

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)**ScienceDirect**

Procedia Chemistry 16 (2015) 495 – 502

**Procedia**  
Chemistry

International Symposium on Applied Chemistry 2015 (ISAC 2015)

# Synthesis of 1,4-butanediol monooleate and 1,4-butanediol, 9-hydroxy-10-methoxy-monostearate from Palm Oil as Modifier of Epoxy Resin for Coating

Evi Triwulandari, Muhammad Ghozali, and Yenny Meliana

Research Center for Chemistry, Indonesian Institute of Science  
Kawasan Puspiptek, Serpong 15314, Indonesia  
Tel. (+62217560929); Fax. (+62217560549); Email: [evi.triwulandari69@gmail.com](mailto:evi.triwulandari69@gmail.com)

## Abstract

1,4-butanediol monooleate (BMO) and 1,4-butanediol,9-hydroxy-10-methoxy-monostearate (BHMMS) were synthesized. BMO was synthesized via Fisher Esterification between oleic acid from palm oil and 1,4-butanediol by using sulfuric acid as catalyst. Furthermore, BMO product was used as raw material for synthesis of BHMMS. BHMMS was synthesis via continuous two-step reaction i.e. epoxidation and hydroxylation. Characterizations of BMO and BHMMS products were conducted by analysis of ester number, acid number, iodine number and FTIR. In this research, obtained product of BMO and BHMMS were used as modifier of epoxy by reacting with epoxy and tolonate to produce polyurethane modified epoxy (PME) based on BMO (PMEBMO) and BHMMS (PMEBHMMS) from palm oil. Characterization of PME was conducted by determine residual isocyanate to calculate the isocyanate conversion and FTIR analysis. Curing process of PME products to obtain film sheets were done by adding versamid 140 as hardener. Characterizations of film sheets were conducted by determine of mechanical properties such as tensile strength and elongation at break. The result showed that mechanical properties of PME were higher than the mechanical properties of unmodified epoxy.

Keywords: epoxy, polyurethane, palm oil, BMO, BHMMS, modification

---

\* Corresponding author. Tel.: +62217560929; fax: +62217560549.  
E-mail address: [evit003@lipi.go.id](mailto:evit003@lipi.go.id)

## 1. Introduction

Corrosion is one of the important issues that led to the depreciation of goods investment. Corrosion on metal can cause great loss. One method for corrosion prevention which is commonly used is coat the metal with a coating material [1,2]. The coating material requires characteristics like ability to inhibit corrosion and resist to weather, ultraviolet light, other light components, heat and chemical. In conventional ways, the coating materials based on organic resin that commonly used are epoxy and polyurethane [3]. Epoxy and polyurethane as material for coating have some advantages and limitations. Epoxy has characteristics such as a good corrosion barrier and a durable and adhesive material. However its properties has some limitations such as brittleness, low impact strength, low elongation at break and chalking. Polyurethane has the features in good appearance, durability and weather ability but it has limitations of moisture sensitive and health hazard (isocyanate) [4-6]. In order to eliminate the limitations of each resin and to combine the durability and hardness of them, this research studies about modification of epoxy with polyurethane which is expected to improve the coating performance.

In general, the polyols used in the manufacture of polyurethanes have been derived from petrochemical derivatives. The demands for petrochemical are increasing but supplies are even more decreasing so that the research of alternative renewable natural resource that can replace petrochemicals needs to be done to produce polyols. Palm oil is one of renewable natural resource that can be used as a raw material for the manufacture of polyols. In their chemical composition, palm oil contains a fatty acid or unsaturated triglycerides (double bond) which can be converted into more reactive groups that is a hydroxyl group [7].

Utilization of vegetable oil for coating applications has been developed [8-12]. Vegetable oil has unique structures which contain unsaturated bond, epoxy, hydroxyl, ether and other functional groups. Therefore the vegetable oil has the opportunity to be chemically transformed into a polymer material with low molecular weight polymeric materials, for example for some alkyds, polyesteramides, polyeteramida, polyurethane, epoxy and polyol that can be applied as a coating material [8]. Specifically for the development of polyurethane for coating from polyol based on vegetable oil was conducted by Sharmin et. al., and Akram et al, using linseed oil and Alam, et. al, using corn oil [9-11]. Therefore, in this study the modification process of epoxy with polyurethane for coating application were done by using the palm oil-based polyols. In this study two kind of palm oil-based polyols e.i 1,4-butanediol monooleate (BMO) and 1,4-butanediol,9-hydroxy-10-methoxy-monostearate (BHMMS) were synthesized. BMO was obtained from esterification of 1,4-butanediol and oleic acid, while BHMMS was obtained from epoxidation and hydroxylation of BMO. Study about the ability of both polyol for polyurethane as modifier of epoxy has been conducted.

## 2. Experiment

### 2.1 Materials

Epoxy diglycidyl ether bisphenol A (epoxy YD 128) with Epoxy Equivalent Weight (EEW) = 185,54 from PT. Sigma Utama, oleic acid (Brataco), 1,4-butanediol (Merck), n-heksana (Merck), acetic acid glacial (Merck), chloroform (Merck), sulfuric acid ( $H_2SO_4$ ) 96% and 50% (Merck), aquadest, methanol (Merck), peroxide acid 35% (Merck), tolonate (from PT. Sigma Utama), versamide 140 as curing agent (from PT. Sigma Utama), potassium Hydroxide (KOH) (Merck), Hydrochloric Acid (HCl) (Merck), potassium iodide (Merck), sodium hydroxide (Merck).

### 2.2. Synthesis of 1,4-butanediolmonooleate (BMO)

Oleic acid (1 mol) was placed in three-necked flask equipped with a thermometer, dean-stark, condenser and magnetic stirrer. Oleic acid was stirred and heated until the temperature of  $140^{\circ}C$ . After these temperature were reached, oleic acid was added with 1,4-butanediol (1 mol) and sulfuric acid (1% from total weight of oleic acid and 1,4-butanediol) and heating was continued for 6 hours. The mixture was washed with aquadest and sodium chloride solution until pH 7 was reached. The organic solution was separated from water phase and then evaporated. The product was characterized by determine acid number (Indonesian National Standard/SNI 01-355-1998), iodine number (Wijs Solution Method, SNI 01-2902-1992), ester number (SNI 01-355-1998). The product were also characterized by analyzing their functional groups using FTIR (IR Prestige-21 SHIMADZU).

### 2.3. Synthesis of 1,4-butanediol,9-hydroxy-10-methoxy-monostearate (BHMMS)

BMO was placed in three-necked flask equipped with thermometer, reflux condenser, and magnetic stirrer and dissolved with hexane. Then glacial acetic acid (1 mol to BMO mol) and 50% sulfuric acid was added into the system and heated until 50°C. Before the temperature reached 50°C, the mixture was added with methanol and after the temperature reached 50°C added with 35% H<sub>2</sub>O<sub>2</sub> slowly. The heating was continued at 65°C for 2 hours. The obtained product was washed with aquadest and NaCl until pH 5 was reached. The organic solution was separated from water phase and then evaporated. The obtained product was characterized by analysis of iodine number (Wijs Solution Method, SNI 01-2902-1992) and functional groups using FTIR (IR Prestige-21 SHIMADZU).

### 2.4. Synthesis of Polyurethane Modified Epoxy Based on 1,4-butanediolmonooleate (BMO) and hydroxyl-methoxy-1,4-butanediol,9-hydroxy-10-methoxy-monostearate (BHMMS).

Polyurethane modified epoxy based on BMO and BHMMS was synthesized by reacting BMO or BHMMS, tolonate (1 mole of tolonate per mole of BMO or BHMMS), epoxy (The total weight of BMO or BHMMS and tolonate was 10% to the epoxy) and 0,1% dibutyltin dilaurate as catalyst in the three-neck flask simultaneously. The reaction was conducted at 50°C for 30 minutes.

### 2.5 Characterization

Characterization of the polyurethane modified epoxy products were conducted by using FTIR analysis (IRPrestige-21 Shimadzu) and free isocyanate (%NCO). Then the polyurethane modified epoxy products was cured by using versamid 140 as curing agent with the composition 0.5 w/w relative to the polyurethane modified epoxy mixture in order to obtain film sheet. The mechanical properties of film sheet were analysis to determine the tensile strength and elongation at break properties using Universal Testing Machine, Orientec Co. Ltd, Model UCT-5T.

## 3. Results and Discussion

### 3.1 Synthesis of 1,4-butanediolmonooleate (BMO)

BMO was synthesis via Fisher Esterification between oleic acid from palm oil and 1,4-butanediol by using sulfuric acid as catalyst. The reaction of synthesis BMO is presented by Fig. 1.

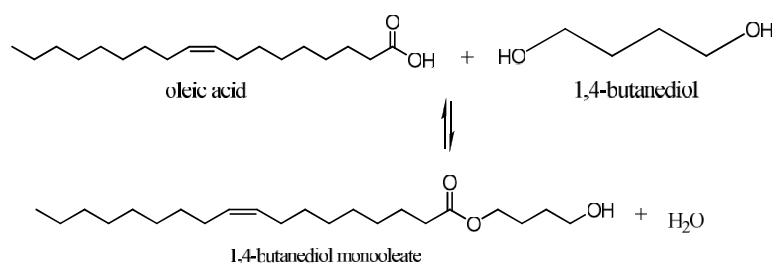


Figure 1. Esterification reaction between 1,4-butanediol and oleic acid

Characterization of ester product was carried out by analysis of acid number, ester number and FTIR. Table 1 showed that the acid number of BMO is lower than acid number of oleic acid with acid number conversion is 72.33%. This data showed that the carboxylic functional group of oleic acid has been successfully converted into ester group and supported by ester number of 1,4-butanediol monooleate about 78.23 g HCl/Sample.

Table 1. Acid Number and Ester Number of Oleic Acid and 1,4-butanediol monooleate

Sample	Acid Number (g KOH/g sample)	Acid Number conversion (%)	Ester number (g HCl/sample)
Oleic acid	208.718		-
1,4-butanediolmonooleat (BMO)	57.75	72.33%	78.23

Qualitative analysis of BMO was conducted by using FTIR analysis. The FTIR spectra of oleic acid and ester product are presented in Fig. 2. From the spectra of ester product there were some new absorption bands that different with the spectra of oleic acid. The new absorption band in wave number  $3462\text{ cm}^{-1}$  represent the O-H stretching vibration from 1,4-butanediol. The ester linkage in the BMO is shown by absorption band in wave number  $1153\text{ cm}^{-1}$  which represent  $\text{-C-O-C-}$  bond and shifted of absorption band of carbonyl ( $\text{-C=O}$ ) from oleic acid at  $1708\text{ cm}^{-1}$  to  $1743\text{ cm}^{-1}$  in the BMO. This data showed that reaction between carboxyl ( $\text{-O-C=O}$ ) functional group of oleic acid and hydroxyl functional group of 1,4-butanediol successfully produced ester compound 1,4-butanediol monooleate.

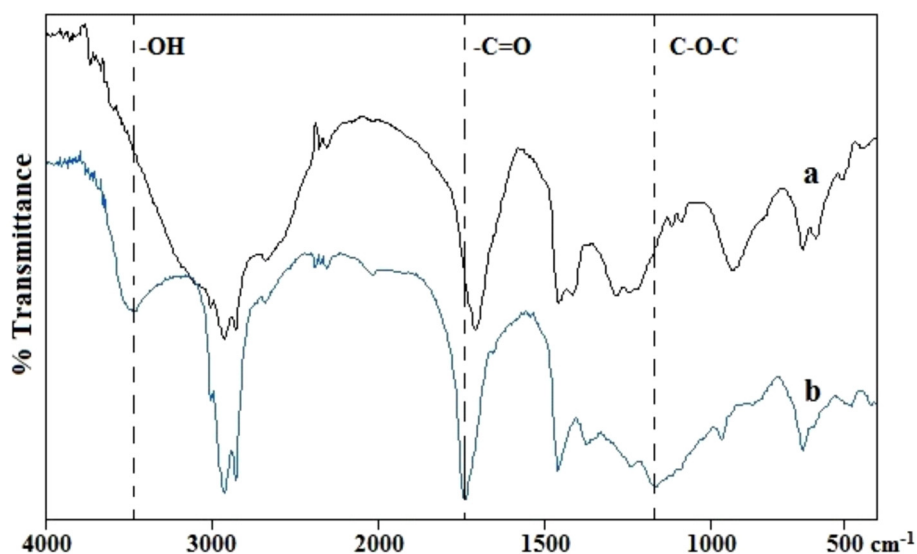


Figure 2. FTIR Spectra of Oleic Acid (a) and 1,4-butanediol monooleate (b)

### 3.2 Synthesis of 1,4-butanediol, 9-hydroxy-10-methoxy-monostearate(BHMMS)

BMO is unsaturated ester compound which has one hydroxyl functional group in its structure. This compound can react with isocyanate to produce one urethane linkage, because of has one hydroxyl functional group. In order to increase the amount of urethane linkage so in this case necessary to increase the number of hydroxyl group. The addition of hydroxyl groups on the ester compound of BMO can be done by converted its unsaturated  $\text{C=C}$  bond into hydroxyl groups. Converted of unsaturated  $\text{C=C}$  bond in the BMO into hydroxyl group in the BHMMS was carried out via continuous two-step reaction i.e. epoxidation and hydroxylation of BMO. The reaction equation of continuous two-step reaction epoxidation and hydroxylation of BMO was shown in the Figure 3:

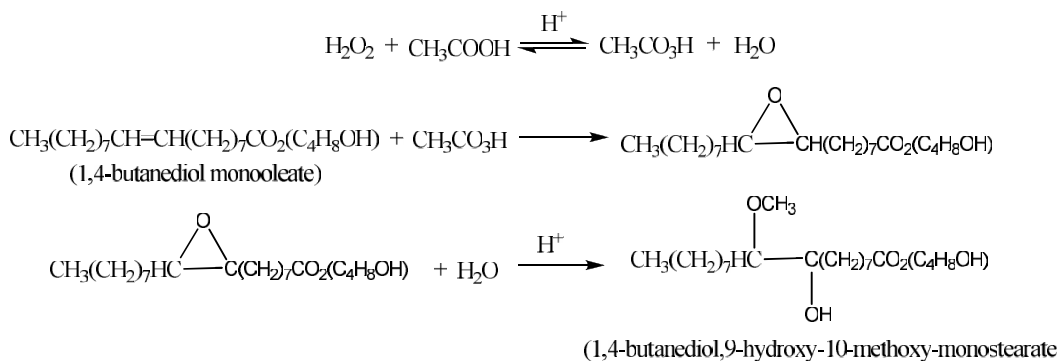


Figure 3. The reaction equation of continuous two-step reaction epoxidation and hydroxylation of BMO

Quantitative analysis of epoxidation and hydroxylation product of BMO was conducted by analysis of iodine value. Determination of iodine value is used to determine the quantities of unsaturation in fatty acids and its derivative. Iodine value shows the mass of iodine (gram) that is consumed by 100 grams of chemical substance. Iodine value of BMO and BHMMS is presented in Table 2. According to this data can be known that after epoxidation and hydroxylation, the iodine number of BMO is decreased. This data showed that unsaturated C=C bond of BMO has been converted into saturated bond in BHMMS compound with conversion 82.16%.

Table 2. Iodin Value of 1,4-butanediol monooleate and 1,4-butanediol monostearate

Sample	Iodine value (g KI/g sample)	Conversion (%)
1,4-butanediol monooleate	75.99	
1,4-butanediol,9-hydroxy-10-methoxy-monostearate	14.55	82.16

Furthermore as support data, structure analysis of epoxidation and hydroxylation product of BMO has been conducted by using FTIR analysis. FTIR Spectra of BMO and BHMMS (epoxidation and hydroxylation product of BMO) are presented in Fig. 4. Significant difference between FTIR spectra of and BHMMS is indicated by the appearance of a sharper broad band of O-H stretching vibration uptake in the wave number at  $3334 \text{ cm}^{-1}$  from the product of BHMMS. The existence of an OH group on the product alleged that the hydroxylation process has occurred. Furthermore, other information which indicates that the hydroxylation has been taken place is a loss of absorption band at  $3003 \text{ cm}^{-1}$  from the  $-\text{C}=\text{C}$ -unsaturated bond. This is indicates that the double bond in BMO has been converted into hydroxyl groups in the BHMMS.

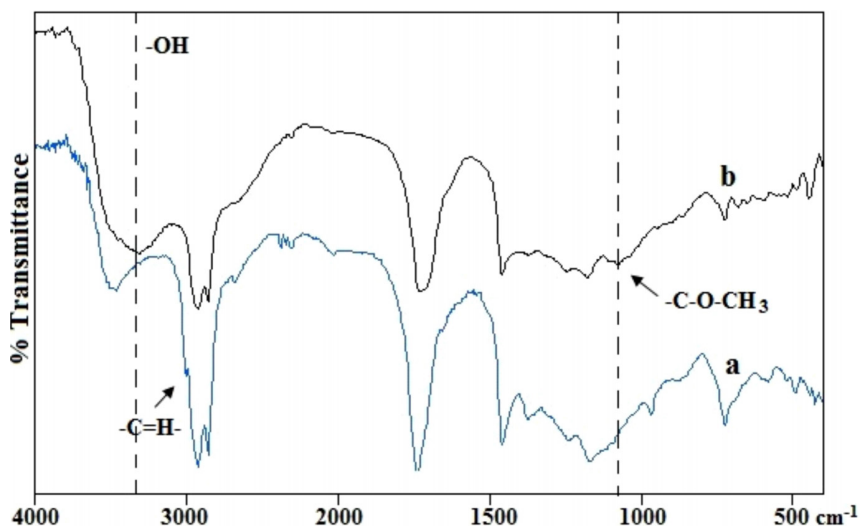


Figure 4. FTIR Spectra of 1,4-butanediol monooleate before (a) and after (b) epoxidation and hydroxylation

### 3.2. Synthesis of Polyurethane Modified Epoxy Based on 1,4-butanediolmonooleate (PMEBMO) and 1,4-butanediol,9-hydroxy-10-methoxy-monostearate (PMEBHMS).

Modification of epoxy with polyurethane based on BMO and BHMMS was conducted by reacted epoxy, tolonate, BMO or BHMMS simultaneously in one step. Epoxy, BMO and BHMMS have hydroxyl group in its structure. This hydroxyl group can react with tolonate to produce urethane linkage. Table. 3 showed the isocyanate content of polyurethane modified epoxy product based on BMO and HMBS. Isocyanate content of polyurethane modified epoxy product indicates the free isocyanate group of tolonate which is not reacted with hydroxyl group of epoxy, BMO or BHMMS. According to Table 3 can be known that isocyanate content of tolonate is decreased after reacted with epoxy and BMO or BHMMS. This indicates that tolonate has reacted with epoxy, BMO or BHMMS. The isocyanate conversion of PMEBHMS product is lower than isocyanate conversion of PMEBMO product. Because of PMEHBM is modified epoxy from BHMMS compound which is the result of the epoxidation and hydroxylation reaction of BMO hence there are additional molecules in structure of BHMMS. The molecule which is added into BHMMS are hydroxyl group (-OH) and methoxy group (-OCH<sub>3</sub>). With the addition of this molecule is allegedly caused the steric hindrance that can inhibit the reaction.

Table. 3. Isocyanate Content of Polyurethane Modified Epoxy Product from 1,4-butanediol monooleate (BMO) and 1,4-butanediol, 9-hydroxy-10-methoxy-monostearate (BHMMS).

Sample	Isocyanate Content (%)	Conversion (%)
Tolonate	31.62	-
Polyurethane modified epoxy based on BMO (PMEBMO)	4.68	85.19
Polyurethane modified epoxy based on BHMMS (PMEBHMS)	20.31	35.76

Figure 5 and 6 presents the FTIR spectra of polyurethane modified epoxy from BMO and BHMMS. FTIR analysis was employed to confirm possible chemical reactions which occur between epoxy, tolonate and BMO or BHMMS. In the FTIR spectra of PMEBMO and PMEBHMS showed the intensity of hydroxyl group peak was decreased, the absorption band from carbonyl group was shifted and there were new

absorption band at wave number  $1689\text{ cm}^{-1}$ . These data implies the formation of urethane linkage (HN-COO-) between hydroxyl group (from epoxy and BMO or BHMMS) and isocyanate group (from tolonate) was occurring. For the figure 6, spectra of polyurethane modified epoxy from BHMMS there were absorption peak at wave number  $2200\text{ cm}^{-1}$  from  $\text{N}=\text{C}=\text{O}$  free of isocyanate. It is showed that isocyanate was not reacted perfectly as shown data by isocyanate content above.

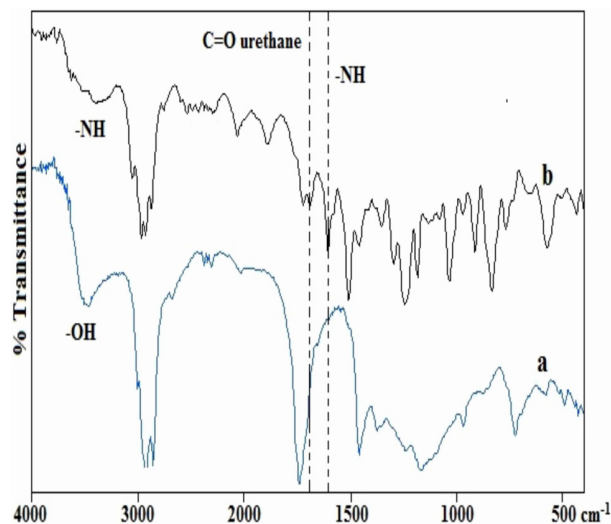


Figure 5. FTIR spectra of BMO (a) and polyurethane modified epoxy from BMO (b)

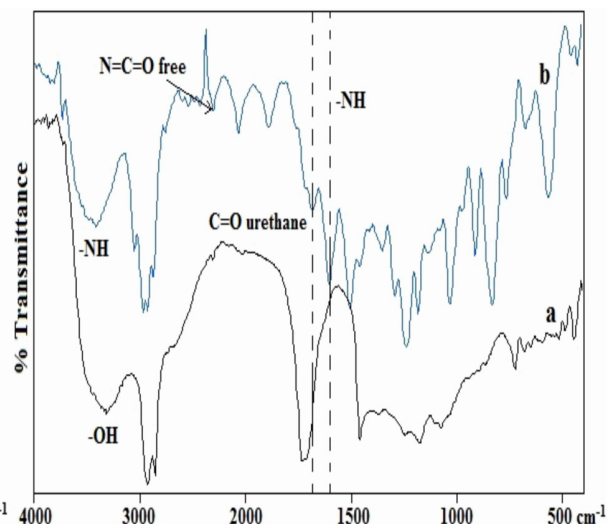


Figure 6. FTIR spectra of BHMMS (a) and polyurethane modified epoxy from BHMMS (b)

The mechanical properties of PMEBMO and PMEBHMMS was characterize by analysis of tensile strength and elongation at break. Before analysis, PMEBMO and PMEBHMMS were reacted with versamide as curing agent to get film form. The Table 4 shown the tensile strength and elongation at break data of PMEBMO and PMEBHMMS film. The tensile strength and elongation at break value of polyurethane modified epoxy were higher than unmodified epoxy. This is due to the addition of polyurethane based on BMO and BHMMS enhance the cross-link density of epoxy resin.

Table 4. Mechanical Properties of PMEBMO and PMEBHMMS Film

Sample	Tensile Strength (MPa)	Elongation at break (%)
Epoxy -OH	6.82	1.88
Polyurethane Modified Epoxy Based on 1,4-butanediol monooleate	10.59	1.75
Polyurethane Modified Epoxy Based on 1,4-butanediol,9-hydroxy-10-methoxy-monostearate	12.23	2.17

## Conclusion

1,4-butanediol monooleat was successfully synthesized via Fisher esterification and confirmed by FTIR, ester number and acid number. Furthermore epoxidation and hydroxylation of 1,4-butanediol monooleate was successfully conducted to produce 1,4-butanediol,9-hydroxy-10-methoxy-monostearate and confirmed by FTIR and

iod number. Modification of epoxy by using polyurethane based on 1,4-butanediol monooleat and 1,4-butanediol,9-hydroxy-10-methoxy-monostearate increased the tensile strength and elongation at break properties of epoxy.

### Acknowledgments

This work has been financially supported by Program Riset Unggulan LIPI 2015. Author also gratefully acknowledge to Herlan Herdiawan and Izhar Ibrahim for their help during this work.

### References

- [1]. Ahmad S, Zafar F, Sharmin E, Garg N, Kashif M. Synthesis and characterization of corrosion protective polyurethanefattyamide/silica hybrid coating material. *Prog. Org.Coat.* 2012: 73: 112– 117
- [2]. Sarmiento V.H.V, Schiavetto M.G, Hammer P, Benedetti A.V, Fugivara C.S, Suegama P.H, Pulcinelli S.H, Santilli C.V, Corrosion protection of stainless steel by polysiloxane hybrid coatings prepared using the sol–gel process. *Surf. Coat. Technol.* 2010: 204: 2689–2701
- [3]. Díaz I, Chico B, de la Fuente D, Simancas J, Vega J.M, Morcillo M, Corrosion resistance of new epoxy–siloxane hybrid coatings. A laboratory study. *Prog. Org.Coat.* 2010: 69: 278–286
- [4]. Prabu A. A, Alaga M, Mechanical and thermal studies of intercross-linked networks based on siliconized polyurethane-epoxy/unsaturated polyester coatings. *Prog. Org.Coat.* 2004: 49: 236–243
- [5]. Kostrzewa M, Modification of Epoxy Resin with Polyurethane and Montmorillonite, Tomas Bata University in Zlin, Faculty of Technology. *Doctoral Thesis.* 2011
- [6]. Shaorong Lu, Jianfeng Ban, Chunhe Yu, and Weixing Deng, Properties of Epoxy Resins Modified with Liquid Crystalline Polyurethane, *Iran Poly J.* 2010: 19 (9): 669-678
- [7]. Azlan A, Prasad K. N, Khoo H. E, Abdul-Aziz N, Mohamad A, Ismail A, and Amom Z. Comparison of fatty acids, vitamin E and physicochemical properties of Canarium odontophyllum Miq. (dabai), olive and palmoils. *J. Food Compos. Anal.* 2010: 23(8) : 772-776
- [8]. Alam M, Ahmad S, Akram D, Sharmin E, Zafar F. Vegetable oil based Eco- friendly coating materials: A review article. *Arab J.Chem.*, 2014;7: 469–479
- [9]. Sharmin E, Zafar F, Akram D, Ahmad S. Plant oil polyol nanocomposite for antibacterial polyurethane coating, 2013: 76: 541– 547
- [10]. Akram D, Sharmin E., Ahmad S. Linseed polyurethane/tetraethoxyorthosilane/fumed silica hybrid nanocomposite coatings: Physico-mechanical and potentiodynamic polarization measurements studies. *Progr Org Coat.* 2014: 77: 957–964
- [11]. Alam M, Alandis N.M. Corn oil based poly(ether amide urethane) coating material—Synthesis, characterization and coating properties. *Industrial Crops and Products.* 2014: 57: 17–28
- [12]. Kong X, Liu G, Qi H, Curtis J.M, Preparation and characterization of high-solid polyurethane coating systems based on vegetable oil derived polyols. *Prog Org.Coat.* 2013: 76 : 1151–1160