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FTIR Characterization and Conductivity Studies of Undoped and Doped Synthesize Polyene from Polyvinylchloride with Sustainable Epoxidised Oil Coating Resin

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ABSTRACT

Dechlorination of polyvinylchloride (PVC) through chemical process is expected to form conjugated carbon-carbon double bonds (CH=CH) along the polymer chain due to elimination of chlorine (Cl). Through the formation of conjugated bond in polymer chain, it may contribute to electrical conduction possibilities. In this research, polyene was synthesized by dechlorination of suspension grade of PVC. Polyene powder is synthesized by the reaction of PVC with tetrahydrofuran (THF) in the presence of polyethylene glycol (PEG) as catalyst. Several reaction times were used. The polyene powder was then doped with 5% of potassium iodide (KI). For conductivity test, modified epoxidised oil (EO) was mixed with the polyene before it was spin coated onto the glass substrate as medium. It was shown that the chlorine content reduces upon longer reaction time up to 4 hours and the formation of conjugated bond was verified by fourier transform infrared (FTIR). Optimum conversion of PVC to polyene was found to be about 2 hours. After doped with 5% potassium iodide (KI), peaks which indicate the presence of conjugated bond were shifted to a range about 1707 cm^{-1} to 1750 cm^{-}1. The highest conductivity observed for undoped polyene with synthesizing time of 2 hours, $1.92x10^{-3}$ Scm^{-1} and after doping with 5% KI, the conductivity was increased up to $3.37x10^{-3}$ Scm^{-1}. From these research, the increase in conductivity maybe affected by the formation of conjugated bond and the electronegativity ability of iodide (I^{-}).

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INTRODUCTION

Polyvinylchloride (PVC) is a vinyl polymer constructed of repeating vinyl groups (ethenyls) having one hydrogen replaced by chloride. Chemical structure of PVC is $[(CH2\text{-}CH\text{-}Cl)_n]$ where *n* is polymerization degree of the materials that plays an important roles in industrial applications. PVC is a common commodity plastic, and the production of the PVC is the third largest, after polyethylene (PE) and polypropylene (PP) (Yoshioka, Kameda, Grause, Imai, & Okuwaki, 2009). PVC through dechlorination treatment could produce the dechlorinated Polyvinylchloride (DPVC) that eliminates the chlorine atoms, resulting in hydrochloric (HCl) removal and black powder of polyene formation (sequence of conjugated double bond). A study by Balci S. *et al*., (2004) reported that PVC is a common insulating polymer but degrades easily via dehydrochlorination by loss of hydrochloric acid (HCl) when exposed to heat, energetic particles or photons (Balci, Birer, & Suzer, 2004). Under definite conditions, dechlorination of PVC may cause alternating single bonds and double bond carbons or conjugated (polyene). DPVC can be doped by iodine into a conductive state and showed the conductivity value up 10^{-3} Scm^{-1} with that various thickness of film (Lin Guo, Shi, & Liang, 1999).

Generally, polymers are insulators, from electronic material point of view; polymers have limited application as they are considered as uninteresting. However, in late 1970s, polyacetylene doped with iodine was reported as the first polymer which capable of conducting electricity and the polymer conductivity can be increased to as high as 15 orders of magnitude by oxidative doping effects. Electrical conduction is measure by the ability of a material or samples to pass a current (Çakmak, Baştürkmen, & Kısakürek, 2004). According to Pauw (1958) for conducting polymers which conductivities less 10^{-8} Scm^{-1} are consider as insulators, conductivities between 10^{-8} $Scm^{-1}$to 10^{3} Scm^{-1} are considered as semi-conductors and for materials with conductivities more than $10^{3}Scm^{-1}$ consider as conductor (JLvd, february 1958). Most of the conductive

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polymers present are based on aromatic ring systems. An example of conducting polymers include polyacetylene, polythiophene, polyaniline(PANi)(10^{-5}Scm^{-1}), polypyrole(PPy)(10^{2}Scm^{-1}) and Polyphenylenevinylene(10^{-13}Scm^{-1}) which possess significant level of electrical conductivity, and versatile promising applications in the field of energy storage, sensors, electrical and optical applications (Guimard, Gomez, & Schmidt, 2007; Yee, Mahmud, Kassim, & Yunus, 2007).

Epoxidised oil (EO) can be obtained by the conversion of unsaturated fatty acids that can be obtained from plant based and this material is vegetable-oil based epoxy material, renewable and environmental friendly. Polymeric materials form natural oils have attracted a lot of attention recently. It becomes more abundance and hence are expected as an ideal alternative chemical feedstock particularly in petroleum based sources (Tsujimoto, Uyama, & Kobayashi, 2010). The modification of EO is done by introducing unsaturated monomer into oxirane groups of the EO leads to possible side reaction was the epoxy ring opening that produced hydroxyl groups formation and formation of derivative group (Habib & Bajpai, 2011). An example of epoxidised oil extracted from plant based is rubber seed oil, soybean oil, jatropha oil and palm oil.

Hence, this study is undertaken with the aim to determine the effect of synthesize polyene with different reaction times and doping effect on structural investigation via Fourier Transform Infrared (FTIR) and conductivity test for coated with modified EO.

Experimentation:

Materials:

Polyvinyl chloride (PVC) powder with grade HP65 is a product of Malaysian Electrochemicals industry (Malaysia). Tetrahydrofuran(THF)(MERCK Malaysia), polyethylene glycol(PEG)(R&M Chemicals Malaysia), potassium hydroxide(KOH)(R&M Chemicals Malaysia), potassium iodide (KI)(SYSTERM Malaysia).

Synthesization of PVC:

Dechlorination of PVC was done in three neck flask reactor consisted of condenser. PVC was dissolved in tetrahydrofuran (THF) and base solution (potassium hydroxide dissolved in PEG). Base solution was dropped into polymer solution and stirred until form a homogeneous solution system. The transparent colour of solution was changed from yellow and finally to dark colour. The black powders were filtered using vacuum pump. Finally, the rough products were then washed with methanol. Then, remaining base solution and salt was extracted out using soxhlet extractor with methanol about 24 hours. The polyene powders were dried under vacuum conditions at 60°C for 24 hours before being characterized. Reaction of dechlorination was varied from 30 minutes, 1 hour, 2 hours and 4 hours reaction time.

Doping of polyene:

Doping of polyene powders was carried out by immersing in 5% potassium iodide (KI) for 1 hour and washed with distilled water. It is finally dried under vacuum conditions at 60°C for 24 hours.

Preparation of modified EO with Polyene:

The polyene powder had been dispersed in modified epoxidised oil (EO) and was cured through ultraviolet (UV) light conveyer machine (F300S MODULAR 6 ULTRAVIOLET), intensity 0.107 W/cm^2 (measured by an IL 390B Light Bug radiometer from International Light Inc.), lamp with 80 W, energy 0.4400J with 2 times at 37 sec per pass.

Characterization:

Fourier transform infrared by Perkin-Elmer IR spectrometer was used to analyze the absorption and peak presence of functional groups which might be produced from dechlorination of PVC. IR band used between 600cm^{-1} to 4000cm^{-1} with 16 scan number (S. J. Park, Jin, & Lee, 2004) and potassium bromide (KBr) pallets used with ratio 1:9 with polyene powder. The electrical conductivity of polyene coated with modified EO was measured by two probe d.c technique on an HIOKI 3532-50 machine. The conductivity of polyene coated with modified EO is calculated from $\sigma = t/R_bA$, where ‘t’ the thickness of the film, ‘A’ the area of the film and R_b the bulk resistance of the material which is obtained from the intercept on the real axis of semicircle (Kiran Kumar *et al*., 2011; Rajendran, Prabhu, & Rani, 2008).

RESULTS AND DISCUSSION

Analysis synthesization of polyene from PVC:

Fourier Transform Infrared spectroscopy (FTIR) analysis:

The FTIR analysis performed had characterized the formation of conjugated (C=C) and the loss of chlorine bond in the components of the polyene and PVC samples. The conjugated bond (C=C) might had been formed during the dechlorination of PVC by releasing the chlorine atoms attached at the polymer chain (C-Cl) at around 600cm^{-1} to700 cm^{-1}.

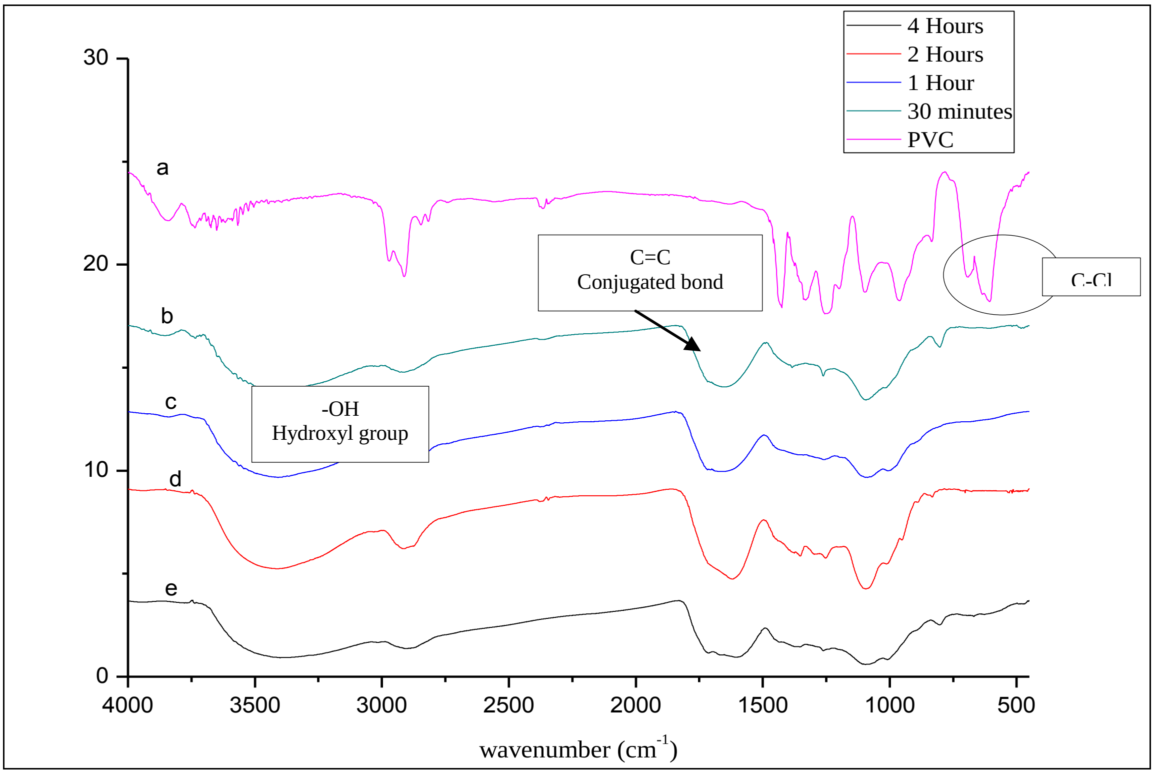

Fig. 1: Shows the FTIR of PVC (a) and the DPVCs obtained by the catalyzation of PEG 400 for 30 minutes (b) 1 hour (c) 2 hours (d) and 4 hours reaction time (e).

As can be seen from Figure 1 (a) there is stretching band of C-Cl at 610cm^{-1} and 684.63cm^{-1} and it also showed a strong characteristic of CH_2 stretching bands in the of 2913cm^{-1} to 2800cm^{-1}. After several comparisons with the reaction times (b, c, d and e), the characteristic of CH_2 stretching bands had became weak and broad. These will confirmed that the reaction of dechlorination process had occurred (L. Guo, 2001).

Besides that, the IR spectra showed strong conjugated C=C stretching bands characteristic is in the range of 1600cm^{-1} to 1680cm^{-1} after several reaction times. The strongest peak of C=C can be seen at Figure 1 (d) 2 hours dechlorination of PVC. In the infrared spectra, the CH_2 bending modes at 1426cm^{-1} at Figure 1a are stronger compared to the spectra after the dechlorination reaction. The decreasing sharp peak of CH_2 bending modes at 1426cm^{-1} after the reaction might be due to the C=C double bond which had overlapped the CH_2 bands, and hence the formation of C=C bands at 1600cm^{-1}. Then, after the dechlorination reaction, the bands at 1426 cm^{-1} became weak, and it indicates that there is CH_2 bands which are located mostly at the last of the polymer chain. Hence after certain reaction times, IR spectra showed an obvious peaks around 1005cm^{-1} to1009cm^{-1} bands of -C-H. Guo, L., Shi, G., & Liang, Y. (2001) implied that the dechlorination of PVC has longer conjugated sequences, because longer polyene segments tend to have more enhanced adsorption of C=C at low frequencies and of -CH at higher frequencies (L. Guo, 2001).

Figure 2 showed that, peaks which centered at 1600cm^{-1} to 1680cm^{-1} of conjugated bond was shifted and the band become broader to the higher frequencies of 1707cm^{-1} to 1750cm^{-1}. During doping process, Iodine help places the hydrogen atoms in the polyene system. Hydrogen atoms recombined with Iodine and produces hydriodic acid (Stejskal *et al*., 2008).

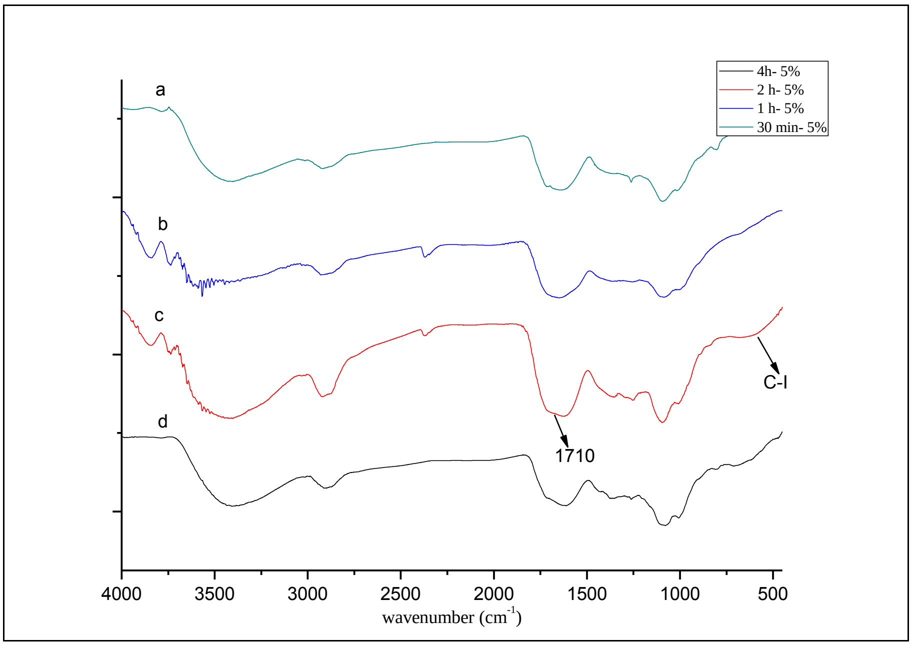

Fig. 2: Shows the FTIR of 30 minutes (a), 1 hour (b), 2 hours (c) and 4 hours (d) reaction time doping with 5% KI.

According to Švorčík, V., Prošková, K., Hnatowicz, V., & Rybka, V. (1999), the maxima absorption peaks (520cm^{-1} to 560cm^{-1}) is typical for C-I bond which indicates that a part of the incorporated iodine atoms is chemically bonded to the polyene system chain via addition onto double bonds. However, the C-I bond is weak and was expected to be easily broken down by the effect of elevated temperature or illumination (Švorčík, Prošková, Hnatowicz, & Rybka, 1999). It can be seen from the IR spectra that the peaks at 520cm^{-1} to 560cm^{-1} does not show obviously after the doping with iodine, this might due to the peaks of iodine was overlapped with nearest chlorine peaks that remained at 610cm^{-1} to 684cm^{-1}.

Figure 3 showed the colour of THF solvent at certain dechlorination reaction time where it started from a transparent solution changing into yellowish after a few second upon pouring the base solution, gradually turning dark red, and finally to dark

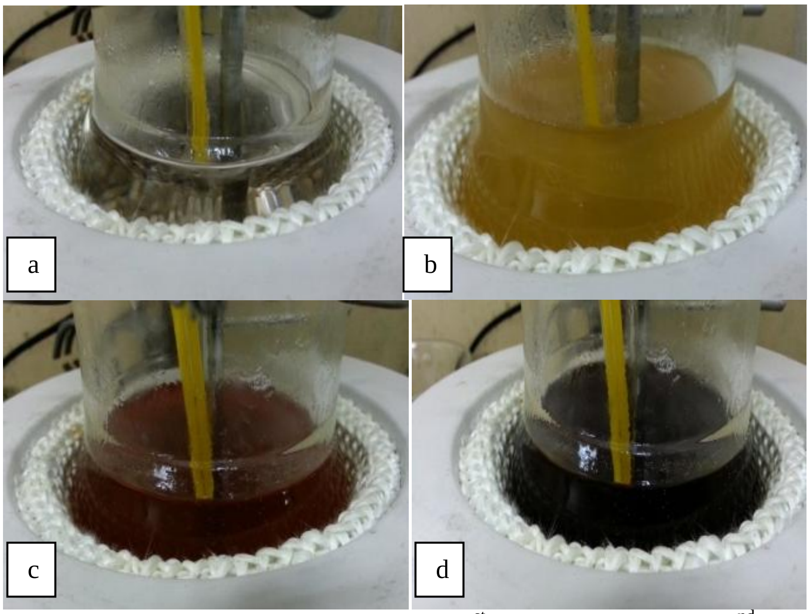

Fig. 3: Colour of solution upon dechlorination reaction time; 1st stage-*colourless* (a), 2nd stage, a few second after poured base solution was administered- *Yellow* (b), 3rd stage, after 2 minutes of reaction – *Dark red* (c), final stage, after 5 minutes of reaction- *Dark* (d).

Electrical conductivity of potassium iodide (KI) doped:

The electrical conductivity of polyene coated with modified EO is calculated from $\sigma = t/RbA$, where't' is the thickness of the film, 'A' the area of the film and R_b the bulk resistance of the material which is determined from the intercept on the real axis of semicircle. (Rajendran *et al*., 2008). The semicircle formed due to the parallel combination of bulk resistance (due to migration of ions) and bulk capacitance (due to immobile polymer chains) (Kiran Kumar *et al*., 2011).

Table 1 lists the electrical conductivity at room temperature of a series of polyene film undoped and doped with 5% KI. From the result on Table 1 it shown that, for undoping polyene the conductivity value is almost at 10^{-3} Scm^{-1}and after doping with KI the conductivity value is about 10 times higher. For undoping polyene 2 hours polyene showed the highest conductivity 1.92 x 10^{-3}Scm^{-1}.

Table 1: Shows Conductivity Value of Polyene Coated Modified EO Undoped and Doped with 5% KI

Samples	Conductivity [Scm^{-1}]	
	Undoped	Doped with 5% KI
30 minutes	1.81x10^{-3}	2.40x10^{-3}
1 Hour	1.87x10^{-3}	2.86x10^{-3}
2 Hours	1.92x10^{-3}	3.37x10^{-3}
4 Hours	1.04x10^{-3}	2.74x10^{-3}

The lower conductivity value of 30 minutes of polyene is probably due to lesser amount of conjugated structure compared to longer reaction time of 1 hour or more. This may be due to addition of conjugated bond formation structure. At 4 hours polyene sample, the conductivity value was decreased to 1.04x10^{-3} Scm^{-1}. It was found that as the reaction time increased, the conductivity increased. Upon higher reaction time at 4 hours, the conductivity was decreased; this might be due to intercrosslink conjugated structure which reduces the conjugated link hence restricting the ion mobility.

Doped samples with 5% KI showed that the conductivity was increased up to 3.37x10^{-3}Scm^{-1} for 2 hours reaction time and the lowest was recorded at 2.40x10^{-3}Scm^{-1} at 30 minutes reaction time. According to Majid and Arof (2007), the conductivity increase is mainly due to an increase in the number density of mobile ion (Majid & Arof, 2007). Regarding to the FTIR test showed that, conjugated bond was diminished and supposedly lower the conductivity. According to Guo and Liang (1999), this behaviour is similar to other conducting polymers such as polyacetylene and polypyrole(PPy), which doping damaged the conjugated double bonds and shorten their sequences (Lin Guo *et al*., 1999). Adhikari, S. and Banerji, P. (2010) report that Iodide (I^-) as an anion dopant may increase the conducitivity which have the ability to increase the conductivity of PANI (Adhikari & Banerji, 2010). In this case, the presence of iodide still can increase the conductivity of the polyene sample but in a small effect. Effect of electronegativity of iodide would make electrolyte pi-orbital (Π) electron transfer better.

Consequently, according to Kumar *et al*, 2011, the increase in conductivity with the addition of salt may contribute by the reduction in crystallinity of polymer and also the increase in number of mobile charge carriers (Kiran Kumar *et al*., 2011). On the other hand, the reduction of crystallinity to amorphous phase which more flexible would resulted in an increase in segmental motion of the polymer hence facilitate the ion mobility (C. Park, 2003).

Conclusion:

Polyene which has conjugated bonds was successfully synthesized from PVC via chemical reaction method. Dechlorination of PVC via chemical methods produced polyene with conjugated bonds. From FTIR analysis, the synthesis resulted in severe morphological alteration peak for conjugated bond that was found at around 1600cm^{-1} to 1680cm^{-1} and the diminishing of chlorine peaks at 630cm^{-1} after several reaction times. For undoped sample, the electrical conductivity of 2 hours reaction time of polyene coated with modified EO showed highest conductivity, 1.92x10^{-3}Scm^{-1}. Meanwhile, after doping with 5% KI, its conducitivity increased to 3.37x10^{-3} Scm^{-1}.

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