

Real-Time Cure Monitoring of Unsaturated Polyester Resin from Ultra-Violet Curing

M.A. Hussein^{#,†,*}, G.S. Tay and H.D. Rozman

Division of Bio-Resource Paper & Coatings Technology, School of Industrial Technology, Universiti Sains Malaysia, Penang, 11800, Malaysia

Abstract: Real time Fourier transform infrared (RTFT-IR) spectroscopy reveals the influence of the nature of the photoinitiator on the kinetics for the polymerization reaction. Real time cure monitoring was used to determine the polymerization rate of ultra-violet cured unsaturated polyester resins (UPR_{1:2-1:5}) based on palm oil and containing styrene as a cross-linking agent in the presence of IRGACURE 184 photoinitiator. Firstly, variable types of UPR_{1:2-1:5} were prepared using various ratios of monoglyceride (MG) monomer to maleic anhydride which used as a source of double bond using polycondensation technique. RTFT-IR spectroscopy was used to characterize the ultra-violet curing kinetics for all the systems. This technique offered a powerful approach for monitoring changes in the chemical properties of the system during the ultra-violet curing. Pseudo first order kinetics for all UPR_{1:2-1:5} curable systems were determined and the rate constant values and regression coefficients were calculated. Furthermore, the thermal behaviour and morphological features for the photo-fabricated UPR_{1:2-1:5} systems were examined. The thermal analyses for the cured films were evaluated by TGA, DTG and DSC in nitrogen atmosphere at a heating rate of 10°C/min. All the formulations showed similar degradation pattern at 40 % and 50 % weight losses ($T_d = 40\%$ and $T_d = 50\%$ respectively) except polymer UPR_{1:5} which had somewhat lower degree in the same range. In addition, the morphological properties for photo-fabricated UPR_{1:2,1:3,1:5} were investigated by using scanning electron microscopy.

Keywords: Real time, kinetic study, ultra-violet curing, unsaturated polyester resins, thermal analyses.

1. INTRODUCTION

Unsaturated polyester resins [1, 2] (UPR) are one of the most important polymers synthesized by step-growth polymerization. UPR are widely used in variable fields including: automotive field, construction and electrical applications and coatings, considered as one of the most widely used thermosets. UPR find use in industrial applications because of their good mechanical properties especially when reinforced with fibres or fillers [3]. UPR, have firmly established themselves as important matrix materials in the field of reinforced plastics and coatings, although phenol formaldehyde type resins are preferred when specific fire and smoke resistance qualities are required [4-6]. Palm oil is a very common cooking ingredient in Southeast Asia. Along with its use in food, it is also used in a wide array of cosmetics and pharmaceuticals and increasingly for biodiesel production. Despite a short-term economic dip, diesel fuel prices are likely to continue to increase over the next decades and so will the demand for alternative sources [7]. The oil palm industry in Malaysia generates large quantities of biomass. Our research team present a variety of

publications that related to oil palm industry using curing technology [8-18]. Most of these investigations show that various products can be produced from the by-products of the palm oil industry, such as oil palm component plastic composite [8], oil palm component-rubber composite [9], sheet moulding compound [10] and pulp-paper [11].

The rapid growth of the ultra-violet (UV) curing industry over the past two decades has stimulated the development of new techniques for analyzing the UV curing process. Less heat, less cost and more life: that seems to be the motto among UV curing equipment manufacturers. However, there still lacks a fundamental understanding of many issues associated with UV curing. For example, the relationship between how the curing conditions and the molecular architecture of the monomers affect the final material properties of the cured polymer are not well understood. As a consequence, formulating UV curable systems for the desired properties is mostly done on an empirical basis. Furthermore, the UV curing technology has found a large variety of applications, in particular to achieve a fast-drying of varnishes and printing inks, a quick setting of adhesives and composite materials [19, 20] and a selective insolubilization of photoresists in microlithography. To improve understanding of the UV curing process, many studies have focused on characterizing the polymerization kinetics by using a variety of analytical techniques. Furthermore, ultraviolet curable systems are used in surface coatings and have

*Address corresponding to this author at the Polymer chemistry lab, 122, Chemistry Department, Faculty of Science, Assiut University, Assiut, 71516, Egypt; Tel: +20 882 41 24 16; Fax: +20 882 34 27 08; E-mail: mahmoud.hussein74@yahoo.com

[#]Permanent address: Polymer chemistry lab, 122, Chemistry Department, Faculty of Science, Assiut University, Assiut, 71516, Egypt

[†]Current address: Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

several distinct advantages such as solvent free, environmentally friendly, and energy saving [21]. The entire curing process occurs at room temperature and hence does not require expensive high temperature equipment for the curing [22]. In addition, UV curing is used to cure coatings and adhesives on many different types of automotive parts and components including: headlamp lenses, lighting reflector housings, body side moldings, under-hood components and interior coatings. Today, UV curing is being done very successfully on complex, three-dimensional parts including automotive lighting assemblies, plastic molded parts such as mobile phone cases and other teletronic devices, contoured wood products, golf balls, electric motor housings and fibreglass composite parts. The cure monitoring of the UV-curable formulation is usually carried out using a combination of techniques. Some of the techniques that have been used for kinetic studies on UV curable systems including: differential scanning calorimetry [23], differential photocalorimetry (DPC) [24, 25] dilatometry [26, 27] fluorescence spectroscopy [28]. In recent years, several academic and industrial groups have investigated the photopolymerization behaviours of cationic, free radical, and hybrid UV curable systems by using a simple and effective technique, RTFT-IR. Most RTFT-IR studies so far have focused on clear systems such as monomers, oligomers, or unpigmented coatings/adhesives [29 - 31]. FT-IR spectroscopy is considered as an important tool which has the ability to monitor the specific changes in chemical structure during UV curing process. This technique provides a fingerprint of the chemical groups present initially in the monomers before reaction and the subsequent changes in chemistry during curing. The FT-IR data can be used to directly determine the rate of polymerization by analyzing the decrease in the infrared absorbance of the reacting functional groups. FT-IR spectroscopy can also measure the reactant conversion more accurately than either DPC or dilatometry. This is accomplished by monitoring the absorbance of the functional groups before and after UV curing.

The great deals of this study was concentrated on the preparation of unsaturated polyester resins of variable formulations based on palm oil using ultraviolet curing technique. Furthermore, we exploit the advantage of RTFT-IR spectroscopy to monitor the UV curing for UPR_{1:2-1:5} formulations. Moreover, the study focused on the creation of spectroscopically derived curing profiles for all systems. These profiles were generated in the real time, that is the data from both

UV curing and FT-IR monitoring were collected simultaneously to follow the time dependent decrease of the double bond. Together with RTFT-IR spectroscopy, the thermal analyses and scanning electron microscope are other powerful tools that can be used to characterize the produced formulations.

2. EXPERIMENTAL

2.1. Materials, Reagents and Solvents

Palm oil was purchased from local market in Malaysia, maleic anhydride (Fluka, Analytical $\geq 98\%$), glycerol reagent plus (Sigma, $\geq 99\%$), 2-methylimidazole (Fluka, $\geq 98\%$) sodium hydroxide (System company $\geq 99\%$), molecular sieve (Fluka, type 3A) styrene (Sigma-Aldrich, $\geq 99\%$), pyridine (Aldrich, $\geq 99\%$), hydroquinone (System company, $> 99\%$) and Photoinitiator IRGACURE 184 (1-hydroxycyclohexyl-phenyl-ketone) was supplied by (Ciba Specialty, Singapore) Pte. Ltd. All of the materials mentioned before were used without purification. Solvents with different solubility parameters and of analytical grade, such as toluene [$8.9 \text{ (cal/cm}^3)^{1/2}$], [32] were used. All the other solvents were purified as reported in literature [33].

2.2. Preparation of Ultra-Violet Cured Unsaturated Polyester Resins (UPR_{1:2-1:5})

2.2.1. Monoglyceride Monomer Preparation (MG)

The main setup consisted of a 500 ml reaction flask equipped with a mechanical stirrer (2000 rpm/min), with dry nitrogen inlet and outlet. A mixture of palm oil (162.26 g) and 0.1 % sodium hydroxide were placed in the reaction flask, 27.74 ml of glycerol (within the molar ratio of palm oil to glycerol 1:2.2 respectively) was put inside the dropping funnel which was fitted to the reaction flask and was added in a drop-wise manner. For the first 5 minutes, nitrogen gas was allowed to flow swiftly. It was then adjusted to slow rate throughout the experiment. The reaction mixture was heated to 220 - 240 °C for 3 – 4 hours. After that, a small amount of reaction mixture was taken out by means of glass rod to measure the solubility in ethanol. The same work was continued until solution was obtained where no emulsion or white spots were observed. Then the mixture was cooled in ice water, and poured into a sealed beaker for the next experiment. Purification and structure elucidation for monoglyceride monomer were reported in our previous study [34].

2.2.2. Polymers Matrices Preparation

A polycondensation technique was used in the preparation of the desired polymer resins as described in our previous work [34]: In a round-bottomed reaction flask equipped with a mechanical stirrer (2000 rpm/min), 1 eq. of MG monomer was heated up to melt, then a mixture of 0.15% of hydroquinone was added to retard any polymerization reaction that may occur. Variable amounts of maleic anhydride (2 – 5 eq.), 2-methylimidazole as catalyst were added to the reaction mixture with constant stirring. The mixture was subsequently stirred at a temperature not more than 90 °C for 5 hrs, and then it was cooled down giving a dark viscous liquid. The resulting UPR_{1:2-1:5} was dried and later poured into sealed beaker for the next experiment. The chemical compositions for the produced UPR according to MG : maleic anhydride ratios as the following: UPR_{1:2} ; UPR_{1:3} ; UPR_{1:4} ; UPR_{1:5}

2.2.3. UV Photo-Fabrication of UPR_{1:2-1:5}

UV curing process for previously prepared UPR_{1:2-1:5} was conducted as described in our previous work [34] using ¹ST UV machine (model M20-1-Tr-SLC) for ten passes (each pass 28.3 x 10 uW/Cm²) at conveyor speed of 5 m/min. The machine consisted of a medium pressure mercury arc lamp with UV radiation wave number of 180–450 nm. The desirable cured UPR_{1:2-1:5} sheets (20 x 20 cm²) were obtained as the following: UPR_{1:2-1:5} (100 g) was mixed with styrene (30 ml, 30%) and photoinitiator (IRGACURE 184, 3 g, 3%). The whole mixture was stirred for 10 min with mechanical stirrer, evacuated under vacuum (30 mmHg, 20 min.) to remove the air bubbles if any. The mixture was then poured into stainless steel holder then sandwiched between two glass panels covered with transparency before being passed through the UV machine.

2.3. Instrumentation

2.3.1. Real-Time Kinetics

The Real-Time kinetic study for all UPR_{1:2-1:5} formulations was tested using Fourier transform infrared (FT-IR) spectroscopy (Nicolet, IS10) equipped with long wave UV-pen accessory [pen-ray ® light source, 90-0012-01(11SC-1), UV radiation wave number of 254 nm]. UPRs were spread over a KBr disk and were placed in the FT-IR machine. The FT-IR scanning started simultaneously with the exposure of the disk to the UV pen. All the FT-IR spectra were recorded in transmittance units within the wavenumber

range of 4000–400 cm⁻¹, with a resolution of 4 cm⁻¹. There were 32 scans for each spectrum.

The disappearance of the functional group was monitored continuously by RTFT-IR spectroscopy, by selecting the proper wavenumber of the IR detection, at 1630 cm⁻¹ for the UPR_{1:2-1:5} double bond. Conversion versus time curves can be readily obtained from the value of the IR absorbance, initially (A_0) and after a given exposure (A_t), by plotting the ratio $A_0 - A_t / A_0$ as a function of the exposure time. All the experiments have been performed at ambient temperature in the presence of air.

2.3.2. Thermogravimetric Analysis (TGA)

The pre-dried photo-fabricated UPR_{1:2-1:5} were tested using Perkin–Elmer thermogravimetric analyzer Pyris,1 TGA. Sample weight in the range of 15 – 20 mg was heated at 10°C/min in the range of 50 – 800°C with nitrogen atmosphere.

2.3.3. Differential Scanning Calorimeter (DSC)

The pre-dried photo-fabricated UPR_{1:2-1:5} were tested using Perkin–Elmer DSC6. Sample weight in the range of 3 – 5 mg was heated at 10°C/min in the range of -60 – 300°C with nitrogen atmosphere. For each sample, two measurements were made.

2.3.4. Scanning Electron Microscopy (SEM)

The fracture surfaces of photo-fabricated UPR_{1:2,1:3,1:5} test samples were investigated with a Leica Cambridge S-360 scanning electron microscope (Leica, Milton Keynes, Buckinghamshire, UK). The specimens were mounted on aluminium stub and sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

3. RESULTS AND DISCUSSION

Prior to polymerization process, MG monomer was prepared by the interaction of 1 mole of palm oil and 2.2 mole of glycerol in the presence of sodium hydroxide as basic catalyst. UPR_{1:2-1:5} based on palm oil were prepared in different compositions according to the amount of maleic anhydride used using polycondensation technique [35] by the interaction of the corresponding MG monomer with different equivalents of maleic anhydride as a source of double bond. This has been carried out in the presence of 2-methylimidazole as catalyst. The general structure for resulting UPR_{1:2-1:5} are represented in Figure 1. The structures of MG monomer as well as UPR_{1:2-1:5}

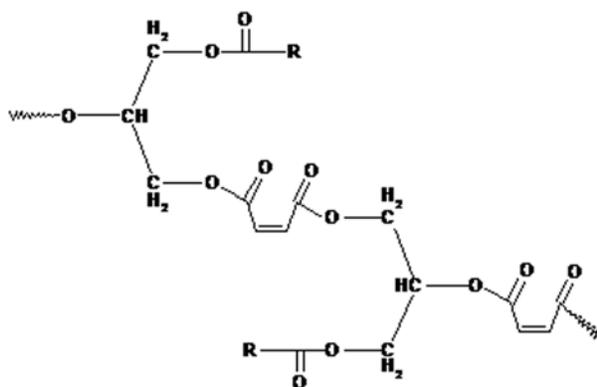


Figure 1: The general chemical structure of the produced $UPR_{1:2-1:5}$ resins.

polymer matrices were confirmed by spectral analysis. Spectral data supported the structural assignments for the obtained $UPR_{1:2-1:5}$ and are in good agreement with expected structures as shown in our previous study [34]. UV photo-fabrication for $UPR_{1:2-1:5}$ with styrene was evaluated using free radical initiator IRGACURE 184 using free radical polymerization technique to produce photo-fabricated formulations. The general structure these formulations is illustrated in Figure 2.

Real time infrared spectroscopy kinetics studies for $UPR_{1:2-1:5}$ were discussed. Furthermore, the thermal and morphological features for the resulting formulations after UV curing were determined and the data were discussed below.

3.1. Kinetics of the Photopolymerization

The kinetics profile of the UV-induced curing for $UPR_{1:2-1:5}$ formulations were studied by RTFT-IR. $UPR_{1:2-1:5}$ formulations were exposed for a short time to the radiation of long wave UV-pen accessory, the UV radiation intensity at the sample position being set at wave number of 254 nm. The extent of the

polymerization reaction upon UV exposure was evaluated quantitatively by RTFT-IR spectroscopy [36, 37] by following the decrease of the IR band at $1630 - 1640 \text{ cm}^{-1}$ characteristic of the $UPR_{1:2-1:5}$ double bond. This analytical method permits one to determine the final conversion, and thus the amount of residual unsaturation in our UPRs. Gradually, as the reaction slows down, the rate of the photopolymerization also slows; showing the cure is near completion. As curing proceeds, the physical nature of the UV curable mixture changes from a Newtonian fluid to a gel and finally a glassy solid [38]. Gelation corresponds to the point at which an infinite network is formed. While the vitrification is the point at which the chains become closely packed and there is insufficient volume for co-operative motion to occur. At vitrification, the material changes from a rubber to a glass and reaction is effectively quenched for those reactions where intramolecular reactions are not important.

Figure 3 shows three-dimensional (3D) and traditional 2D representations of the time dependence upon UV exposure of IR band at 1636 cm^{-1} of the $UPR_{1:2}$ double bonds respectively as selected example. It is clear that, there is a decrease of the IR bands at 1636 cm^{-1} , characteristic of the UPR double bonds as the time increases and reaches minimum at around 20 min. The radical polymerization of $UPR_{1:2-1:5}$ curable formulations which are exposed to UV radiation in the presence of styrene as cross-linking agent and IRGACURE 184 as photoinitiator are shown in Figure 4. It should be noted that all the curable systems have nearly the same pattern of conversion. All the $UPR_{1:2-1:5}$ curable formulations show higher reactivity toward the cross-linked free radical polymerization with styrene in the first half of the exposure time than that occurred in the second part of time where the conversion is somewhat slower. The conversion rate for $UPR_{1:3}$

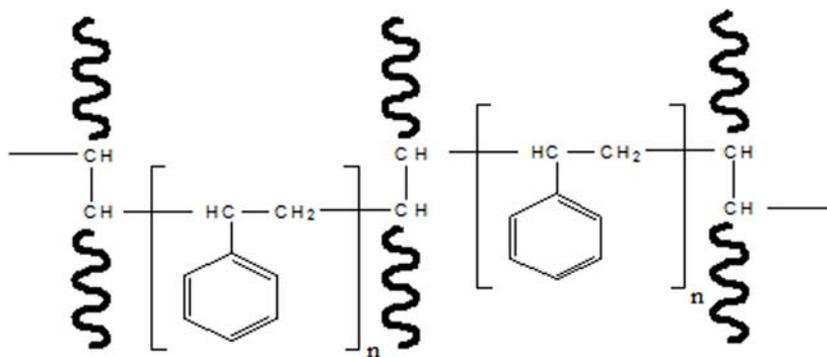


Photo-fabricated unsaturated polyester resins

Figure 2: UV photo-fabrication for $UPR_{1:2-1:5}$.

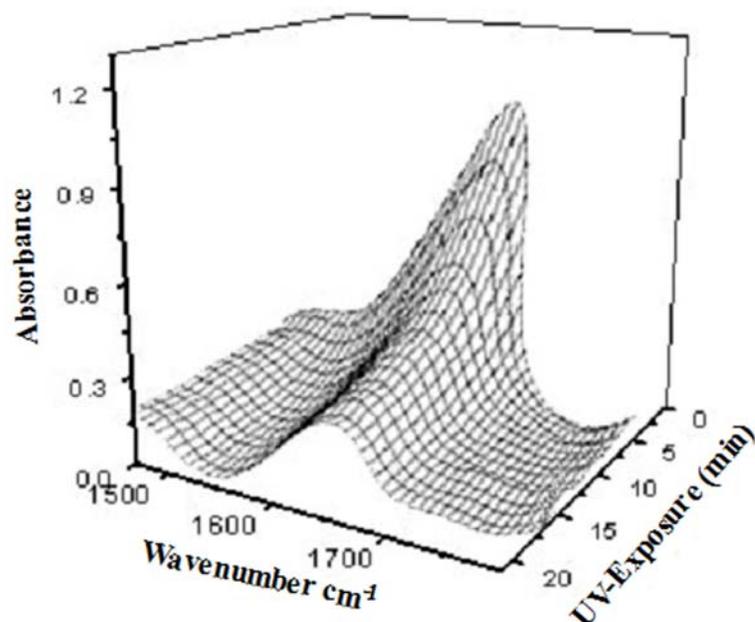


Figure 3: Polymerization 3D profiles recorded by RT-IR spectroscopy for the curable UPR_{1:3} exposed to UV radiation wave number of 254 nm.

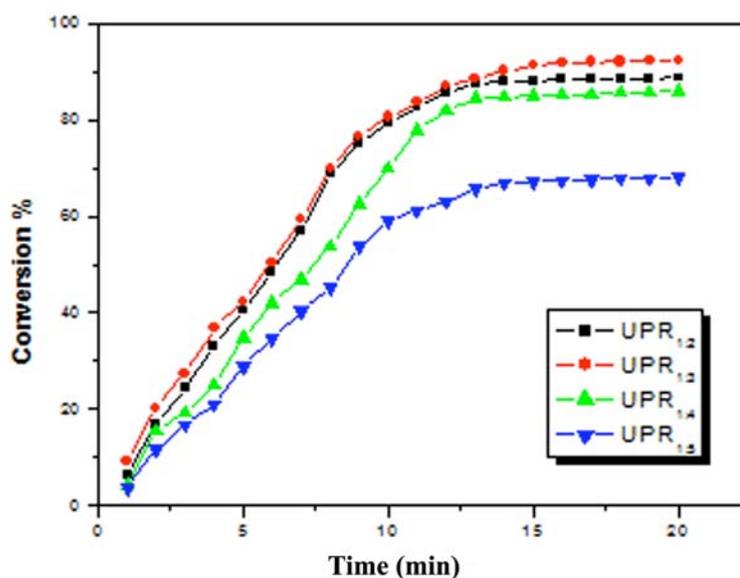


Figure 4: Conversion versus time profiles of curable UPR_{1:2-1:5} recorded by RTFT-IR.

reaches up to 80 % after 10 min. and finally reach 92 % after 20 min. The introduction of such curable polymer resins have generated a significant introduction period. Therefore, it takes less than one min. for the UV light to penetrate into the polymer matrix, react with the photoinitiator, and generates free radical before the cross-linked polymerization reaches a critical limit which can be observed on the RTFT-IR curves. A nearly complete polymerization of the majority of UPR double bond is achieved after 20 min UV-irradiation of the curable systems, while the conversion values were levelling off at around 85 – 92 % in the neat curable

systems. UPR_{1:5} has the lowest conversion value for all the tested UPR_{1:2-1:5} systems, where the conversion value was levelling off at around 65 %. It is obvious that 100 % conversion of the curable systems is not achieved. This may be attributed to the lower UV light emitted from the pen accessory where, the UV radiation wave number is only 254 nm compared to those photo-fabricated formulations produced using the normal experimentation condition for 1ST UV machine as illustrated in the experimental part (section 2.2.3.). More studies will be done for variable UV radiations in the near future.

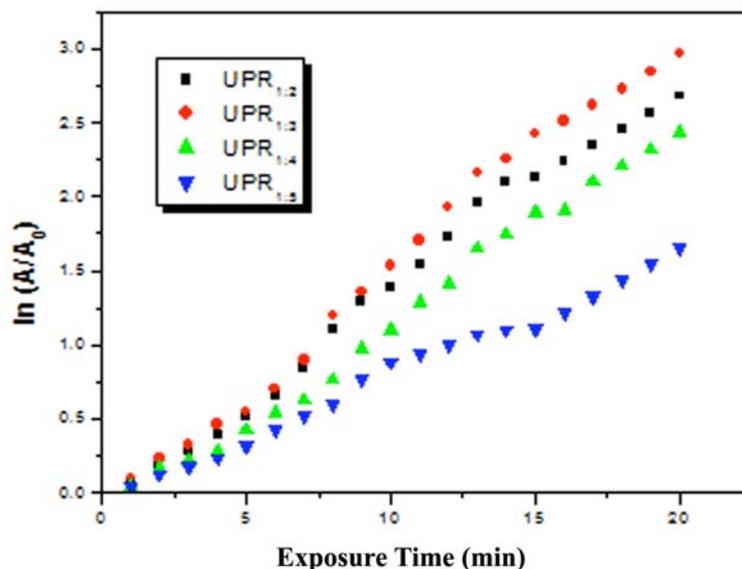


Figure 5: Pseudo first order kinetic plots for the UPR_{1:2-1:5}.

A comparison of the normalized UPR_{1:2-1:5} conversion (A/A_0) profiles for all the prepared formulations exhibited no noticeable trends suggesting that the alkyl ester side chain length does not significantly affect the activation-deactivation equilibrium controlling the cross-linking polymerization process. In addition, the pseudo first order kinetics for UPR_{1:2-1:5} curable systems were determined as given in Figure 5 and the resulting observed rate constant (K_{obs}) and regression coefficient (R^2) values are shown in Table 1. The rate constant values vary from one formulation to the other. UPR_{1:5} shows the lowest (K_{obs}) value. This trend may be due to the degree of the free radical polymerization that may depend on the total number of the double bonds supplied by maleic anhydride within the polymer matrix. However, examination of the polymerization kinetics for the other formulations UPR_{1:2-1:4} revealed little significant difference between the observed rate constants.

3.2. The Thermal Behaviour

The thermal behaviour of photo-fabricated UPR_{1:2-1:5} was evaluated by thermogravimetric analysis (TGA),

differential thermogravimetry analysis (DTG) and differential scanning calorimetry (DSC) at a heating rate of 10°C/min under nitrogen atmosphere. Table 2 gives the temperatures for various percentages of weight loss for all formulations. All UPR formulations show similar pattern on decomposition. TGA curves show a small weight loss in the range 1, 2%, starting at 90 until 130°C, which may be attributed to loss of absorbed moisture and entrapped solvents. The thermographs also indicate that, all the cured formulations decompose in two stages depending upon the nature of the unsaturated polyesters [39, 40]. The first stage between 145 and 185°C, the second stage of degradation occurs between 350 and 420°C. The rate of degradation in the second stage is slightly faster than in the first stage. The first degradation step involves the scission of cross-links/weak links with the liberation of free linear chains. The second step involves a random scission of the free linear chains into smaller fragments. This observation is in agreement with that observed by Bansal *et al.* [41]. The initial decomposition temperature (IDT) [42] corresponds to the temperature at which the initial degradation may

Table 1: Pseudo First Order Rate Constants and Regression Coefficients for the UPR_{1:2-1:5}

Polymer Symbol	$K_{obs} (min^{-1})$	R^2
UPR _{1:2}	0.386	0.9807
UPR _{1:3}	0.415	0.9881
UPR _{1:4}	0.345	0.9692
UPR _{1:5}	0.197	0.9819

K_{obs} = Rate Constant; R^2 = Regression Coefficients.

occur, IDT for all the formulations appeared before the $T_d = 10\%$ and ranging between $145^\circ\text{C} - 180^\circ\text{C}$. $T_d = 10\%$ represent the temperature at which 10% weight loss occurs and it is considered to be the polymer decomposition temperature (PDT) [35, 43]; it occurs in the range 186°C to 275°C . Therefore, the data in Table 2 indicate that the thermal stabilities at $T_d = 10\%$ are in the order $\text{UPR}_{1:3} > \text{UPR}_{1:2} > \text{UPR}_{1:4} > \text{UPR}_{1:5}$. The rate of degradation for the $\text{UPR}_{1:3}$ is the most thermally stable formulation which is clearly indicated at $T_d = 10\%$ and $T_d = 20\%$. Moreover, $\text{UPR}_{1:5}$ is the lowest stable formulation in the same range due to no more cross-linking between the polymer matrix and styrene is formed. The maximum polymer degradation temperature (PDT_{max}) corresponds to the temperature at which the maximum rate of weight loss occurred and appeared in the range $400 - 420^\circ\text{C}$. Moreover, it is clearly to say that, as the temperatures for various percentages of weight loss are increased the thermal behaviour for all formulations seems to be the same. On comparison for the $T_d = 40\%$ and $T_d = 50\%$ values of $\text{UPR}_{1:2-1:5}$, it is found that all the formulations have the same thermal stabilities up to 390 & 400°C for $T_d = 40\%$ and $T_d = 50\%$ respectively except, $\text{UPR}_{1:5}$ formulation which has slightly lower stability than the others. That may be attributed to lower degree of curing due to the lower number of double bonds and cross-linking that may present in this formulation which is in agreement with that illustrated in our previous work concerning the gel content and mechanical properties for this formulation [34]. On the other hand, the higher the double bond supplied by maleic anhydride to the polymer structure the higher the styrene content for cross-linking in the final composition. The PDT_{max} increases as the cross-linking process within the photo-fabricated UPR structure increases until $\text{UPR}_{1:3}$ and after this composition, the PDT_{max} decreases as shown in Table 2. This behaviour is associated with the cross-linking density. The highly cross-linked nature of the three dimensional polymer

networks enhances the thermal resistance of the resin at high temperatures [44]. The cross-linked resins, irrespective of the composition of polyester polymer, undergo spontaneous decomposition near 400°C , even in the absence of oxygen. This is a characteristic of all vinyl polymers which are degraded into monomeric units at high temperatures, unlike nonvinyl cross-linked thermosets, such as the phenolic and epoxy resins, which tend to carbonise [45].

Glass transition temperatures (T_g) for all formulations were calculated from the corresponding typical DSC traces as given in Table 2. The dependence of T_g on the cross-linking reaction which in turn depends on the number of double bond within the polymer matrix is shown. The increase of cross-linking reaction shifts the glass transition of different phases to higher temperatures. $\text{UPR}_{1:3}$ have higher T_g due to the higher the cross-linking reaction for higher double bond within the structure. The broad ascending exothermic curves were attributed to thermal degradation because TGA thermograms of these polymers showed a considerable rate of weight loss at the respective temperatures. The DSC curve of each polymer showed a broad exothermic which appeared above 240°C . This exothermic could be attributed to the curing reactions involving the olefinic bonds inside the polymer matrices that may be still present [46].

3.3. Morphology

The morphological features for photo-fabricated $\text{UPR}_{1:2,1:3,1:4,1:5}$ were tested by using scanning electron microscopy. All the formulations have nearly the same morphology features except $\text{UPR}_{1:5}$. The study of the $\text{UPR}_{1:5}$ surface shows that, the surface still contain little oil droplets within the polymer matrix as illustrated in Figure 6a,b with the magnification $X = 5.00\text{K}$ for Figure 6a and with higher magnification $X = 10.00\text{K}$ for Figure 6b. These oil droplets may be attributed to the presence of styrene and uncured polymer matrix which

Table 2: Thermal Properties of Photo-Fabricated $\text{UPR}_{1:2-1:5}$

Polymer Symbol	^a T_g ($^\circ\text{C}$)	^b PDT_{max}	^c Temperature ($^\circ\text{C}$) for various percentage decompositions				
			10%	20%	30%	40%	50%
$\text{UPR}_{1:2}$	38	413	256	342	375	390	400
$\text{UPR}_{1:3}$	44	420	275	348	375	391	400
$\text{UPR}_{1:4}$	39	405	246	339	373	388	398
$\text{UPR}_{1:5}$	42	408	186	257	343	374	390

^aDetermined from DSC curves.

^bDetermined from the derivative of thermogravimetric curves.

^cThe values were determined by TGA at heating rate of $10^\circ\text{C min}^{-1}$.

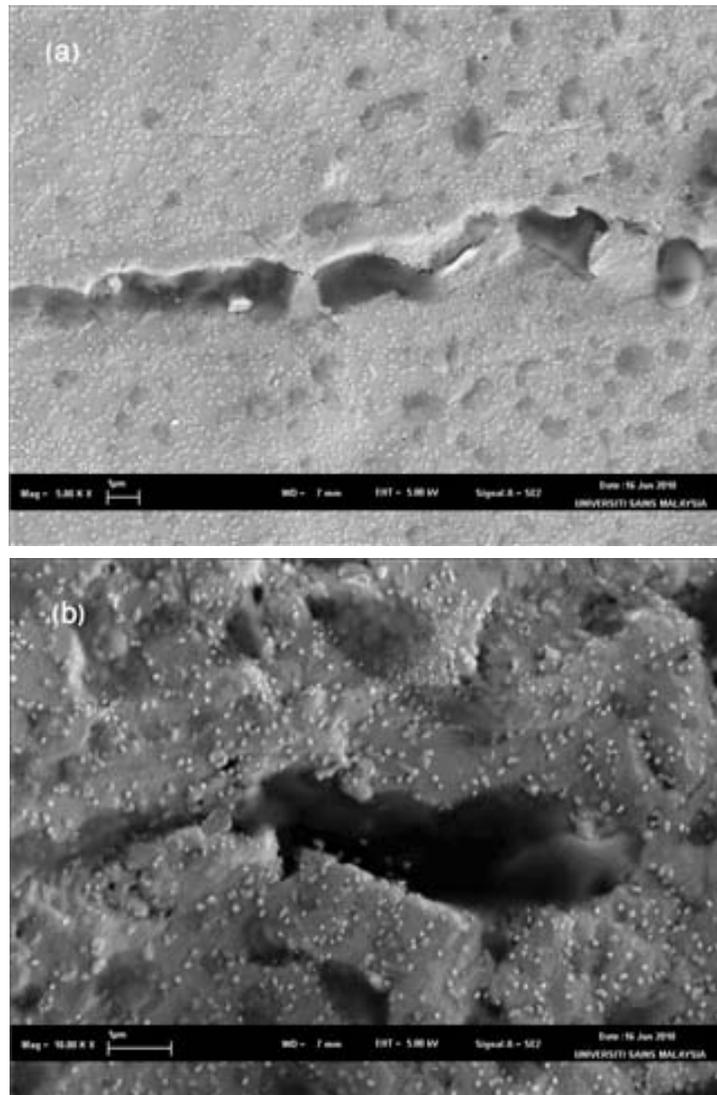


Figure 6: SEM micrographs of photo-fabricated UPR_{1:5} with magnification (a) X = 5.00K and (b) X = 10.00K.

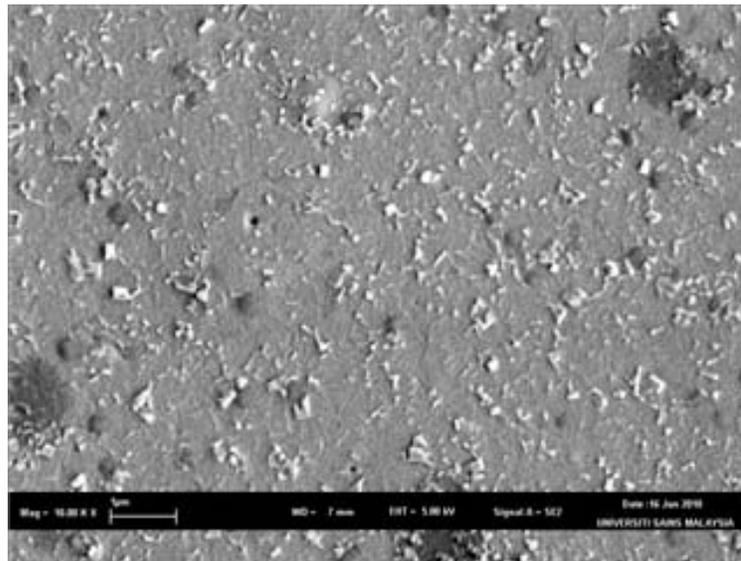


Figure 7: SEM micrograph of photo-fabricated UPR_{1:2} with magnification X = 10.00K.

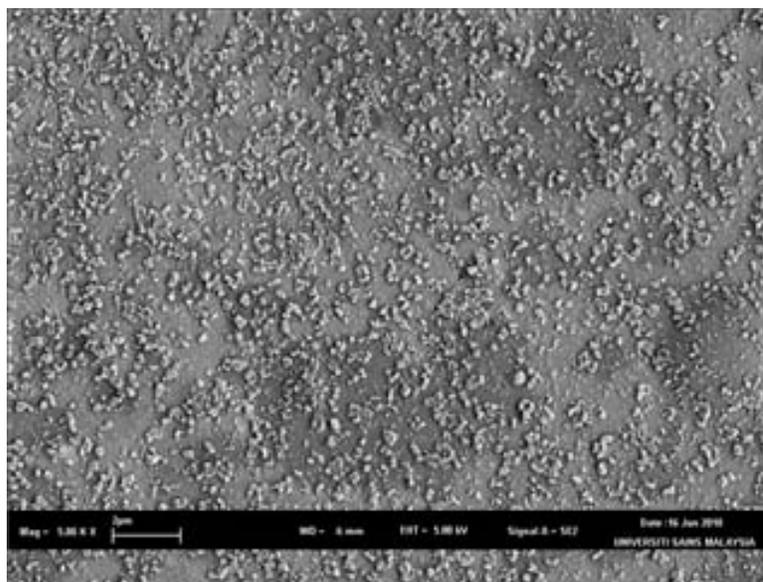


Figure 8: SEM micrograph of photo-fabricated UPR_{1,3} with magnification X = 5.00K.

considered as an evident indicated that, such polymer resin is not fully cured under the same conditions used for all the other formulations. SEM surface features for the other formulations have no oil drops even with the higher magnification as shown in Figure 7 with magnification X = 10.00K and Figure 8 with magnification X = 5.00K for UPR_{1,2} and UPR_{1,3} respectively. This result again, is in agreement with that observed in our previous study for the same formulations concerning the gel fraction, hardness and mechanical properties studies [34].

4. CONCLUSION

UPR_{1:2-1:5}, of variable formulations from ultra-violet curing were obtained in the presence of styrene and IRGACURE 184 as photoinitiator using ¹ST UV machine. The rates of polymerization of UV curable UPR_{1:2-1:5} were determined using real time cure monitoring. UPR_{1:2-1:5} showed pseudo first order kinetic behaviour, while the polymerization kinetics revealed little significant difference between the observed rate constants. The conversion values were levelling off at around 85 – 92 % in the UPR_{1:2-1:4} curable systems. Furthermore, UPR_{1:5} had the lowest conversion value where the conversion value was levelling off at around 65 %. Pseudo first order kinetics for UPR_{1:2-1:5} curable systems were determined. The observed rate constant (K_{obs}) and regression coefficient (R^2) values were calculated. UPR_{1:5} shows the lowest (K_{obs}) value. On the other hand, thermal analyses, and scanning electron microscope studies for photo-fabricated formulations were conducted and the data were discussed. UPR_{1:2-1:5} formulations decomposed in two

stages depended upon the nature of the unsaturated polyesters. The rate of degradation for the UPR_{1,3} showed that it was the most thermally stable formulation. The thermal stabilities at $T_d=10\%$ were in the order of UPR_{1,3} > UPR_{1,2} > UPR_{1,4} > UPR_{1,5}. The glass transition temperature increased as the cross-linking reaction increased.

REFERENCES

- [1] Selley J. Unsaturated polyesters. In: Mark, HF. editor. Encyclopedia of polymer science and engineering; Wiley: New York 1988; vol. 12: pp. 256-90.
- [2] Kramer H. Polyester resin, unsaturated. In: Elvers B, Hawkins S, Schulz G, editors. Ullmann's encyclopedia of industrial chemistry; VCH: Weinheim 1992; vol. A21: pp. 217.
- [3] Bascom WD. Interphase in fibre reinforced composites. In: Lee I, Stuart M, Eds. International encyclopedia of composites; VCH: New York 1990-1991; vol. 2: pp. 411-22.
- [4] Sinha Ray S, Kundu AK, Ghosh M, Maiti S. A new route to synthesize polyamideimide from rosin. Eur Polym J 1985; 21: 131-33.
[http://dx.doi.org/10.1016/0014-3057\(85\)90042-4](http://dx.doi.org/10.1016/0014-3057(85)90042-4)
- [5] Sinha Ray S, Kundu AK, Maiti S. Polymers from renewable resources-13. Polymers from rosin acrylic acid adduct. Eur Polym J 1990; 26: 471-74.
[http://dx.doi.org/10.1016/0014-3057\(90\)90055-9](http://dx.doi.org/10.1016/0014-3057(90)90055-9)
- [6] Sinha Ray S, Kundu AK, Ghosh M, Maiti S. Polymers from renewable resources. II. Synthesis of polyamideimides by triphenylphosphine-polyhalo compound activated polycondensation. J Polym Sci Polym Chem Ed 1986; 24: 603-12.
<http://dx.doi.org/10.1002/pola.1986.080240403>
- [7] Carter C, Finley W, Fry J, Jackson D, Willis L. Palm oil market and future supply. Eur J Lipid Sci Technol 2007; 109: 307-14.
<http://dx.doi.org/10.1002/ejlt.200600256>
- [8] Rozman DH, Tay SG, Abubakar A, Kumar NR. Tensile properties of oil palm empty fruit bunch-polyurethane composites. Eur Polym J 2001; 37: 1759-65.
[http://dx.doi.org/10.1016/S0014-3057\(01\)00063-5](http://dx.doi.org/10.1016/S0014-3057(01)00063-5)

- [9] Ismail H, Jaffri MR, Rozman DH. Oil palm wood flour filled natural rubber composites: fatigue and hysteresis behaviour. *Polym Int* 2000; 49: 618-22. [http://dx.doi.org/10.1002/1097-0126\(200006\)49:6<618::AID-PI418>3.0.CO;2-#](http://dx.doi.org/10.1002/1097-0126(200006)49:6<618::AID-PI418>3.0.CO;2-#)
- [10] Kumar NR, Wei ML, Rozman DH, Abubakar A. Fire resistant sheet moulding composites from hybrid reinforcements of oil palm-fibres and glass fibre. *Int J Polym Mater* 1997; 37: 43-52. <http://dx.doi.org/10.1080/00914039708031476>
- [11] Rushdan I. Chemical composition of alkaline pulps from oil palm empty fruit bunches. *Oil Palm Bull* 2002; 44: 19-24.
- [12] Rozman HD, Rozyanty AR, Tay GS, Kumar, RN. The effect of glycidyl methacrylate treatment of empty fruit bunch (EFB) on the properties of ultra-violet radiation cured EFB-unsaturated polyester composite. *J Appl Polym Sci* 2010; 115: 2677-82. <http://dx.doi.org/10.1002/app.29791>
- [13] Taib RM, Ramarad S, Mohd Ishak ZA, Rozman HD. Effect of immersion time in water on the tensile properties of acetylated steam-exploded acacia mangium fibers-filled polyethylene composites. *J Thermoplas Compo Mat* 2009; 22: 83-98. <http://dx.doi.org/10.1177/0892705708091609>
- [14] Rozman HD, Tay GS. You have full text access to this content. The effects of NCO/OH ratio on propylene oxide-modified oil palm empty fruit bunch-based polyurethane composites. *J Appl Polym Sci* 2008; 110: 3647-54. <http://dx.doi.org/10.1002/app.28881>
- [15] Tay GS, Rozman HD. Swelling properties of chemically modified oil palm empty fruit bunch based polyurethane composites. *J Appl Polym Sci* 2008; 108: 995-1004. <http://dx.doi.org/10.1002/app.28881>
- [16] Rozman HD, Faiza MA, Kumar RN. A preliminary study on ultraviolet radiation-cured biofiber composites from oil palm empty fruit bunch. *Polym Plast Tech and Eng* 2008; 47: 358-62. <http://dx.doi.org/10.1080/03602550801897414>
- [17] Rozman HD, Ahmad Hilme KR, Abubakar A. Polyurethane composites based on oil palm empty fruit bunches: Effect of isocyanate/hydroxyl ratio and chemical modification of empty fruit bunches with toluene diisocyanate and hexamethylene diisocyanate on mechanical properties. *J Appl Polym Sci* 2007; 106: 2290-97. <http://dx.doi.org/10.1002/app.25119>
- [18] Tay GS, Rozman HD. Chemical modification of oil palm empty fruit bunch: Determination of optimum condition and characterization. *J Appl Polym Sci* 2007; 106: 1697-706. <http://dx.doi.org/10.1002/app.26825>
- [19] Davidson RS. Exploring the Science Technology and Applications of UV and EB Curing, SITA Technology: London 1999.
- [20] Decker C. In: Meijer HEH. Ed. *Materials Science and Technology*, VCH Verlag: Weinheim 1997; Vol 18: p. 615.
- [21] Paul P. *Surface coating: science and technology*, 2nd ed., Wiley: New York 1996.
- [22] Crivello VJ, Narayan R, Sternstein SS. Fabrication and mechanical characterization of glass fiber reinforced UV-cured composites from epoxidized vegetable oils. *J Appl Polym Sci* 1997; 64: 2073-87. [http://dx.doi.org/10.1002/\(SICI\)1097-4628\(19970613\)64:11<2073::AID-APP3>3.0.CO;2-G](http://dx.doi.org/10.1002/(SICI)1097-4628(19970613)64:11<2073::AID-APP3>3.0.CO;2-G)
- [23] Voytekunas-Abadie VY, Ng FL. Alternative curing methods for structural epoxy resins. SIMTech Technical Reports 2010; 11: 53-58.
- [24] Kloosterboer JG, Lijten GFCM. Thermal and mechanical analysis of a photopolymerization process. *Polym* 1987; 28: 1149-55. [http://dx.doi.org/10.1016/0032-3861\(87\)90258-8](http://dx.doi.org/10.1016/0032-3861(87)90258-8)
- [25] Hoyle CE, Hensel RD, Grubb MB. Laser-initiated polymerization of a thiol-ene system. *Polym Photochem* 1984; 4: 69-80. <http://dx.doi.org/10.1002/pol.1984.170220808>
- [26] Bowman CN, Peppas NA. Polymers for information storage systems. II. Polymerization kinetics for preparation of highly crosslinked polydimethacrylates. *J Appl Polym Sci* 1991; 42: 2013-18. <http://dx.doi.org/10.1002/app.1991.070420727>
- [27] Kinkelaar M, Lee LJ. Development of a dilatometer and its application to low-shrink unsaturated polyester resins. *J Appl Polym Sci* 1992; 45: 37-50. <http://dx.doi.org/10.1002/app.1992.070450105>
- [28] Nelson EW, Carter TP, Scranton AB. Fluorescence monitoring of cationic photopolymerizations: divinyl ether polymerizations photosensitized by anthracene derivatives. *Macromole* 1994; 27: 1013-19. <http://dx.doi.org/10.1021/ma00082a020>
- [29] Decker C, Decker D. Photoinitiated Polymerization of Vinyl Ether and Acrylate Monomer Mixtures. *J Macromol Sci – Pure Appl Chem* 1997; A34: 605-25. <http://dx.doi.org/10.1080/10601329708014988>
- [30] Yang DB. Direct Kinetic Measurements of Vinyl Polymerization on Metal and Silicon Surfaces Using Real-Time FT-IR Spectroscopy. *Appl Spectro* 1993; 47: 1425-1429. <http://dx.doi.org/10.1366/0003702934067739>
- [31] a) Crivello JV, Yang B, Kim WG. Chemosselective hydrosilylations. I. Synthesis and photopolymerization of 1-propenyl ether functionalized siloxanes. *J Polym Chem Part A: Polym Chem* 1995; 33: 2415-23; b) Crivello JV, Yang B, Kim WG. Synthesis and electron-beam polymerization of 1-propenyl ether functional siloxanes. *J Macromol Sci Part A, Pure Appl Chem* 1996; 33: 399-415. <http://dx.doi.org/10.1002/pola.1995.080331414>
- [32] Grundert F, Wolf BA. In: *Polymer Handbook*. Brandrup J, Immergut EH, Eds. Wiley: New York 1989; p. VII/173.
- [33] Perrin DD, Armarigo WLF, Perrin DF. *Purification of laboratory chemicals*. 2nd ed. Pergamon: New York 1980.
- [34] Mahmoud AH, Tay GS, Rozman HD. A Preliminary Study on Ultraviolet Radiation-Cured Unsaturated Polyester Resin Based on Palm Oil. *Polym Plast Tech Eng* 2011; 50: 573-80. <http://dx.doi.org/10.1080/03602559.2010.543740>
- [35] Al-Muaikel NS, Aly KI, Hussein MA. Synthesis, characterization and antimicrobial properties of new poly(ether-ketone)s and copoly(ether-ketone)s containing diaryliidenecycloalkane moieties in the main chain. *J Appl Polym Sci* 2008; 108: 3138-47. <http://dx.doi.org/10.1002/app.27963>
- [36] Decker C. Kinetic Study and New Applications of UV Radiation Curing, *Macromolecular Rapid Commun* 2003; 23: 1067-93. <http://dx.doi.org/10.1002/marc.200290014>
- [37] Decker C, Bianchi C, Decker D, Morel F. Photoinitiated polymerization of vinyl ether-based systems. *Progress in Organic Coatings* 2001; 42: 253-66. [http://dx.doi.org/10.1016/S0300-9440\(01\)00203-X](http://dx.doi.org/10.1016/S0300-9440(01)00203-X)
- [38] Mijovic J, Kenny J, Maffezzoli A, Trivisano A, Bellucci F, Nicolais L. The principles of dielectric measurements for in situ monitoring of composite processing. *Compos Sci Technol* 1993; 49: 277. [http://dx.doi.org/10.1016/0266-3538\(93\)90109-T](http://dx.doi.org/10.1016/0266-3538(93)90109-T)
- [39] Abd-Alla MA, Aly KI Hammam AS. Arylidene Polymers IV. Synthesis, Characterization and Morphology of New Polyesters of Diaryliidenecyclohexanone. *High Perform Polym* 1989; 1: 223-37.
- [40] Abd-Alla MA, Aly KI. Arylidene Polymers-X. Preparation and Properties of New Polyesters of Diaryliidenecycloalkanes

- Containing Symmetrical Bis-Azomethine Groups in the Polymer Backbone High Perform Polym 1990; 2: 181-88.
- [41] Bansal RK, Mittal J, Singh P. Thermal stability and degradation studies of polyester resins. *J Appl Polym Sci* 1989; 37: 1901-908.
<http://dx.doi.org/10.1002/app.1989.070370713>
- [42] Al-Muaikel NS. Synthesis and characterization of new unsaturated polyesters and copolyesters containing azo groups in the main chain. *Eur Polym J* 2003; 39: 1025-33.
[http://dx.doi.org/10.1016/S0014-3057\(02\)00304-X](http://dx.doi.org/10.1016/S0014-3057(02)00304-X)
- [43] Aly KI, Abbady MA, Mahgoub SA, Hussein MA. New polymer syntheses, Part 44: Synthesis, characterization, and corrosion inhibition behavior of new polyurea derivatives based on diaryl ether in the polymers backbone. *J Appl Polym Sci* 2009; 112: 620-28.
<http://dx.doi.org/10.1002/app.29106>
- [44] Sancheza EMS, Zavagliaa CAC, Felisberti MI. Unsaturated polyester resins: influence of the styrene concentration on the miscibility and mechanical properties. *Polym* 2000; 41: 765-69.
[http://dx.doi.org/10.1016/S0032-3861\(99\)00184-6](http://dx.doi.org/10.1016/S0032-3861(99)00184-6)
- [45] Paul DR, Barlow JW, Keskkula, H. *Encyclopedia of polymer science and engineering*. Wiley: New York 1986.
- [46] Mikroyannidis JA. New styrylpyridine-based polyesters and polyurethanes. *Eur Polym J* 1988; 24: 1093-99.
[http://dx.doi.org/10.1016/0014-3057\(88\)90070-5](http://dx.doi.org/10.1016/0014-3057(88)90070-5)

Received on 20-08-2012

Accepted on 06-10-2012

Published on 31-10-2012

DOI: <http://dx.doi.org/10.6000/1929-5995.2012.01.01.5>