparable with the blend ratio. The presence of Maleic anhydride increases the mechanical and thermal properties of Recycled PP / Reclaimed EPDM coconut pith composites and hence MA-g-EPDM should be used while preparing the ternary recycled composites. Morphological analysis through SEM revealed that there is an increase in interaction between coconut pith and Reclaimed EPDM / Recycled PP after the addition of maleic anhydride has addition of MA in the form of MA-g-EPDM decreases the inter phase interaction and there is more compatibility in the blends formed. After 20 phr addition of coconut pith there is a decrease in dispersion of coconut pith into the Recycled PP / Reclaimed EPDM matrix which leads to detrimental effects on the properties of the composites and hence 20phr loading is optimum for 60:40 (RPP:REPDM) polymer matrix. Hence I conclude that - Presence of coconut pith and MA – g – EPDM as a grafting agent in Recycled PP/ Reclaimed EPDM composites improves the properties which are applicable to footwear application.

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