Mechanical and Thermal Properties of Hybrid Coating Products from Polyurethane and/or Polysiloxane Modified Epoxy Based on Acrylic Polyol and Tolonate

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Abstract. Hybrid coating products were synthesized from polyurethane and/or polysiloxane modified epoxy based on acrylic polyol and tolonate. Hybrid coating which synthesized were epoxy-polyurethane, epoxy-polysiloxane and epoxy-polyurethane-polysiloxane. Hybrid coating from epoxy-polyurethane was synthesized by reacting epoxy, acrylic polyol and tolonate. The second hybrid coating from epoxy-polysiloxane was synthesized by reacting epoxy and polysiloxane by using γ-aminopropyl triethoxysilane (γ-APS) as cross-linking agents. And the third hybrid coating from epoxy-polyurethane-polysiloxane was synthesized by reacting epoxy with monomer constituent of polyurethane and polysiloxane via simultaneous reaction. Characterizations of hybrid coating products were using FTIR and 1H-NMR spectroscopy. Curing process of hybrid coating products to obtain film sheets were done by adding versamid 140 as hardener. Characterizations of film sheets were conducted by determination of mechanical properties such as tensile strength and elongation at break and thermal properties by using thermogravimetric analysis (TGA). The mechanical and thermal properties of hybrid coating products have been compared with the unmodified epoxy. Mechanical properties of epoxy-polyurethane and epoxy-polyurethane-polysiloxane hybrid coating were higher than the mechanical properties of unmodified epoxy. The highest thermal property was shown by the epoxy-siloxane hybrid coating thermogram.

Keywords: Hybrid coating; epoxy; polyurethane; polysiloxane; acrylic polyol; tolonate

Introduction

Epoxy and polyurethane are binders that usually used in the formulation of protective coating. Epoxy and polyurethane are used as multilayer in paint system, whether epoxy usually as primer or intermediate coat and polyurethane as the top coat [1,2]. Although epoxy has good mechanical properties and chemical resistant but it has some weakness. The weaknesses of epoxy are brittle, low impact strength and low elongation at break so it has limitation when applied for high performance applications [3-5]. Several researches about modified epoxy had been done to improve the characteristic of epoxy. One of the methods for modification of epoxy is by reacting epoxy with another polymer (binder) and/or inorganic material to produce hybrid coating. Hybrid coating is a new technology in coating method. This technology develops a new binder system by combining two binders or more that have different properties to improve their characteristic as a coating for corrosion protection [3,6,7]. Polyurethane resin that usually used as the top coat in paint system can be used as modifier of epoxy resin because it has excellent properties. When the epoxy resin was modified with polyurethane it produces a new resin system, the process application of this coating can be done only using one layer and not multilayer again [3-5, 8-10]. It has been reported that modification of epoxy using polyurethane improved the toughness of epoxy, for example thermal resistant and mechanical property [4].

Modification of epoxy resin via organic-inorganic hybrid coating concept has also been studied. Modification of organic resin with polysiloxane has generally been recognized as a new class of high-performance coatings. Siloxane is an inorganic system, it is more resistant in degradation mechanism, and it is also based on that structure consists of a silicone resin with a stable polysiloxane backbone [- (Si-O) n-Si-]. The chemical bonding of Si-O is stronger than C-C chemical bond of the organic coating structure, where the strength of Si-O bond is 108 kcal / mole and the strength of C-C bond is 83 kcal / mole. It requires large energy to break the Si-O bonds therefore coating based on siloxane will have excellent properties such as thermal stability, weather and UV resistance, durability and chemical attack [1,11].

Epoxy-siloxane hybrid is a kind of organic-inorganic hybrid coating that has been studied and commercialized. This new resin combines the properties of epoxy as organic polymer and siloxane as inorganic polymer. It has been reported that epoxy-siloxane hybrid have anticorrosive performance in acid, saline and organic solvent environments in general and in alkaline environments [1, 11-15]. Another research about hybrid coating also has been reported by modified epoxy with other organic polymer and siloxane. Polyurethane is an organic polymer that can be used in modified epoxy with siloxane to produce hybdrid coating [3, 16]. Polyurethane is widely used as a coating material because it has excellent mechanical, physical and abrasion resistant properties. The addition of polyurethane in the process of modified epoxy with siloxane resin can improve the properties of the resulting resin respectively. It has been reported that the mechanical and thermal properties modified epoxy-polyurethane-siloxane hybrid coating increase [3, 4, 17]. Several researches about synthesis of hybrid coating based on epoxy-polyurethane-siloxane are still limited and it needs further studies especially by using other constituent monomer of polyurethane. Different kind of constituent monomer will affect the properties and characteristic of polyurethane resin. The scope of this research is synthesis hybrid coating from polyurethane and/or polysiloxane modified epoxy by using acrylic polyol and tolonate as the constituent monomer of polyurethane. Comparison properties and characteristic between unmodified epoxy, epoxy-polyurethane, epoxy-polysiloxane and epoxy-polyurethane-siloxane hybrid coating also have been studied.

Experimental

Materials

Epoxy diglycidyl ether bisphenol A (epoxy YD 128 with Epoxy Equivalent Weight (EEW) = 180-190), acrylic polyol (Evercryl 2901 with a hydroxyl number = 47.28 mgKOH / g), Tolonate HDT (% NCO = 31.6155%), versamid 140 (curing agent), hydroxyl terminated polydimethylsiloxane (HTPDMS, Aldrich), γ-aminopropyl triethoxysilane (γ –APS, Merck).

Synthesis of Epoxy-Polyurethane Hybrid Coating (Polyurethane Modified Epoxy)

Epoxy-polyurethane hybrid coating was synthesized by reacting epoxy, acrylic polyols, and tolonate in the three-neck flask simultaneously. The ratio of NCO/OH of tolonate and acrylic polyol as the components of polyurethane used in this research is 2.5. The total weight of acrylic polyol and tolonate was 20% relative to the epoxy. The reaction was conducted at 50^{o}C for 30 min.

Synthesis of Epoxy- Polysiloxane hybrid coating

Epoxy-polysiloxane hybrid coating was synthesized by reacting epoxy with hydroxyl terminated HTPDMS (10%) and γ–APS (1%) as silane cross-linking agents. The reaction was conducted at 50^{o}C for 20 min.

Synthesis of epoxy-polyurethane-polysiloxane hybrid coating

Epoxy-polyurethane-polysiloxane hybrid coating was synthesized by reacting epoxy, acrylic polyols, tolonate and HTPDMS (10% relative to the epoxy) in the three-neck flask simultaneously. The ratio of NCO/OH of isocyanate and polyol as the components of polyurethane in this research is 2.5. The total weight of acrylic polyol and tolonate was 20% to the epoxy. The reaction was conducted at 50^{o}C for 30 min.

Characterization

Before characterization, the resulting mixture was cured by using versamid 140 as curing agent with the composition 0.5w/w relative to the hybrid coating mixture to obtain film sheet. The film sheet product has cured for 7 d prior to analysis. Characterization of the hybrid coating products were conducting by using FTIR analysis (IRPrestige-21 Shimadzu) to determine the functional groups which were formed, and analysis of ^{1}H-NMR (JNM ECA-500 Brand JEOL) to determine the proton chemical shifts. The mechanical properties were analysis to determine the tensile strength and elongation at break properties using Universal Testing Machine, Orientec Co. Ltd, Model UCT-5T and thermal analysis using TGA Instrument Q50.

Results and Discussion

Synthesis of Epoxy-Polyurethane Hybrid Coating

Modification of epoxy with polyurethane can be done by reacting with the polyol and isocyanate as constituent monomer of polyurethane. Because of epoxy diglycidyl ether bisphenol A contain hydroxyl group in its structure, so it can act as a polyol which will react with isocyanates group in tolonate. Modification process of epoxy by using polyurethane was conducted via simultaneous reaction where epoxy, acrylic polyol and tolonate were reacted in one step. The reaction between epoxy, acrylic polyol and tolonate are shown in Fig. 1.

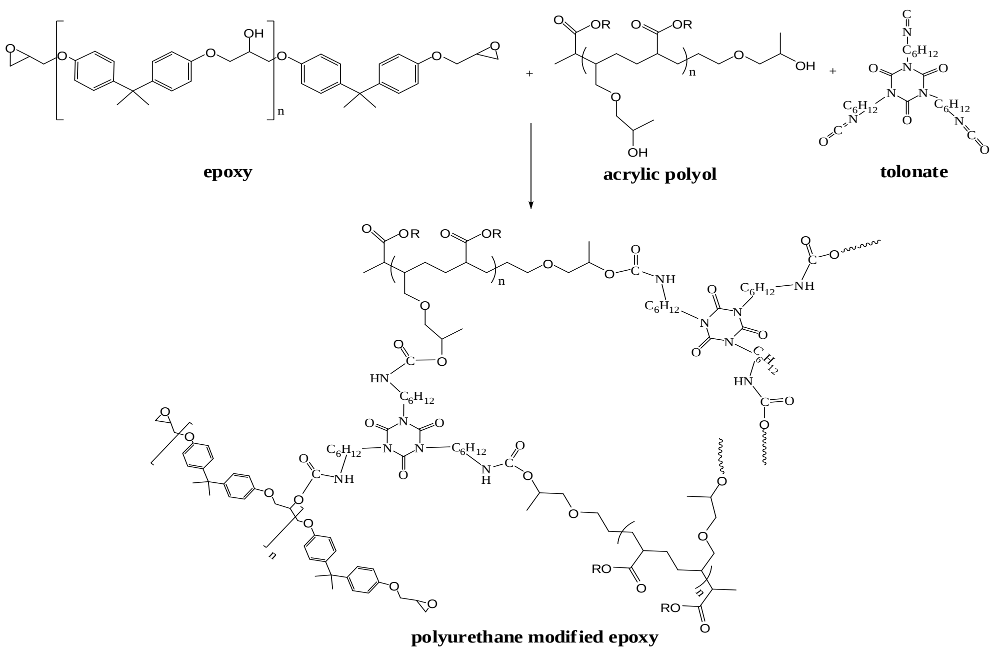

Figure 1. Synthesis of Epoxy-Polyurethane Hybrid Coating

Fig. 1 showed how epoxy and acrylic polyol can react with tolonate to form a new compound called epoxy-polyurethane hybrid coating (polyurethane modified epoxy). The isocyanate groups (two groups) from tolonate reacted with two hydroxyl groups from acrylic polyol and one hydroxyl group from epoxy. It is assumed due to the hydroxyl groups on the acrylic polyol is a primary alcohol while hydroxyl groups on the epoxy is a secondary alcohol, so it is suspected that acrylic polyol more reactive to form urethane bonds than the reaction with epoxy.

Fig. 4 showed the FTIR analysis of raw material (epoxy and polysiloxane) and the hybrid coating products. Figure 4D is the unmodified epoxy before reaction. The FTIR spectra of the unmodified epoxy has wide absorption peak in the wave number 3500 cm^{-1} which is the absorption peak of the –OH group. While, The FTIR spectra of polyurethane modified epoxy (Fig. 4B) has sharper absorption peak in the wave number 3437 cm^{-1} from the absorption peak of –NH group. The appearance of –NH group in the polyurethane modified epoxy product indicates that the -OH groups from epoxy and polyol have reacted with isocyanate and formed urethane bond. Fig. 4B from the spectra of the polyurethane modified epoxy showed a new absorption peak appeared at wave number 1726 – 1722. This new peak is from C = O group absorption of the urethane bond (-NH-(C = O)-O-) which is formed from the reaction between isocyanate (N = C = O) with hydroxyl group (-OH) of the epoxy and polyol.

Fig. 5 showed the H-NMR analysis of unmodified epoxy (5A) as raw material and the hybrid coating products (5B and 5C). There were new chemical shifts at 2.3 ppm which indicated the $–CH_2$ bonding from acrylic polyol and at 1.25 ppm from the $–CH_2$ of tolonate.

Synthesis of Epoxy- Polysiloxane hybrid coating

Modification of epoxy with polysiloxane has been conducted by using hydroxyl terminated polydimethylsiloxane (HTPDMS) as polsiloxane and γ-aminopropyl triethoxysilane (γ-APS) as cross-linking agents. The reaction between epoxy and polysiloxane is shown by Figure 2.

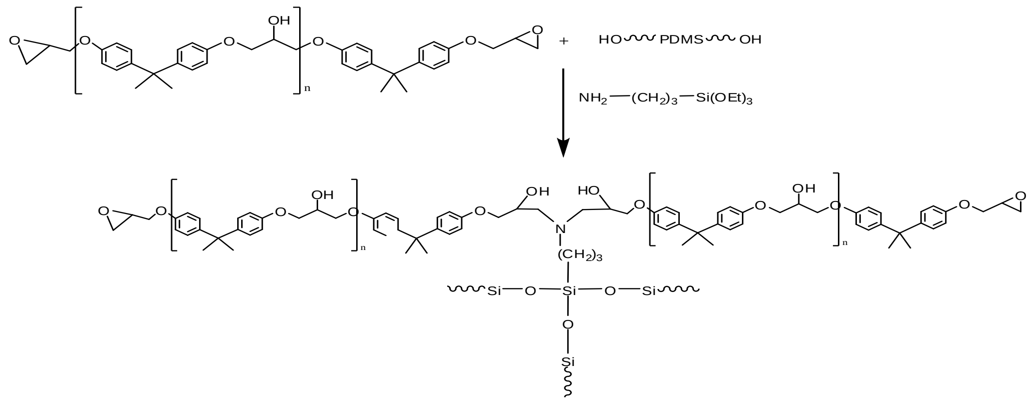

Figure 2. Synthesis of epoxy- polysiloxane hybrid coating.

In this reaction, the oxirane ring of epoxy reacted with the amine group in γ-APS and the oxirane ring cleavage and produced hydroxyl group. The next reaction was the ethoxy groups in γ-APS reacted with hydroxyl group in HTPDMS to produce Si – O- Si linkage. According to the overlay data of FTIR spectra from unmodified epoxy (Fig. 4D) and epoxy-polysiloxane hybrid coating (Fig. 4C) can be figured that in the spectra of epoxy-polysiloxane hybrid coating there is new absorption peak in the wave number 1099 cm^{-1} from the absorption peak of Si-O-Si. This new absorption peak from Si-O-Si showed that reaction between ethoxy groups in γ-APS and the hydroxyl group in HTPDMS has occurred. Reaction between oxirane ring of epoxy and the amine group in γ-APS was shown by the decreasing intensity of absorption peak from oxirane ring in the wave number 912 cm^{-1} because of the oxirane ring cleavage after reacted with amine group.

Synthesis of epoxy-polyurethane-polysiloxane hybrid coating

This synthesis process of epoxy-polyurethane-polysiloxane hybrid coating is similar with the synthesis process of polyurethane modified epoxy above. Where there was not addition of γ-APS as cross linking in this reaction. Because of hydroxyl terminated polydimethylsiloxane contain hydroxyl group in its structure, so it can act as a polyol which will react with isocyanates. Isocyanates which added in the process synthesis reacted with hydroxyl group of epoxy, polyol and HTPDMS. The reaction between epoxy, acrylic polyol, tolonate and HTPDMS are shown by Fig. 3. Urethane linkage that being produced from the reaction between N=C=O group of isocyanate and hydroxyl group of epoxy, polyurethane, and HTPDMS are shown by absorption peak in wave number 1724-1687 cm^{-1} from C=O group and 1581 cm^{-1} and 3433-3292 cm^{-1} from N-H group. Reaction between hydroxyl group of HTPDMS and N=C=O group of isocyanate produced (-NH-(C = O)-<u>O-Si</u>-) linkage which is shown by absorption peak in the wave number 1157 cm^{-1}

(Figure 4A). From the [1]H-NMR spectra there were new chemical shift at 2.3 ppm which indicated the $–CH_2$ bonding from acrylic polyol and at 1.26-1.25 ppm from the $–CH_2$ of the tolonate (Figure 5B).

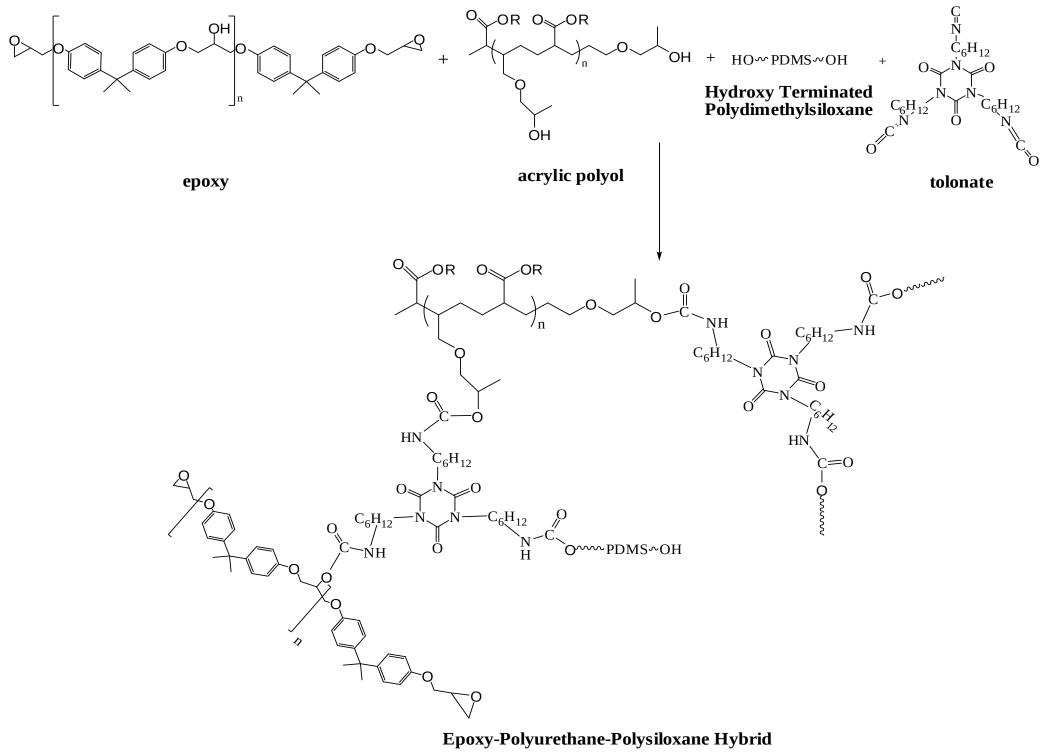

Figure 3. Synthesis of epoxy-polyurethane-polysiloxane hybrid coating.

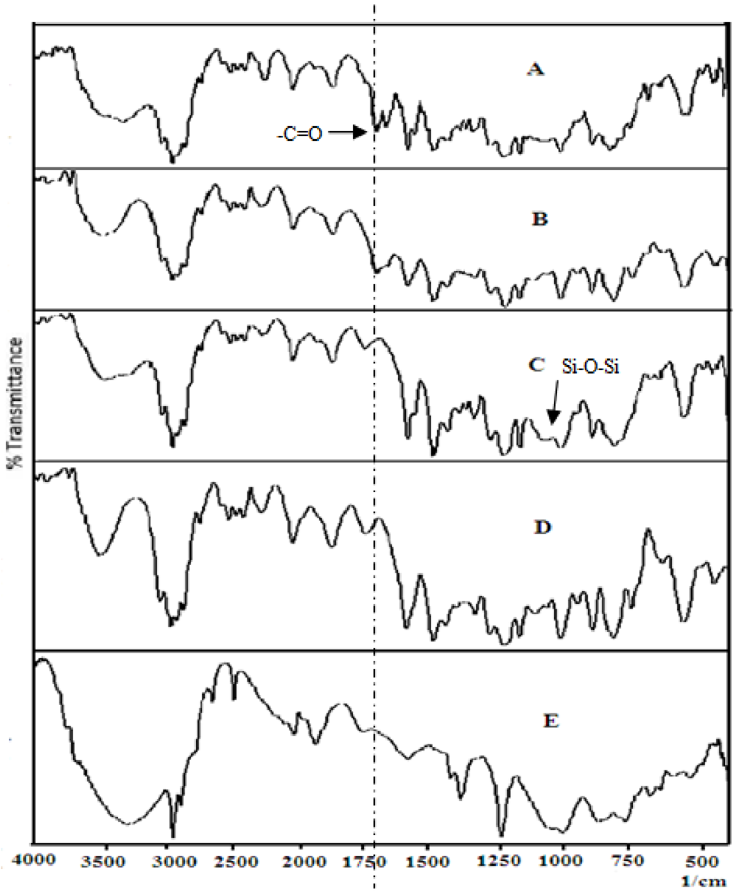

Figure 4. FTIR Spectra of Epoxy-Polyurethane-Polysiloxane Hybrid Coating (A), Epoxy-Polyurethane Hybrid Coating (B), Epoxy-Polysiloxane Hybrid Coating (C), Unmodified Epoxy (D), and hydroxyl terminated polydimethylsiloxane (E).

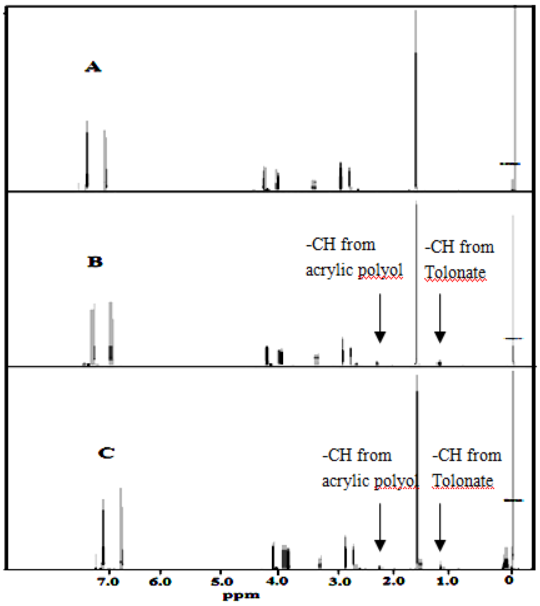

Figure 5. ^{1}H-NMR spectra of Unmodified Epoxy (A), Epoxy-Polyurethane-Polysiloxane Hybrid Coating (B), Epoxy- Polyurethane Hybrid Coating (C).

Mechanical Properties

The mechanical properties of unmodified epoxy and modified epoxy have been conducted by using tensile strength and elongation at break analysis. Mechanical properties comparison between unmodified epoxy, epoxy-polyurethane, epoxy-polysiloxane and epoxy-polyurethane-polysiloxane hybrid coating films are shown at Table 1. The highest value of tensile strength and elongation are from epoxy-polyurethane hybrid product. This is due to the addition of polyurethane enhance the cross-link density of epoxy resin. Moreover the addition of polysiloxane into epoxy resin was not significantly affect the tensile strength of epoxy but affect the increasing of elongation at break value. It is suspected because of polysiloxane has flexible –Si–O–Si– linkage, therefore the siloxane moiety functioning can act as an internal plasticizer. The tensile strength of epoxy-polyurethane-polysiloxane was smaller than epoxy-polyurethane hybrid but had the same elongation at break value. These data showed that the addition of polysiloxane into epoxy-polyurethane hybrid decreases its tensile strength due to the flexibility of –Si–O–Si– linkage [3, 18].

Table 1. Mechanical Properties of Unmodified and Modified Epoxy

Film	Thickness (μm)	Tensile Strength (MPa)	Elongation at break (%)
Unmodified Epoxy	283.53	6.82	2.29
Epoxy-Polyurethane Hybrid	239.22	11.29	2.92
Epoxy-Polysiloxane Hybrid	280.2	6.62	2.5
Epoxy-Polyurethane-Polysiloxane Hybrid	263.925	10.8	2.92

Thermal Properties

The thermal stability of unmodified epoxy and modified epoxy is illustrated in Figure 6. As seen in the figure, for all of the samples have similar degradation thermogram. The thermal stability of epoxy-polyurethane hybrid and unmodified epoxy overlap and has tendency to be similar. Therefore the addition of polyurethane into epoxy resin was not significantly affecting the mechanical properties. The thermal stability of epoxy resin improved when it was modified with polysiloxane and polyurethane-polysiloxane. At temperature 500°C the weight loss of unmodified epoxy and epoxy-polyurethane hybrid is smaller than the weight loss of epoxy-polysiloxane hybrid and epoxy-polyurethane-polysiloxane hybrid. At temperature 500°C the weight of unmodified epoxy and epoxy-polyurethane hybrid is 10%, the weight of epoxy-polyurethane-polysiloxane hybrid is 22% and the weight of epoxy-polysiloxane hybrid is 34%. Polysiloxane has ability to delay the thermal degradation process because of its high bond energy and thermal stability of –Si-O-Si linkage [3].

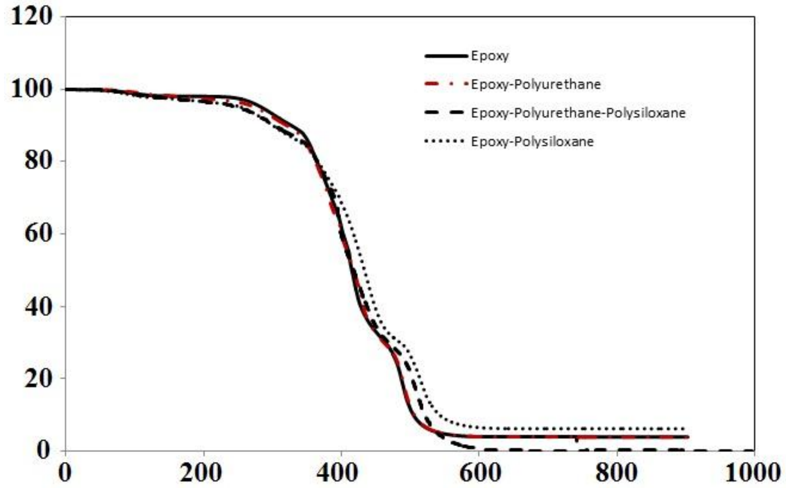

Figure 6. TGA curves of Unmodified Epoxy and Hybrid Coating

Conclusions

The hybrid coating products from polyurethane and/or polysiloxane modified epoxy based on acrylic polyol and tolonate were successfully synthesized via simultaneous reaction and confirmed by FT-IR and ^{1}H-NMR spectra. Modification of epoxy by using polyurethane and polyurethane-polysiloxane increased the tensile strength and elongation at break properties of epoxy. Whereas modification of epoxy by using polysiloxane have not significant effect on change in tensile strength, but increased the elongation at break and have highest thermal properties.

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