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Preliminary Study on Degree of Conversion of UV Curable Maleinated Acrylated Epoxidised Palm Oil Pressure Sensitive Adhesives Synthesised with Isobornyl Methacrylate Monomer via FTIR-ATR Analysis

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UV curable PSA of maleinated acrylated epoxidised palm oil (MAEPO) from palm oil via UV LED lamp has been introduced with the existence of Chivacure 300 as photoinitiator. By involving the isobornyl methacrylate (ISBMA) as a monomer in the PSA formulation, the degree of conversion recorded low percentage of conversion, which was below 50 % although the loading of photoinitiator has been raised to 5 parts per hundred (phr). The ISBMA has affected to the slow curing speed on the maleinated PSA and restricted the conversion of C=C to more than 50 % even though the curing time and photoinitiator loading has been increased up to 300 min and 5 phr. It is expected that the double bonds are still present in the synthesised of PSA which indicated that most molecules were bonded at one end of another in methacrylate group. In the present study, real-time FTIR-ATR spectroscopy was used to follow the crosslinking process of the adhesive and the adhesive properties of the cured coatings.

1. Introduction

Pressure sensitive adhesives (PSA's) are a class of materials that have ability to adhere quickly to any surface under a minimum pressure load. The special property of PSA that only requires pressure applied compare with the common adhesives has improved its value among consumer. According to definition these category of adhesives is aggressively tacky in dried form and permanently adhere to any kind of surface. Polymer exhibits viscoelastic form and develops adhesion to material and cohesion (shear) resistant debonding (Sowa et al., 2014). Petroleum based PSA is used in many areas such as general purpose labels, note pads, automobile trim, packaging and medical application. Tong et al. (2014) synthesised PSAs for medical application from petrochemical source. These synthetics PSAs have been existed since the past forty years ago, in order to replace the PSAs made from natural rubber and resins. The development in medical area has been improved since few years back such as paper tape, transparent dressing, vapour permeable (MVP) PSAs and transdermal drug delivery system (TDDS) (Czech et al., 2011b). Liu (2012) studied the development of the existing medical PSA for human skin until it was upgraded to a comfortable removal. The introduction of ultraviolet (UV) technology on medical applications PSA has improved the thermal stability on PSA. There is a big wave on studies of producing adhesives or pressure sensitive adhesive (PSA) from vegetable oil such as soybean, which promise the competitive properties with conventional PSAs from petrochemical source. Epoxidised fatty oils and their derivatives have shown a promising effect when it was used as reactive resins (Habib and Bajpai, 2011). In recent years, there are growing trends in using palm oil as raw materials in radiation curable resins production. Most of the radiation curable resins available commercially are derived from synthetic raw materials. Only a few known acrylated oils are obtained from indigenous raw materials such as soybean, tung and linseed oils. Some successful efforts were reported in developing PSA from acrylated resins from palm oil (EPOLA) products (Mahmood et al., 2004) but still no

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researches on further modification of EPOLA for PSA synthesise was reported. Since epoxidised palm oil (EPO) falls in a same group of triglyceride as epoxidised soybean oil (ESO), it also can be a potential material to be explored in producing PSA. As the palm oil has a short chain compared to the soybean oil, thus the modification is needed. The palm oil contains unsaturated chain can be chemically modified through simple reactions which involved the introduction of polymerisable groups such as epoxy or acrylates to give a practical, useful properties and good characteristics products. The modification on palm oil such as epoxidation, acrylation and maleinisation reactions have increased the reactive double bond onto triglyceride and introduced acid functionality on triglyceride backbones thus, added more cross-link sites (Fakhari et al., 2014). According to Pelletier et al. (2006), among the photoreactive systems, free-radical polymerisations of acrylates and methacrylates are the most reactive monomers, which play a very important role. It was proven through the free radical polymerisation of acrylated soybean oil by ultra violet (UV) and led to the improvement of photoactivity where the crosslinked photopolymers formed within a few seconds. In this research, the approach highlights further modification on epoxidised palm oil (EPO) to increase reactive sites for free radical polymerisation via UV curing and investigate the improvement on the PSA properties such as tack, shear and peel strength of adhesives. In order to satisfy the properties, the degree of conversion should record good and high percentage of conversion. As reported by Czech et al. (2011a), with the increased of photoinitiators concentration, the monomers conversion has been increased until 99.6 %. The main ingredient needs to be modified into maleinated acrylated epoxidised palm oil (MAEPO) with expectations to produce PSA for medical application. The UV LED was used in this study has low temperature and radiation effect as the substitution of mercury lamp from conventional method for curing process. This preliminary study is the string of the previous study of Mahmood et al. (2001) on acrylated epoxidised palm oil (EPOLA), who reported that adhesive properties by ISBMA were high. This study evaluated the degree of conversion of modified EPOLA, maleinated acrylated epoxidised palm oil (MAEPO) PSA under the curing mode in time interval from 20 min up to 300 min.

2. Materials, methods and characterisation

2.1 Materials

MAEPO resin was synthesised from two stages modification of EPO which was purchased from Budi Oil Sdn. Bhd. (Selangor, Malaysia). Isobornyl methacrylate (ISBMA), isobornyl acrylate (ISBOA) and acrylic acid (AA) were purchased from Sigma Aldrich (Selangor, Malaysia), which was used as a monomer and reactive diluents. “Type I” photoinitiator; Chivacure 300 was purchased from Chitec Technology Corp. (Taiwan).

2.2 Experimental

The PSA coating materials with the recipes 50 : 50 of MAEPO: ISBMA/ISBOA/AA was recorded in weight percent with 85 % / 10 % / 5 % represented the monomer ratio from the total weight which was followed from Mahmood (2001) who studied the effect of monomers on the properties of epoxidised palm-oil acrylated (EPOLA) radiation curable PSA. In this study, the formulation was prepared through normal mixing method which involved the sonicator bath to mix the photoinitiator (Chivacure 300, in parts per hundred (phr)) homogenously with the other ingredient before adding the high viscosity MAEPO resin and purged N_2 gas for the formation of partially polymerised resins until the mixture increased in viscosity. Chivacure 300 as photoinitiator was varied from 1 phr to 5 phr as suggested by supplier. The high viscosity adhesives were then coated onto polyethylene terephthalate (PET) films with thickness of 30 – 40 µm with a casting knife, giving around 50 µm thickness of MAEPO adhesives. The coated films were then exposed to UV irradiation by using non-dynamic UV LED chamber with the fixed light-cured distance between the light tip and the surface of the PSA.

2.3 Characterisation

FTIR-ATR (Fourier Transform Infrared Spectroscopy-Attenuated Total Refluctance) spectra of the MAEPO PSA were recorded in the range of 4,000 - 370 cm^{-1} using IR Tracer-100 FTIR Shimadsu using 40 scans at 2 cm^{-1} resolution. Figure 1 recorded the spectra of 50 : 50 of MAEPO: monomer with 1 phr of chivacure 300 at 0 minute. The curing behaviour was investigated by following the IR absorption band at 810 cm^{-1} in the FTIR spectrum, corresponding to C=C twisting, of the liquid and cured films, at different exposure times to the UV radiation. The conversion percentages were calculated using the following Eq(1):

$$\text{Degree of Conversion, \%} = \frac{A_0 - A_t}{A_0} \times 100\ \% \quad (1)$$

where, A_0 is the C=C absorption peak intensity at 810 cm^{-1} before exposing to UV energy (uncured film), and A_t is the C=C peak intensity after an exposure time (t) with the CH_3 peak at 2,924 cm^{-1} was used as an internal standard (Salih et al., 2015).

By following the curing time from the study of David et al. (2009) on the oleo-based PSA, the time of irradiation from 0 min to 60 min were chosen for every loading contents of Chivacure 300 to observe the percentage degree of conversion.

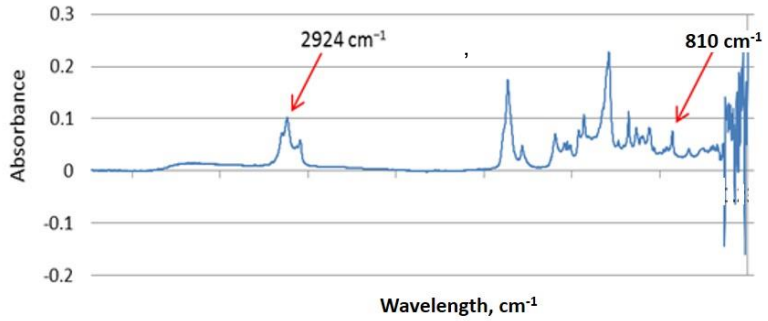

Figure 1: 50 : 50 of MAEPO: monomer with 1 phr of chivacure 300 at 0 min

3. Result and discussion

In the present study, real-time FTIR-ATR spectroscopy was used to follow the crosslinking process of the adhesive. FTIR-ATR is an established method to determine residual double bond and it must be emphasised that the remaining double bond is not directly related to the amount of residual (co) monomer. The most important factors to achieve an appropriate DOC of photoactivated materials are the light intensity and irradiation time. The effect of the irradiation time with low temperature of UV LED on the adhesive properties was studied where these findings corresponds quite well to the observations by FTIR-ATR spectroscopy. Figure 2 shows the values of degree of conversion (DOC) and trends of each loading contents of Chivacure 300 until 60 min. The degree of conversion of C=C double bonds of the methacrylate based monomers measured with FTIR-ATR was significantly increased with the polymerisation time. The DOC recorded the similar trend for every loading contents of Chivacure 300 until 60 min which were not exceeded 50 %. But the DOC increased as the loading content of photoinitiator increased. As can be seen, at 4 phr and 5 phr of photoinitiator loading the trends of DOC were lower than 3 phr of Chivacure 300. It might be due to the exceeded the optimise loading of photoinitiator on MAEPO-ISBMA adhesives. With the long interval of irradiation, it was expected to have higher degree of conversion of at least more than 50 %. As reported by Mahmood et al. (2001), the methacrylate monomers promised the good and high adhesion properties but have slow curing speed. The irradiation time was dragged until 120 min (2 h) at 1 phr of Chivacure 300 for the same observation.

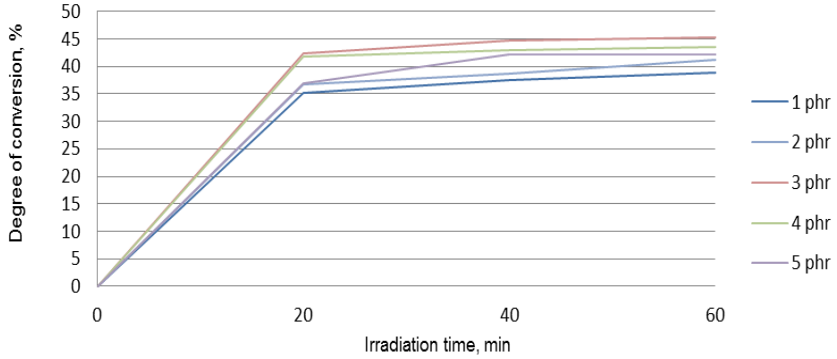

Figure 2: Curing time versus degree of conversion at different loading of photoinitiator (phr) until 60 min

It is expected, with the increasing of time-irradiation on adhesives will give a high result of degree of conversion. From Figure 3, the DOC tends to increase as the time increased. Unfortunately, similar result recorded with the previous observations on the percentage of conversion which still below 50 %. In order to observe the degree of conversion percentage up from 120 min, the irradiation time was then increased until 300 min (5 h) at 3 phr of loading content of Chivacure 300 as shown in Figure 4. The DOC indicated slow increment in the percentage of conversion until at 160 min before it was slowly decreased. It could be due to

the degradation occurred on MAEPO PSA as the longer time of irradiation. Cheong et al. (2009) reported that the cured polymer tends to degrade at higher radiation when initiated at higher dose of irradiation. In this case of non-dynamic irradiation, the dose of radiation depends on the time of curing.

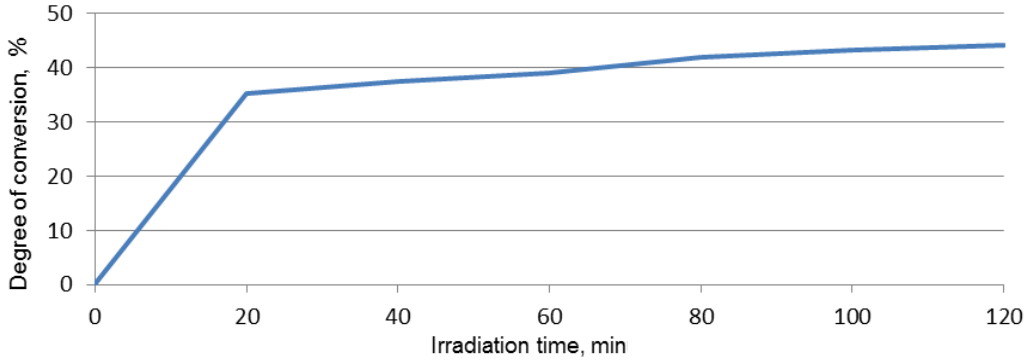

Figure 3: Curing time versus degree of conversion at 1 phr until 120 min

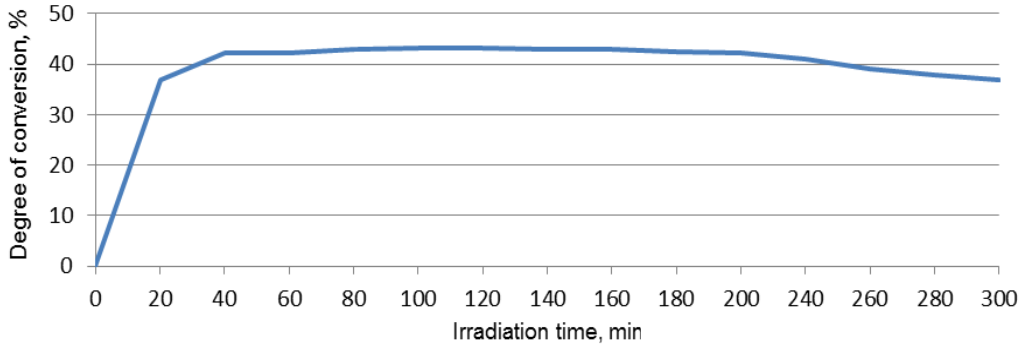

Figure 4: Curing time versus degree of conversion at 3 phr until 300 min

According to Emami et al. (2003), methacrylate molecules can be crosslinked but it does not always react with free monomer due to its potential to react with one end of another methacrylate group. DOC, which was determined based on unreacted double bonds are still available. If the conversion values recorded 50 - 70 %, it meant that 50 - 30 % of double bonds are still present which indicated that many molecules bonded at one end only. From Ruyter and Oysaed (1982) study, if DOC was 50 %, theoretically there would be one single polymer chain along with the second methacrylate groups of each dimethacrylate molecule with its carbon double bond formed a side group. There is no single monomer molecule present despite a degree of conversion of only 50 %. This example is of course an extreme situation, and if the degree of conversion is as low as 50 % it is expected that some leachable monomer molecules are still present. The mechanism of reaction has been proposed by Ruyter and Oysaed (1982) as shown in Figure 5. The main challenge in producing the oleo-based pressure sensitive adhesives technologies is the longer curing time which is not acceptable in industry (Ahn et al., 2011). Even though the curing time and loading content of Chivacure 300 have been increased, the degree of conversion was still not exceeded 50 %. Mahmood et al. (2001) reported that the ISBMA gave good adhesion properties which affected by the good degree of conversion, but slower curing speed on EPOLA PSA. It produced the bad conversion of C=C on MAEPO resin. The used of LED light source also lead to the lower degree of conversion of PSA. Ozturk et al. (2013) concluded in their study that the DOC really dependent on both light source and materials itself. The characteristics of PSA were most considerate than the light source type. The lower light energy like LED lamp indicated the lower degree of conversion value compared to the other light sources such as plasma arc curing (PAC) and quartz tungsten halogen (QTH) lamp.

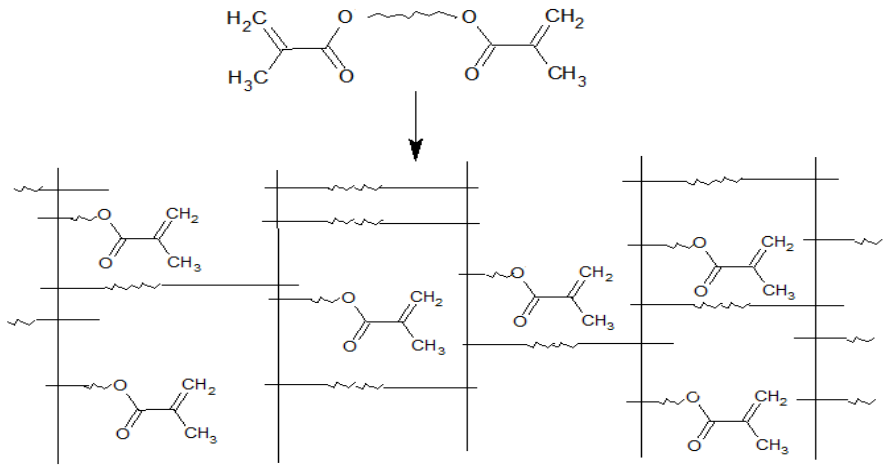

Figure 5: Simplified and idealised structure of polymerised dimethacrylated with remaining unsaturated groups (Ruyter and Oysaed, 1982)

4. Conclusion

The DOC in percent of C=C double bonds of the methacrylate based monomers measured with FTIR-ATR was significantly increased with the polymerisation time. The shortest curing time required to achieve a clinically satisfactory DOC has not been specifically established. The hypothesis in the present study is that the extended curing time would prolong the excitation of photoinitiator molecules and increased the DOC of MAEPO PSA. Up to 160 min curing time and 3 phr of Chivacure 300, the DOC value tends to reduce. This could be due to the light transmission that may have been disturbed and decreased with time. UV cured MAEPO PSA via UV LED synthesised with ISBMA monomer could be preceded with the inexistence of another type of monomer in recipe and the addition or modification in methodology in the future study.

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