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Oven Ageing versus UV Ageing Properties of Natural Rubber Cup Lump /EPDM Rubber Blend with Mangosteen Powder (MPP) as Natural Antioxidant

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Abstract. Natural Rubber (NR) are susceptible to oxidation due to the presence of diene double bond. Improvement of NR properties can be enhanced by presence of antioxidant. Natural antioxidant can be a new source of additives to prevent and delay oxidation process. In this work, mangosteen powder (MPP) is exploited to be good potential additive in improving the aging properties of NR cup lump (NRCL) blended with EPDM rubber. Blended NRCL with EPDM rubber as a sealant had been studied with and without MPP. Aging effects upon thermal and weather exposure after two weeks had been analyzed by FTIR. Increasing amount of MPP had retained the diene bonds upon further rubber degradation. The broad band absorbance peak at 3410 cm^{-1} corresponds to O-H stretching with H-bond which indicates the existence of phenols in the MPP. Carboxylate groups and amine presence in MPP also found to exhibit absorbance peak at 1028 and 1608 cm^{-1} respectively. MPP contained polyphenol proven to be effective antioxidant agent in reducing degradation upon thermal and sunlight exposure. Oven and weathering tests performed for two weeks showed different aging behavior with weathering exposure found to have greater degradation effect due to radical attack by free radical from UV sunlight.

Keywords: Natural antioxidant, Cup lump, Mangosteen powder peel, EPDM, Tackiness

1. Introduction

During the eighteenth century, rubber was known throughout Europe as rubber had greater properties which can be benefitted. Systematic tapping process cause the latex to be extracted regularly and which name it Natural Rubber Cup Lump (NRCL) without process [1].

Initially, there are four types of field coagula that can be derived from Natural Rubber (NR) which are cup lump, tree lace, smallholders' lump and earth scrap. Each of them has their own significant into converting as final products. Cup lump is widely available and preferable to be used as raw material because it is cheap in cost and versatile to be converted into higher grade or Technically specified rubber (TSR) such as SMR20 and TSR20 [2]. Ethylene-propylene-diene monomer (EPDM) rubber is the type of synthetic rubber that are based on 5-ethylidene 2-norbornene (ENB). It is more stable than conventional elastomers-(butadiene, isoprene rubber) as it has sensitive that are very important for subsequent crosslinking by peroxide or sulfur. Applications of EPDM include blending with NR for automotive tires, side walls, cover strips, wires, cables, hoses, belting, roofing barriers and sporting goods [3].

Hevea Brasiliensis is a major commercial source of NR that has been extensively used to manufacture high quality rubber products for instances, tires, gloves, liners, catheters and the



tube. NR is a type of renewable source where a lot of ongoing research had been done to refine its processing offering varieties of rubber products. The rubber plantation has been expanding rapidly as there were many high-quality rubber products can be made from NR. The cup lumps are typically collected daily and sorting this raw material to produce various rubber grades is largely based on its moisture content (MC)[4]. The STR 20 is mainly produced from field coagulum or cup lump and has good processing characteristics and physical properties. The raw material for STR 20 is formed either by the coagulation of field latex with acid, or by the evaporation of water from latex in a collection cup. EPDM rubber is used as it has weather resistant properties. Previous studies had shown the poor compatibility of blending NR and EPDM rubber, but the problem can be overcome by incorporating compatibilizer into the rubber blends. Study by El-Sabbagh, he found that grafting the maleic anhydride (MAH) with EPDM /NR introduce greater compatibility and greatly improved the rheological properties of rubber blends [5]. Then, another study was made to add the compatibilizer agent for NR/EPDM blends which uses maleic anhydride grafted with ethylene propylene monomer (EPM). This time the result shows improvement for mechanical properties by adding 5 pphr of MAH-EPM [6]. The tack ability for vulcanized EPDM rubber having hydrocarbon resin found to be compatible at higher concentration (32% wt), better dispersion, lower softening point and better peel strength [7].

In blends, inherent properties of polymer components are retained and most dominant polymer and its properties will stand out. NR/EPDM blend show that TBBS as accelerator is good choice for vulcanizing the blends since the result reveals both processability and mechanical properties [8]. Benefits of blending are, they can be used to lower the compound cost, for ease of fabrication and to improve the performance of the industrial rubber. NR and EPDM rubber have been blended for a long time for these reasons [9].

Degradation of unstabilized organic polymers occurs rapidly upon exposure to UV and weathering. The function of this antioxidant is to retard the auto-oxidation which can prolong the useful life of the host substrate. Hindered phenols are the example of the stabilizers which accept the unpaired electron of free radicals. Use of Natural antioxidants are important additives that can confer environmental friendly additive as compared to other antioxidants available in the market. Phenolics and amines are scrutinized as carcinogenic. Hindered phenols, hindered amines and quinolones are mostly used in rubber industries. [10] Examples of antioxidants used in rubbers include

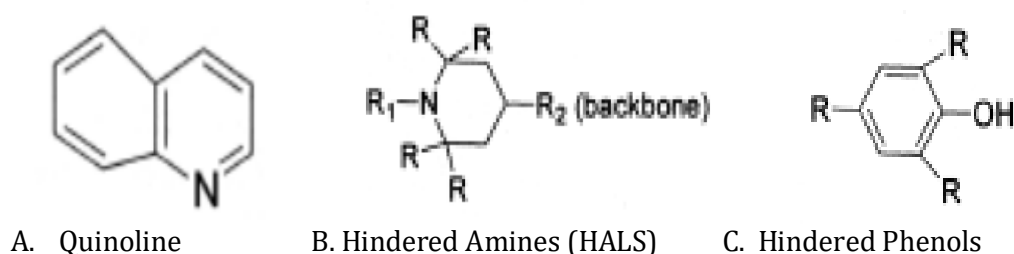


Fig. 1. Examples of Antioxidants for rubbers (a) quinolone (b) HALS (c) Hindered Phenols

Upon reacting with free radicals, phenolic are considered as primary antioxidants. Typical loading rates are 0.25 to 2.0 pphr and they are effective in most polymer and sulfur cure systems. Quinoline are particularly useful in rubber goods requiring resistance to high temperatures. They are also used as a copper and manganese inhibitors and provide anti flex cracking properties.

Accelerated ageing of styrene-butadiene rubber nanocomposites stabilized by phenolic antioxidant had been investigated by Bellas et.al [11]. Synthesis of a new nanosilica-based antioxidant and its influence on the anti-oxidation performance of natural rubber had been performed by Lei H [12]. Cibulkova Z, et al had also found the stabilization effect of potential antioxidants on the thermooxidative stability of styrene butadiene rubber (SBR). [13] Oxidation Degradation Study and Use of Phenol and Amina Antioxidant Compounds in Natural Rubber had been investigated and been extensively use [14]

Mangosteen from the fruit carp grown in Thailand , Malaysia and ASEAN countreis, can be extracted .The extract have the phenolic natural xanthenes called α -mangostin and γ - mangostin structure . It is a hindered phenol which are suitable to replace the use of synthetic hindered phenols or amine. Fig. 2 shows the structure of mangostin xanthone; type of hindered phenols. It had been investigated to have antibacterial properties too [15]

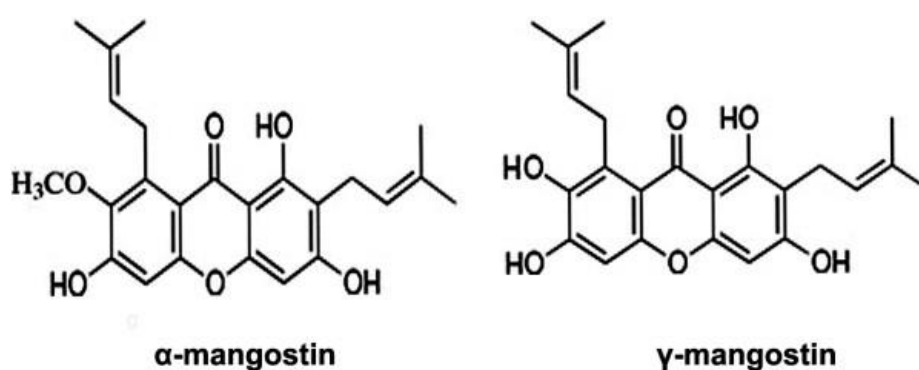


Fig. 2. Structure of Structure of α -mangostin and γ - mangostin xanthone [15]

This research involve the blending of NR cup lump with EPDM rubber and added with natural antioxidant. In this study, NRCL will be blended with EPDM rubber to produce a new environment friendly sealant. Natural antioxidant is added to enhance the ageing properties of elastomer blend. Rahmah et al, [16, 17] had previously use natural additives as antioxidant and can also act as Prodegradant for the polyolefin degradant masterbatch

2. Materials and Methods

In this study, NR cup lump supplied by small holder rubber tapper, EPDM rubber grade VS 3666 supplied by Exxon Mobil Chemical Ltd., natural antioxidant, Mangosteen powder from carp sieved to 50 micron, Phenolic resin tackifier from Malaysian Adhesive & Chemicals Sdn Bhd, Toluene and methyl ethyl ether peroxide (MEKP) from Sigma Aldrich Inc. The formulation mixture of NR cup lump, EPDM rubber and other chemicals are being made as shown in Table 1.

2.1 Preparation of NR cup lump into solution

Raw NRCL were washed, sheared and cleaned thoroughly to remove dirt, sand, twigs and tree bark. The cleaned cup lump was cut into small pieces or as strips and put into oven to dry. Dried cup lump was removed from the oven and they were masticated for about 10-15 minutes to reduce viscosity and molecular weight. Masticated rubber was cut into smaller pieces for easy dissolution with toluene for 2 days. EPDM rubber was cut into smaller size for dissolution into toluene forming EPDM rubber solution.

Table 1. The formulation of NRCL rubber sealant

Ingredient (part by weight)	Control sample	Sample 1 (S1)	Sample 2 (S2)	Sample 3 (S3)
NR cup lump (g)	10	10	10	10
EPDM rubber (g)	2	2	2	2
Natural antioxidant (g)	0	2	4	6
Phenolic resin (g)	0	1.5	1.5	1.5
MEKP (%)	2	2	2	2
Toluene (ml)	100	100	100	100

NRCL solution was mixed with EPDM rubber solution and stirred thoroughly to get homogenous mixture. Then, a tackifier which was add into mixture to give a better tackifying properties. After that, natural antioxidant was added into this mixture at different composition as in Table 1 to improve the ageing properties of rubber blends. MEKP acted as a curing agent that was responsible to cure the rubber blends also added into this mixture. Polymer blend were poured onto the glass and will be left for 1 day to cure the mixture. Then, the sample undergone aging by thermal exposure and weather for 14 days. Upon completion of exposure the samples undergone characterization and testing.

2.2 Characterization and testing

The sample prepared went under characterization and testing to test the properties of sample made. The sample undergoes FTIR characterization test to identify the presence of certain functional groups in a molecule. Standard test for characterization test method is ASTM D3403. The samples which were known as control sample, S1, S2 and S3 were tested after they undergone oven exposure for 0, 2, 7 and 14 days aging at 60°C as according to ASTM D573-(04). Standard Test Method for Rubber—Deterioration in an Air Oven.

The weight loss test is to determine the antioxidative ability of antioxidant affecting properties of sample made. Samples were weighed by using analytical balance before and after aging test for 0, 2, 7 and 14 days. Samples were exposed to weathering process under Malaysian weather having high humidity and temperature between April and May 2017. Recorded humidity ranges between 64% to 94% and min temperature about 25°C and max temperature about 32°C were found for the week mentioned. (Data collected from meteorological website).

Retention and percent were calculated based on percent weight loss upon exposure to sunlight and oven for each duration of 0, 2, 7 and 14 days.

$$\text{Retention, \%} = 100\% - \text{percentage weight loss}$$

$$\text{Percent weight loss} = \frac{\text{Initial weight, g} - \text{Final weight, g}}{\text{Final weight, g}} \times 100\%$$

3. Result and Discussion

Table 2 below shows the tabulated data for percentage of weight loss and percentage of retention weight experienced by the sample for 0, 2, 7 and 14 days during ageing process for both conditions' oven and weathering using weight loss data from Fig. 3 and 4 .

Table 2. Tabulated data of percentage weight loss and retention percentage for each sample under oven and UV weathering aging up to 14 days

	Oven								Weathering							
	Weight loss (%)				Weight Retention (%)				Weight loss (%)				Retention (%)			
Duration (days)	0	2	7	14	0	2	7	14	0	2	7	14	0	2	7	14
Control sample	0	3.75	25	50	100	96.3	75	50	0	6.3	38.8	87.5	100	93.7	61.2	12.5
S1	0	0	13.8	18.8	100	100	86.2	81.2	0	0	16.3	25	100	100	83.7	75
S2	0	0	6.3	15	100	100	93.7	85	0	0	8.8	21.3	100	100	91.2	78.7
S3	0	0	0	0	100	100	100	100	0	0	0	0	100	100	100	100

3.1 Weight Loss Test

Fig. 1 shows weight loss of sample undergone by oven ageing process at different loading of MPP. Initial weight for control sample before aging was 0.8 g. Weight loss was reduced to 0.4 g with 50 % weight retention after 14 days. With S1 and S2 of 5%MPP loading and below, the % weight retention are high ~80% and highest loading of 6% MPP for S3 had retained its original weight.

Upon exposure to weathering, for S1, the weight before aging was 0.8 g exhibiting least % of about 12.4% after 14 days. For 2% MPP (S2) the percent retention is 75% which improved the weight loss while for S3, no change in weight loss was observed. Comparing the two conditions of exposure, MPP is significantly effective in improving the weight retention especially for weathering exposure which can retain the weight by more than 4x compared to heat aging exposure. Ultra violet light which is the agent of degradation of rubber samples which can cause the breaking down of rubber chain can be impeded by incorporating MPP. Heat exposure had caused less change of structural crosslink integrity than weathering; however both samples for oven and weathering retain their original weight with no signs of weight loss.

Li et al [16] had investigated similar work on the thermal ageing of nitrile-butadiene rubber (NBR) reinforced with different graphene (GE)/The mechanical properties, chemical changes, and thermal stability of ageing samples and neat samples were evaluated and found integrity crosslink were affected by variation in GE used at temperature fixed at 100°C. Oven or thermal aging for this work do not affect the integrity of crosslink for high MPP loading but significantly affect the control and with less than 5% loading of MPP.

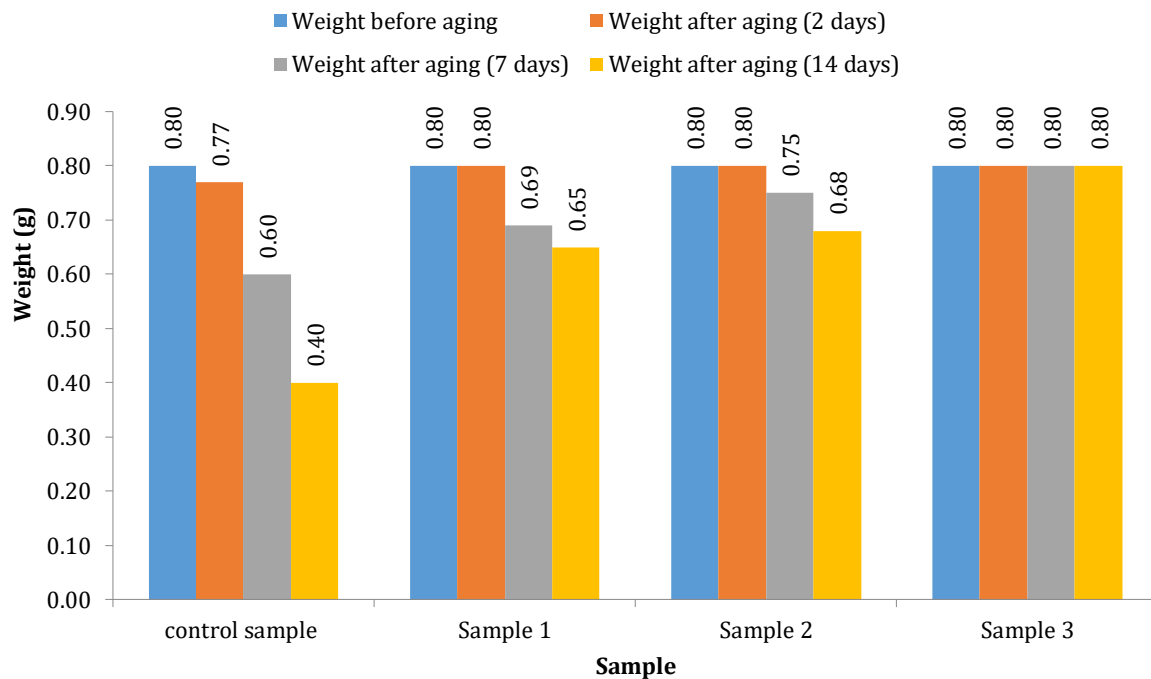


Fig. 3. Graph of weight loss versus percentage loading of MPP by Oven Aging

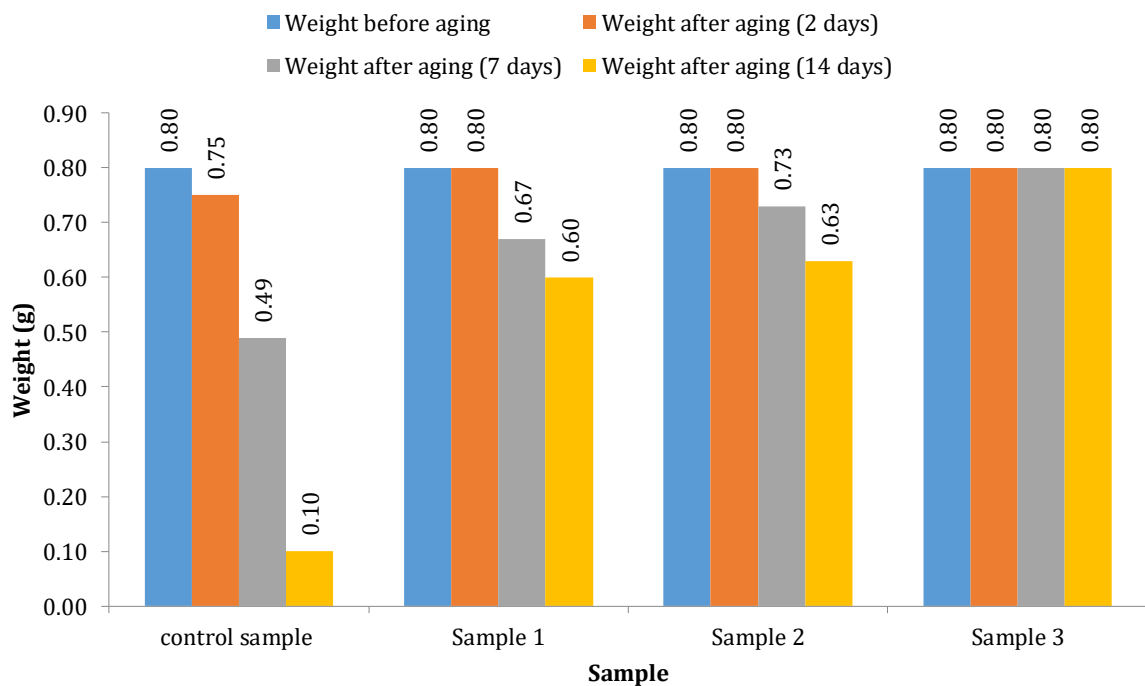


Fig. 4. Graph of weight loss versus percentage loading of MPP by Weathering.

Li et al [16] had investigated similar work on the thermal ageing of nitrile-butadiene rubber (NBR) reinforced with different graphene (GE) / The mechanical properties, chemical changes, and thermal stability of ageing samples and neat samples were evaluated and found integrity crosslink were affected by variation in GE used at temperature fixed at 100°C. Oven or thermal aging for this work do not affect the integrity of crosslink for high MPP loading but significantly affect the control and with less than 5% loading of MPP.

Control NRCL sample lose weight easily because there is no antioxidant (AO) presence. Without AO, structural integrity of rubber upon expose can be attacked as the diene groups of *cis*-polyisoprene could not withstand the high radiation under UV light or high accelerated oven temperature to form free radical. This free radical can attack the double bond of rubber blend causing oxidation, which leads to degradation. With higher amount MPP added into sample, improved rubber aging properties were attained after undergoing weathering for 14 days. This happened because natural AO which was MPP having high rich polyphenols acted as uv interceptor causing effective resistance to oxidation.. MPP had prevented free radical attack and prevented degradation. According to Li et al, oxidative degradation prevention for NR is by addition of AO. Natural rubber with AO exhibited 12 times more stability towards oxidative degradation. The action of MPP xanthone structure is postulated to follow hindered phenol mechanism.

3.2 FTIR Analysis

FTIR spectra of Natural Rubber (NR) and EPDM rubber are depicted in Fig. 5 and 6 respectively. For the NR graph based on Fig. 5, the functional group present were CH, C=C.CH₂ and CH₃. The functional group of NR were detected at the absorption peaks of 290 cm⁻¹, 1662 cm⁻¹, 1444 cm⁻¹, 1374 cm⁻¹ and 839 cm⁻¹. The best region to identify presence of *cis*-Polyisoprene was the absorption at 2960 cm⁻¹ (C-H₃ group) and 1444 cm⁻¹ (C-H deformation).

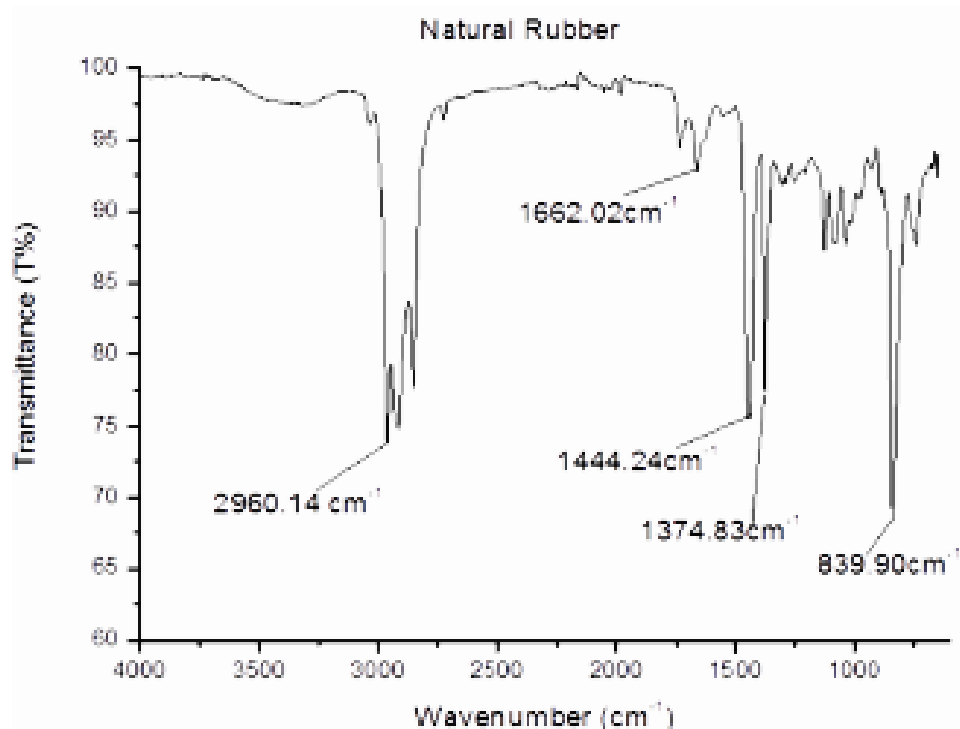
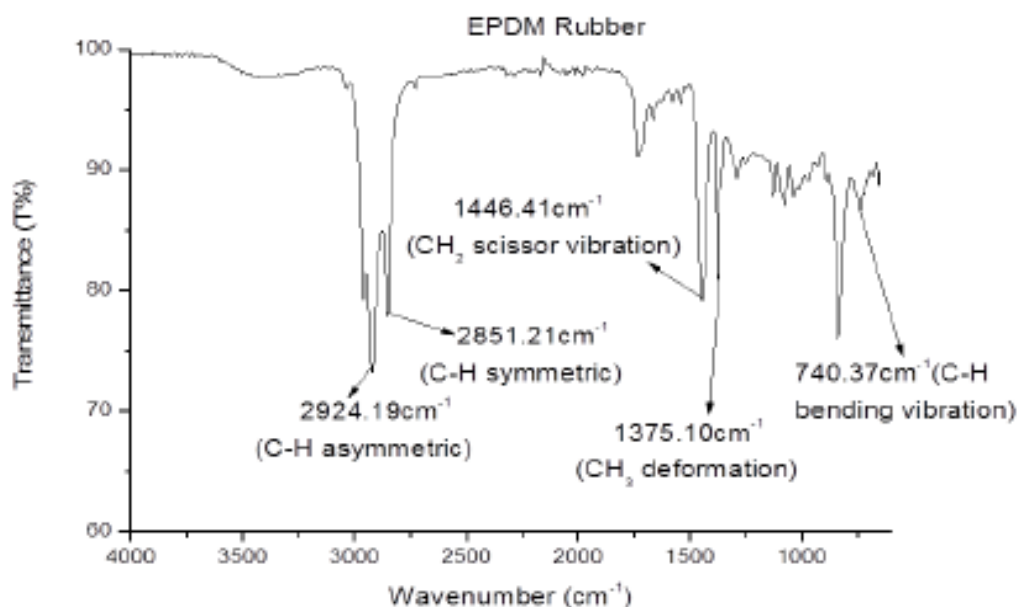


Fig. 5. FTIR spectra for Natural Rubber (NR)

Table 3. Analysis of NR FTIR spectra

Band intensity wavenumber	Wavenumber cm^{-1}	Absorption	Assignment
strong	2960	CH	Stretching vibration
medium	1662	C=C	Stretching vibration
medium	1444,1374	CH ₂	CH ₂ and CH ₃ deformation
medium	839	CH ₃	Out of plane bending

**Fig. 6.** FTIR spectra for EPDM rubber

Stretching vibration of CH are visible at wavenumber 2960-2924 cm^{-1} for NR and EPDM rubber while rubber has medium to strong peak at $\sim 1662 \text{ cm}^{-1}$ representing C=C diene bond which is inherent in NR rubber. For EPDM rubber, strong to medium peak are exhibited around 2850 and significant peaks around CH deformation with bending peak at 740 cm^{-1} .

Table 4. Analysis of EPDM FTIR spectra

Band intensity wavenumber	Wavenumber cm^{-1}	Absorption	Assignment
strong	2924	CH	Stretching vibration
medium	2851	CH	Stretching vibration
medium	1446,1375	CH ₂	CH ₂ and CH ₃ deformation
medium	740	CH ₃	Bending vibration

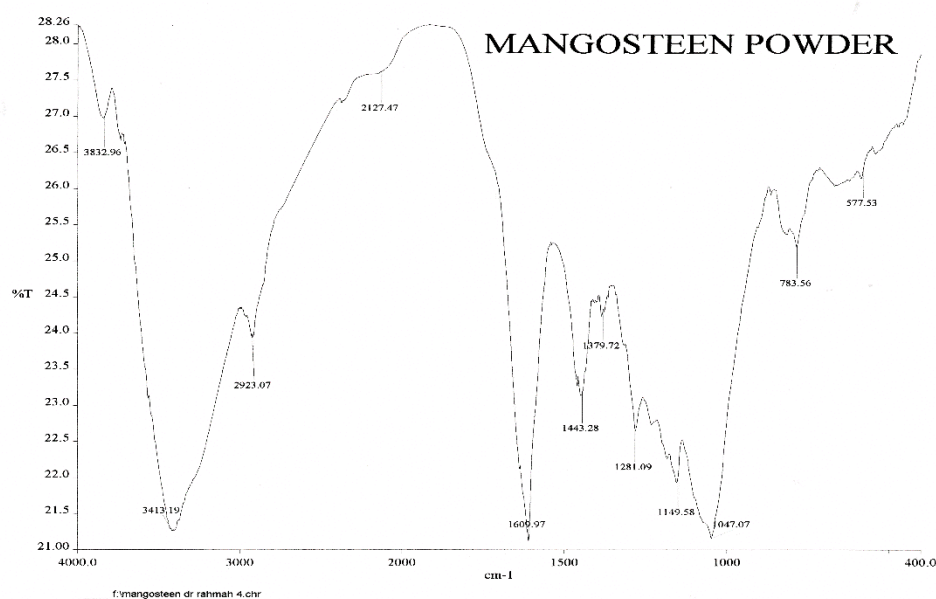


Fig. 7. FTIR spectrum of mangosteen powder

Fig. 7 shows the graph of mangosteen powder with high intensity of OH, C-O and C=O peak of xanthenes which shows strong α -mangostin and γ -mangostin peaks. The MPP blended NRCL before aging are shown in Fig. 8. Fig. 9(a) showed MPP absorption peaks which have intensity absorption of strong to medium at 3410, 2918 representing OH phenolic groups and CH bending while 1608, 1337 and 1048 cm⁻¹ represents the carbonyl deformation and C-O ether of mangosteen functional groups. The broad peak of OH bonding for all samples was diminished after undergo aging for 2 days because of the sample exposed to sunlight which cause the samples dried but OH bonding formed again after the samples undergone for 7 days aging probably because of the samples exposed to the rain and dew which cause the samples absorb the water.

Referring to Fig. 9(c) to 9(d), the peaks at 3210 cm⁻¹ and 967.2 cm⁻¹ increased in intensity remarkably upon weathering, possibly because most of the antioxidants in the NRCL samples had been consumed. The peak at 3210 cm⁻¹ was mostly due to O-H symmetric stretching vibration and C-H deformation vibration indicating that hydroxyl groups were produced for weathering samples when the NRCL was exposed to weathering which exhibit increased in degradation compared to oven ageing environment. This similar pattern were exhibited by Li et al [17] who investigated with Nitrile rubber exposed to thermal aging condition.

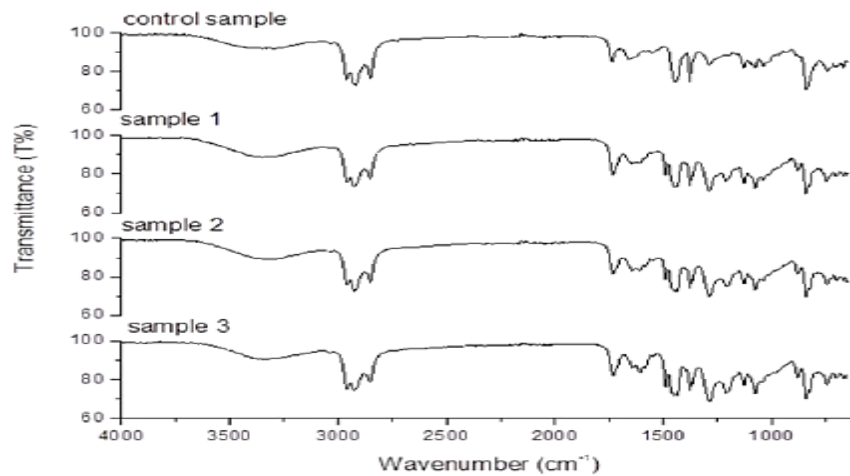
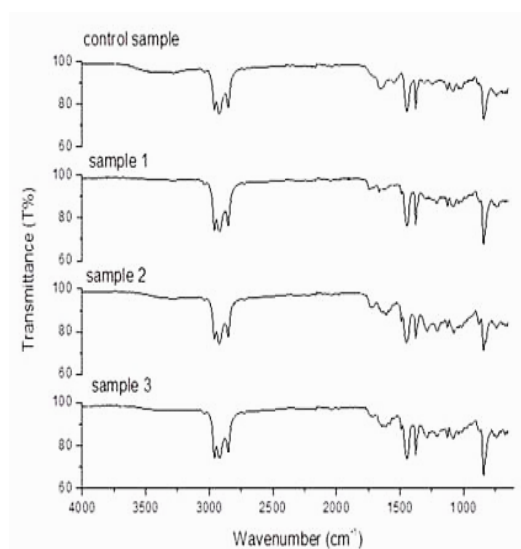
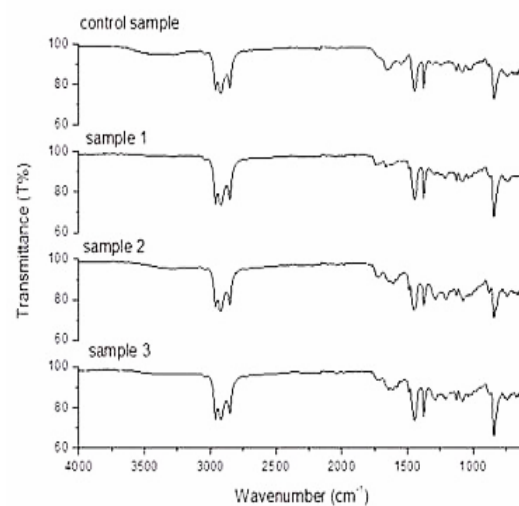


Fig. 8. FTIR spectra of rubber blend for 0 days aging

At 1400 cm^{-1} to 1200 cm^{-1} , more peaks were observed, having more CH deformation. For aging 14 days in Fig. 9(e), the result showed many structural vibration differences with unexposed samples. For samples aged by oven in Fig. 9(b), the functional group presenting in sample coupled with natural antioxidant was diminished. Based on Fig. 9(c), the broad peak which represent for OH bonding at 3200 cm^{-1} was diminished when the samples undergo aging since the first 2 days. This indicated that the samples became dried after exposed to thermal exposure. For the samples undergone aging for 14 days, the result showed that only broad peak which were represent OH bonding only diminished. This showed that the sealant is not easily degrade if they only exposed to the thermal exposure compared to the samples that undergo aging by weather where they were exposed to the UV light, rain and dew.



(a)



(b)

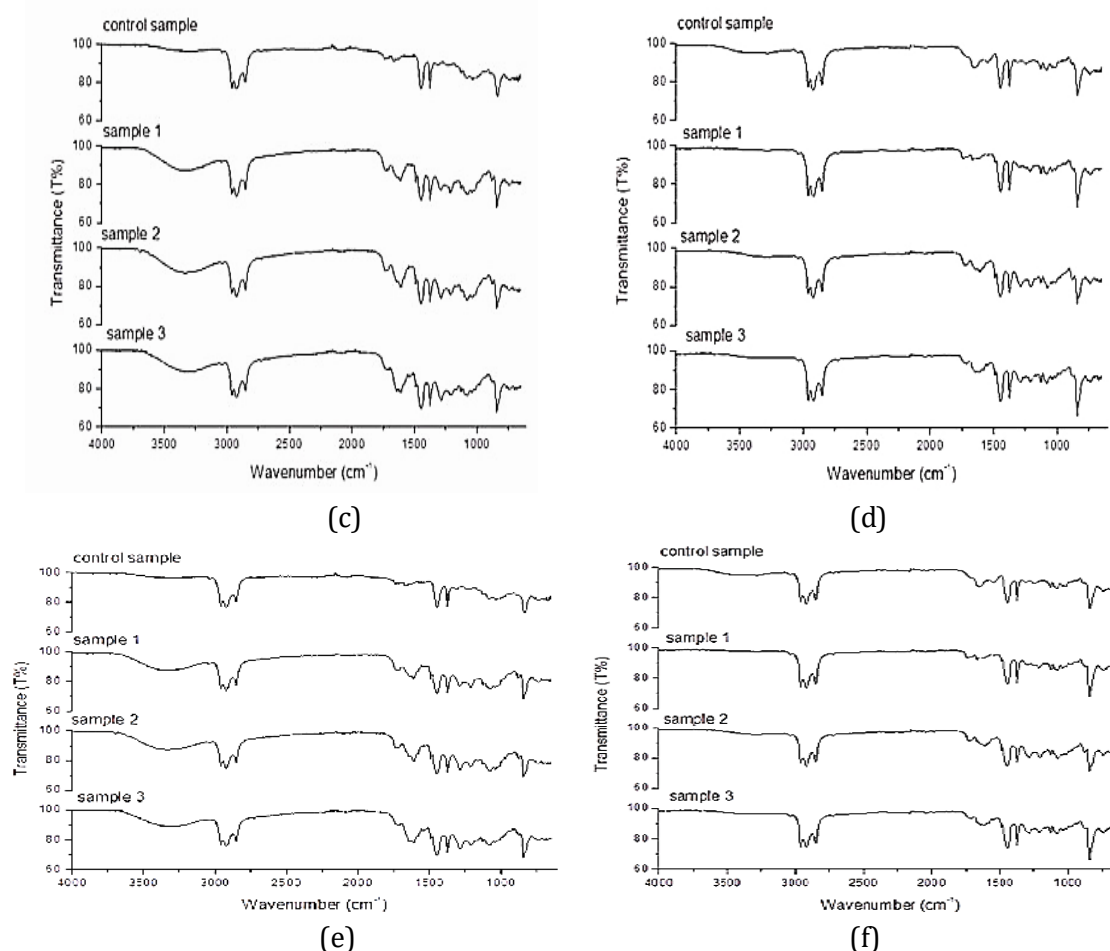


Fig. 9. FTIR spectras of rubber blend at (a) 2 days by weathering (b) 2 days by oven (c) 7 days by weathering (d) 7 days by oven (e) 14 days aging by weather (f) 14 days aging by oven

4. Conclusion

In conclusion, the addition of MPP as natural antioxidant in the sealant improved the aging resistance as these sealants can reduced their weight loss and maintained their appearance. Its ability as a good sealant was not likely affected by the aging through weather or thermal exposure as high amount of MPP can act as its antioxidant and prevent degradation. High amount MPP added into the sealant prevent degradation to rubber compounds as from structural analyzed by FTIR. Oven and weathering tests showed different behavior on aging. Weathering had greater degradation effect as compared to thermal aging.

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