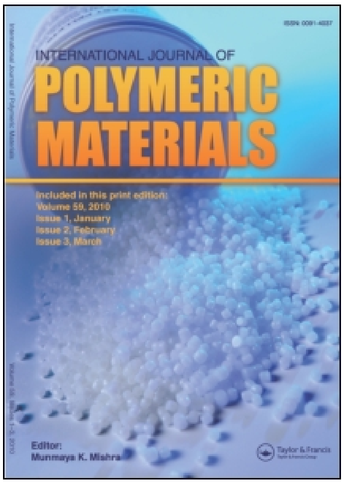

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

OIL PALM EMPTY FRUIT BUNCH FILLED POLYPROPYLENE COMPOSITES

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To cite this Article Wirjosentono, Basuki , Guritno, Purboyo and Ismail, Hanafi(2004) 'OIL PALM EMPTY FRUIT BUNCH FILLED POLYPROPYLENE COMPOSITES', International Journal of Polymeric Materials, 53: 4, 295 — 306
To link to this Article: DOI: 10.1080/00914030490429942
URL: http://dx.doi.org/10.1080/00914030490429942

International Journal of Polymeric Materials, 53: 295–306, 2004
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ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490429942

OIL PALM EMPTY FRUIT BUNCH FILLED POLYPROPYLENE COMPOSITES

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Oil palm empty fruit bunch (EFB), nowadays, has not been fully utilised economically and is always subjected to environmental concern, whereas its handling in the palm oil mill also consumes unproductive cost and energy. In this work oil palm empty fruit bunch filled polypropylene composites were prepared using solution technique and reactive processing in a screw extruder. Results indicate that in the first technique, tensile strength of the composites increases with increasing oil palm empty fruit bunch loading up to 20% (by weight) in the presence of 3% (by weight) of acrylic acid and 0.01 mol ratio of dicumyl peroxide. However the elongation at break shows decreasing trend. Similar observation was also obtained for composites prepared in a single screw extruder. Results from SEM, GPC and IR spectra show that better compatibility between oil palm empty fruit bunch and polypropylene was achieved in the presence of acrylic acid.

Keywords: oil palm empty bunch, polymer fillers, polypropylene, peactive processing, mechanical properties

Received 27 March 2001; in final form 6 April 2001.

We wish to convey our sincere thanks to: The Director of Research and Public Services, General Directorate of Higher Education, Department of Education and Culture, of The Republic of Indonesia for providing the research grant, through "Project of Research and Study for Applied Sciences" (Hibah Bersaing V/3, 1996–1999).

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INTRODUCTION

Oil palm solid wastes, such as empty fruit bunches (EFB), have not been utilised economically, and are even creating environmental problems especially in the mill site. Recent handling of the solid wastes, which accumulate up to 250 tons per day per palm oil mill, using incineration technique is not only no longer accepted but also wasting reusable natural resources. On the other hand, thermoplastic materials, like polypropylene (PP) have been consumed intensively for packaging, *i.e.*, films bags, bottles, and containers to fulfill increasing demands of cheap materials in modern civilisation. Thermoplastic composites made from lignocellulosic materials such as wood and cellulose are becoming more important. Lignocellulosic derived fillers have many advantages compared to inorganic fillers. These include lower density, greater deformability, flexibility during processing with no harm to processing equipment and lower cost per unit volume. In addition, these fillers are derived from renewable resources [1–5]. Thermoplastic materials and wood or other plants tissue fillers are principally two incompatible polymeric materials, because of considerable difference in their polarity. Hence, to produce homogenous blends from both materials, the processing cannot be carried out using conventional methods, which only involve physical mixing between the components of the composites. Brown [6] outlined general techniques to improve compatibility of the blends, *i.e.*, through modification processes such as: *in-situ* crosslinking, addition of compatibiliser, and copolymerisation of functional groups in both polymer and filler. These can be done in processing machines, which also function as modification reactor, by varying processing condition to obtain optimum reaction products. Modification of polymeric materials using this technique is known as “Reactive Processing Technique” [7], which is defined as processing of polymer materials with additives or modifiers involving not only physical but also chemical reactions. This technique has been developed by Al-Malaika *et al.* [8] and can be applied in various areas of polymer technology ranging from mixing, blending, processing and modification, rubber technology, stabilisation, degradation, adhesion and laminating. Modification procedures of polymers using reactive processing technique have been reported by researchers. Rozman *et al.* [9] used three types of coupling agents to improve mechanical properties of polypropylene-oil palm empty fruit bunch-glass fibre hybrid composites. Various attempts have been made to graft anhydride into polymeric materials to improve polarity, hydrophilicity, adhesion, and susceptibility to crosslinking [10]. Final result of the modification reactions is improvement of compatibility of the polymeric materials with various fillers and other polymer materials. Grafting reaction of the maleic anhydride in polypropylene has also been performed by Minuora *et al.* [11], using a peroxide in an organic solvent. In addition, mechano-chemical grafting of the maleic anhydride during polymer processing, without peroxide has been reported by researchers from Nippon Oil Laboratory [12], although with low degree of grafting. In this work the utilization of oil palm empty fruit bunch as a filler in polypropylene composite has been studied. The mechanical properties, compatibility and characteristics of the composites were studied using mechanical, thermal and surface properties testings as well as spectroscopic and chromatographic techniques.

EXPERIMENTAL

Materials

Raw materials were chopped, pressed and dried oil palm empty fruit bunches, and commercial polypropylene resin HF 10 TQ. Chemicals used were acrylic acid, dicumyl peroxide, xylene, acetone, dichloromethane, cellulose, paraffin, and stearic acid. All chemicals were obtained from Aldrich Chemicals and were used as received.

Preparation of Polymer Fillers from Oil Palm Empty Fruit Bunches

Oil palm empty fruit bunches from palm oil mill were chopped, pressed and dried. Then they were milled and sieved to produce filler flour with particle diameter range of 40–90 μm and were further dried under vacuum at 40°C. Chemical composition of the flour was then analysed and their physical characteristics were measured, which include: fibre length and diameter, specific gravity, and surface properties using an electron microscopy.

Reactive Processing in Laboratory Scale

The reactive processing in a laboratory scale was developed using solution technique. Polypropylene was dissolved in xylene and added with filler flour at various compositions and particle sizes. The mixtures were then refluxed at various times with and without dicumyl peroxide as an initiator and acrylic acid as a compatibiliser to obtain optimum compatibility. After evaporation of the xylene, chemical composition of the mixtures was analysed and their physical properties were characterised, which include tensile strength, elongation at break, colour and appearance, as well as degree of compatibility using scanning electron microscopy and infrared spectroscopy.

Reactive Processing in a Single Screw Extruder

To simulate processing condition in production scale, reactive processing of polypropylene composites with the fillers were carried out in a single screw extruder (constant rotation speed at 40 rpm). Parameters affecting effectiveness of the modification reaction were explored to study mechanism of the reactive processing, *i.e.*, processing temperature, 160°–200°C; residence times; die diameters 2–5 mm; initiator concentrations 0–5%; compatibiliser contents 0–10%; and filler contents 0–50%. Optimisation of the compatibility of the blends was also performed by the addition of paraffin wax and stearic acid (0–20 phb: per hundred blend) as dispersing agents. After reactive processing, the polymer blends were granulated and then compression moulded at 180°C for 3 minutes without pressure and additional 3 minutes with 100 kN load to form polymer films for microscopic, spectroscopic and mechanical properties (according to ASTM standard D 638-72 type IV). Degree of homogeneity was measured from distribution of the filler phase using Scanning Electron Microscopy (SEM).

Investigation of Compatibilisation Mechanism

Mechanisms of action of acrylic acid as a compatibiliser in polypropylene and EFB system were studied through measurements of molecular weight distribution gel permeation chromatography (GPC), tensile strength, elongation at break, scanning electron microscopic (SEM) and infrared spectroscopic properties of the polymer blends. The proposed mechanism was also based on the infrared spectra data of the blends before and after exhaustive Soxhlet extraction in acetone and dichloromethane for 24 hours.

RESULTS AND DISCUSSION

Preparation of Polymer Fillers from Oil Palm Empty Bunches

Results of chemical composition and physical parameters of oil palm empty bunches are shown in Tables 1 and 2 respectively.

TABLE 1 Chemical Composition of Oil Palm Empty Fruit Bunches

No.	Component	Concentration (%)
1	Ash content	6.04
2	Lignin content (solubility in aqueous sodium carbonate)	15.70
3	Solubility in alcohol-benzene	5.00
4	Solubility in cold water (30°C)	11.46
5	Solubility in hot water (100°C)	14.79
6	Solubility in aqueous sodium hydroxide 1%	31.17

TABLE 2 Physical Parameters of Oil Palm Empty Fruit Bunches

No.	Parameters (unit)	Value
1	Average fibre length (mm)	1.20
2	Outer fibre diameter (mm)	15.01
3	Fibre content (%)	72.67
4	Nonfibre content (%)	27.33
5	Mass density (Kg/m^3)	177.98

Reactive Processing of Polypropylene and Cellulose Filler in a Laboratory Scale

Data for tensile strength and elongation at break of the blends are shown in Table 3. It can be seen that increasing the filler content (up

TABLE 3 Tensile Strength and elongation at Break of Polypropylene Blends Processed with Various Concentrations of EFB Filler, Acrylic Acid (Weight Ratio to Filler: 0.1) in the Presence of Dicumyl Peroxide (Mol. Ratio to Acrylic Acid: 0.01), Measured Under Load Range of 100 kgf and Speed 50 mm/minutes

No.	EFB (weight %)	Acrylic Ac. (weight %)	Peroxide (mol. ratio)	Tensile strength (MPa)	Elongation at break (%)
1	0	0	0	17.2	328
2	5	0.5	0.01	19.1	254
3	10	1.0	0.01	20.5	106
4	15	1.5	0.01	21.1	66
5	20	2.0	0.01	21.4	60
6	30	3.0	0.01	18.0	11
7	20	2.0	0	19.2	40
8	20	0	0	18.0	25
9	0	2.0	0.01	17.9	228

to 20%) increased the tensile strength but decreased the elongation at break when the blends were processed in the presence of acrylic acid and dicumyl peroxide as an initiator. However, further increase in the filler contents caused a decrease in tensile strength, which may be due to decrease in compatibility. Therefore, the optimum composition of the composites is one containing 20% of filler, processed in the presence of 2% acrylic acid and small amount of dicumyl peroxide.

Processing of Polypropylene with Fillers from Oil Palm Empty Bunches in Single Screw Extruder

Reactive processing of polypropylene and oil palm empty fruit bunch fillers was carried out in a single screw extruder using die diameter 3.5 mm, since using smaller die diameter (longer resident time) may lead to decomposition of the filler. It was found that increasing the filler content resulted an increase of the tensile strength, but decrease in elongation at break of the composites as shown in Table 4. This may be due to decrease in homogeneity and the lack of phase interaction between the filler powder and polypropylene matrix. Processing using higher filler content also showed darker appearance of the blends, which indicated decomposition of the filler. Therefore, optimum standard condition of the reactive processing was chosen at barrel setting temperature 160°C, die diameter 3.5 mm, and filler content 20%.

From the Table 4 results, the main problem found during the reactive processing involved the effectiveness of filler distribution throughout the bulk phase of the composites, especially at higher filler content (>20%). Kiatkamjornwong *et al.* [13] has used epolene wax and soyabean oil as dispersants in the processing of polyethylene and cassava starch filler. Using computer simulation technique, Wang and

TABLE 4 Characteristics of Polypropylene Composites Processed at Standard Condition (Barrel Temperature 160°C, Die Diameter 3.5 mm) with Various Concentrations of Oil Palm Empty Fruit Bunch Filler

Filter (weight %)	Tensile strengh (MPa)	Elongation at break (%)	Colour appearance
0	16.2	32.8	clear
2	16.5	28.1	light yellow
5	20.5	21.5	dark yellow
10	20.2	14.0	light brown
20	23.0	14.1	brown
30	20.1	10.5	dark brown

TABLE 5 Effect Dispersant Contents (per hundred blend: phb) to the Characteristics of Polypropylene Composites Processed at Standard Condition with 30% EFB

Dispersant (phb)	Tensile strength (MPa)	Elongation at break (%)	Appearance
Without dispersant Paraffin:	22.1	10.5	dark brown
5	20.2	15.2	brown
10	20.8	19.0	light brown
20	18.2	28.5	light brown
Steric acid:			
5	21.9	19.2	brown
10	20.5	13.1	brown
20	19.4	20.3	dark brown

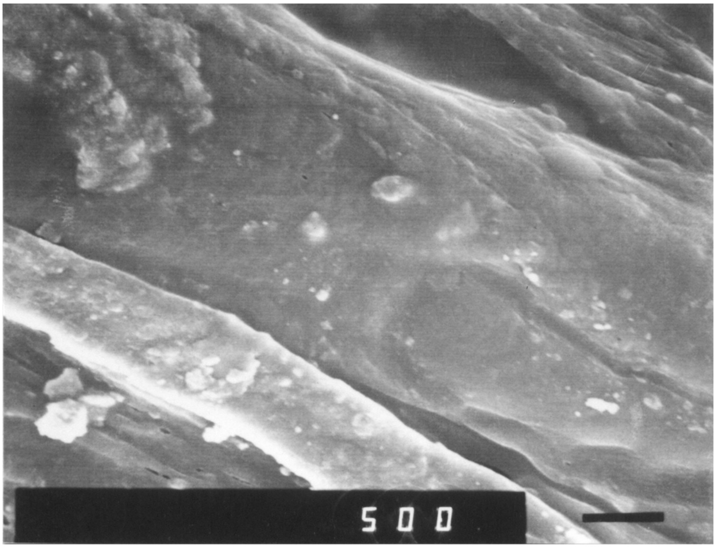
Pereira [14] have reported that the "wetting ability" of dispersant is an important factor affecting filler distribution in polymer matrix. In our work, paraffin and stearic acid were used as dispersan ts during processing of the polypropylene composites. Characteristic data of the composites is given in Table 5.

After addition of paraffin as a dispersant, it was found that the composites visually showed clearer appearance and better homogeneity. On the other hand, physical texture of the composites looked softer with lower tensile strength and higher elongation of break which indicat e that the paraffin can function as a plasticizer. Optimum paraffin dispersant content which gave good appearance, homogeneity, elongation at break, and considerable tensile strength is between 5–10 per hundred blend (phb). Stearic acid dispersant was added due to its dipolar property, in which its carboxylic group may bind onto the ligno-cellulosic filler surface, whereas its alkyl group possesses better compatibility with the polypropylene matrix. However, as shown in Table 5, this was not the case, since the composites containing stearic acid exhibited darker appearance when compared to those containing paraffin dispersant. It shows that stearic acid acts as an internal plasticizer in the composites.

Mechanistic Investigation of Compatibilisation Action by Acrylic Acid

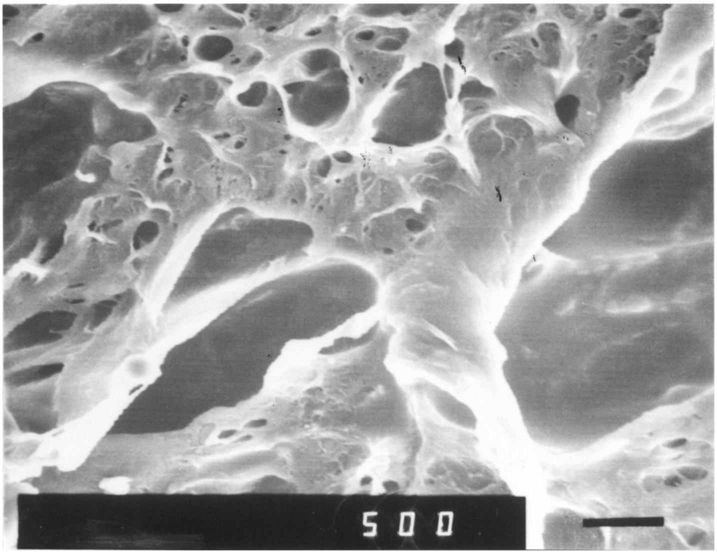
The mechanism of reactive processing of polypropylene system with EFB filler in the presence of acrylic acid and dicumyl peroxide was investigated by analyzing the composites through microscopic (SEM) measurements, molecular weight distribution (GPC), and infrared spectroscopy. Scanning electron microscopy (SEM) of polypropylene composite containing 20% cellulose, 2% acrylic acid, and 0.02% dicumyl peroxide in Figure 1a, showed that the acrylic moiety accumulated on the cellulose surface. The presence of the acrylic compatibilizer moiety can also be seen from SEM photograph of polypropylene processed with acrylic acid as above but without cellulose filler in Figure 1b.

From molecular weight measurement using GPC technique in dichlorobenzene, various molecular weight distribution curves were obtained as shown in Figure 2. Polymer samples were dissolved in 1,2-dichlorobenzene at 140°C, filtered and injected into 30 cm GPC column (PL gel 2x, Mixed gel, 20 micron packing), flow rate 1.0 mlsol;minutes. Curve 2b is for polypropylene composites processed with only 0.1% of dicumyl peroxide which show lower polydispersity and also shifting of the molecular weight distribution toward lower value when compared to that of commercial polypropylene, Curve 2a. This is mainly due to the presence of dicumyl peroxide which promotes chain scission of the polymer molecules. Interestingly, distribution curve of polypropylene composites processed with 10% acrylic acid and 0.1% peroxide (Curve



(a)

FIGURE 1A SEM photograph of polypropylene composite processed with 20% of filler, 2% acrylic acid and 0.002% of dicumyl peroxide at magnification 500x.



(b)

FIGURE 1B SEM photograph of polypropylene composite processed with 2% of acrylic acid and 0.02% dicumyl peroxide but without filler at magnification 500x.

2c) exhibited additional peak at higher molecular weight. This may be related to grafting and crosslinking of acrylic acid of the polypropylene molecular chains.

To investigate further the occurrence of grafts of acrylic acid on the polypropylene matrix during reactive processing, films of the polypropylene composite processed with 10% acrylic acid and 0.1% dicumyl peroxide were exhaustively Soxhlet extracted in acetone and in dichloromethane for 24 hours and were analysed using infrared spectroscopy. Figure 3 shows infrared spectra of the polypropylene films before extraction (Spectrum A), after extraction in acetone (Spectrum B), and after extraction in dichloromethane (Spectrum C). Spectrum A, *i.e.*, before extraction, exhibited absorption peak of: $-$OH group (broad peak at 3000$-$3500 cm^{-1}), >C=O group at 1700 cm^{-1}, but not the >C=C< peak of acrylic acid at around 1600 cm^{-1}. The above spectrum indicates that all acrylic compatibilizer molecules have reacted during processing with polypropylene matrix. After exhaustive extraction in acetone (Spectrum B) and in dichloromethane (Spectrum C), both spectra also exhibited intensive peaks of carbonyl (>C=O) group at 1700 cm^{-1}. When absorbencies of the

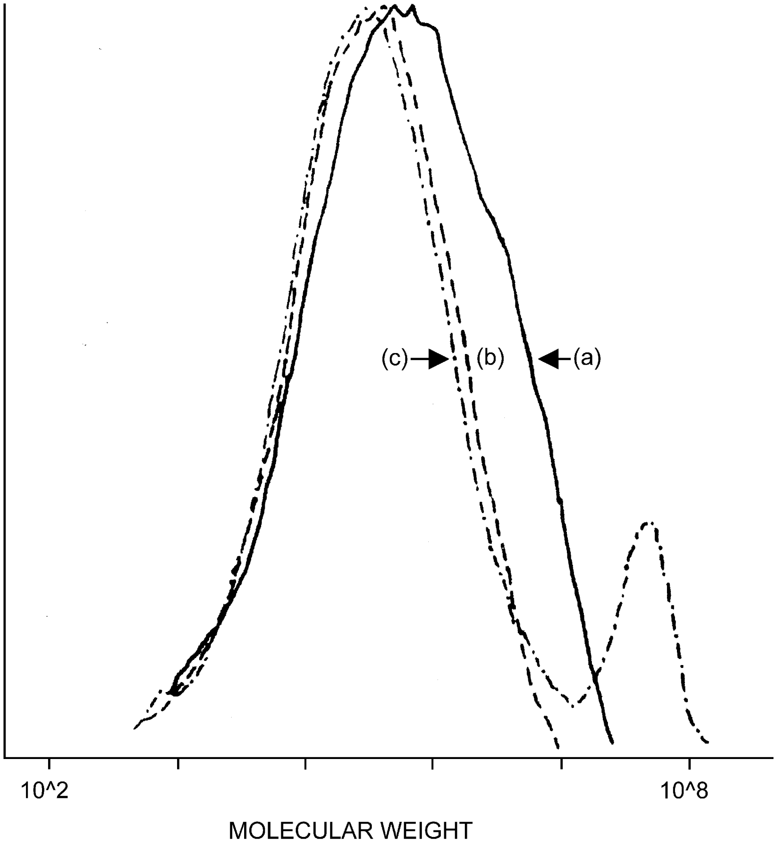


FIGURE 2 Molecular weight distribution curves of: (a) commercial polypropylene, (b) polypropylene processed with 0.1% dicumyl peroxide, (c) polypropylene processed with 10% acrylic acid and 0.1% dicumyl peroxide.

carbonyl peaks were compared to that of before extraction (Spectrum A), it was found that the carbonyl groups still remain (90–95%) in the polymer matrix after exhaustive extractions. In other words, the acrylic compatibiliser was able to bind in high degree to polypropylene matrix during reactive processing in the presence of the peroxide. However, it is still not clear how the binding of acrylic acid taken place in the polymer. The acrylic acid may not only be grafted or crosslinked, but also homopolymerised and then interpenetrated or physically bound to the polymer molecules. The reaction mechanism may be visualised as in the following reaction scheme, (Scheme 1).

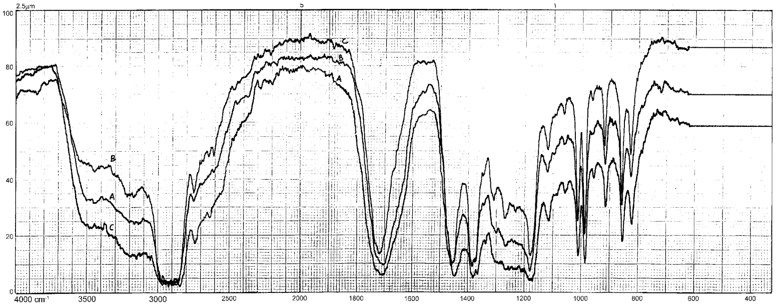
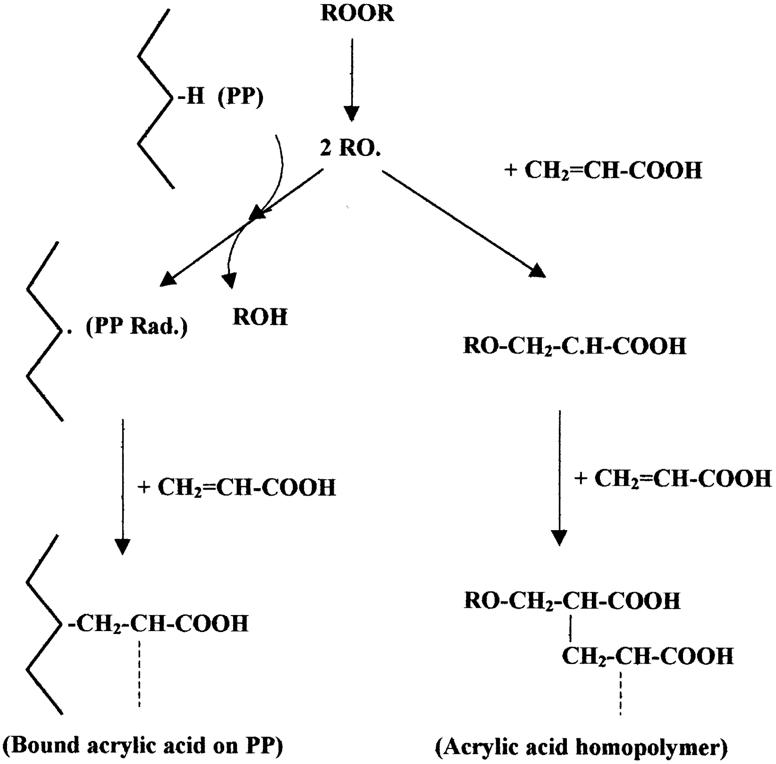


FIGURE 3 Infrared spectra of polypropylene films processed in the presence of 10% acrylic acid and 0.1% dicumyl peroxide at standard condition: (a) before extraction, (b) after exhaustive Sokhlet extraction in acetone, (c) and in dichloromethane.



SCHEME 1 Proposed reaction mechanism of physico-chemical binding of acrylic acid during processing of polypropylene in the presence of 10% acrylic acid and 0.1% dicumyl peroxide at standard condition.

CONCLUSIONS

Oil palm empty fruit bunch can be used as a filler to produce polypropylene composites. The maximum tensile strength of the composites was obtained at 20% wt of filler. However the elongation at break shows decreasing trend with increasing filler loading. The presence of acrylic acid was found to improve the compatibility between the filler and polypropylene.

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