

## Synthesis, Structure, and Mechanical Properties of Castor Oil-Based Polyamidoamines Toughened Epoxy Coatings

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**ABSTRACT:** A series of toughened epoxy systems was prepared via crosslinking of diglycidyl ether of bisphenol A with castor oil-based polyamidoamines as curing agents. To this aim two series of polyamidoamines were synthesized in two steps from the reaction of castor oil with triethylenetetramine and then reaction of these products with dissolved salicylic acid in dimethyl formamide (DMF). The structure of the compounds was confirmed by FTIR spectra, GC-Mass and <sup>1</sup>H-NMR spectroscopy. The mechanical properties, adhesion and water resistance of polyamine and polyamidoamines cured epoxy systems were studied. It was found that significant improvement in toughness and adhesion of the epoxy films was achieved by using polyamidoamines as curing agents. The results showed a great enhancement in toughness and adhesion properties of the epoxy coats proportional to increasing castor oil weight ratio, and/ or using salicylic acid and DMF. Furthermore, polyamidoamines cured samples showed higher water resistance and less degradation in hot water immersion tests than polyamine cured samples. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4023–4030, 2013

**KEYWORDS:** coatings; crosslinking; mechanical properties; viscosity and viscoelasticity

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### INTRODUCTION

Epoxy resins, particularly those prepared from bisphenol A and epichlorohydrin, are considered as one of the most important classes of thermosetting polymers and are extensively used for their many good properties, which include high stiffness and strength, creep resistance, chemical resistance, and good adhesion to many substrates. These resins have found wide uses in various fields of coatings, high performance adhesives, advanced composites for the aerospace, electronic industries, and the other engineering applications. Once cured, they are characterized by high chemical and corrosion resistance as well as good mechanical and thermal properties. However, in many applications they have one major drawback; they are very brittle with poor resistance to crack propagation and low impact strength, and therefore, they exhibit low toughness. They have fracture energies of about two orders of magnitude lower than those of engineering thermoplastics and other high performance materials in the cured state.<sup>1–4</sup>

In principle, it is possible to increase elasticity of epoxy resin systems externally, by adding second phase, or internally, by

reducing the crosslinking density. Indeed, the crosslinking density can be reduced by adding some components, which react with the epoxy resins or hardeners.<sup>5,6</sup>

Most of the reported studies in this field have been carried out the addition of a suitable inorganic filler into the pure epoxy, such as glass beads,<sup>7</sup> layered silicates<sup>8–10</sup> and carbon nanotubes,<sup>11</sup> or rubber such as liquid hydroxyl terminated<sup>12,13</sup> and epoxy terminated<sup>14</sup> polybutadiene, amine-terminated,<sup>15,16</sup> carboxyl-terminated,<sup>17</sup> hydroxyl-terminated,<sup>18</sup> epoxy-terminated<sup>19</sup> copolymers of butadiene and acrylonitrile, or through the use of thermoplastics (polyphenyl oxide),<sup>20</sup> liquid crystalline polyurethane,<sup>21</sup> and interpenetrating polymer networks structures.<sup>22,23</sup>

Another approach in this regard is the use of polyamides and polyamidoamines as curing agents in epoxy resins systems. Both of mentioned curing agents are reaction products of aliphatic amines that should be included in the sub-classification of modified amines. Polyamide curing agents are produced by reaction of dimerized fatty acids and aliphatic amines. The flexibility, moisture resistance, and adhesion of cured epoxies are improved when polyamides are used instead of aliphatic amines

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as curing agents. However, the polyamide cured epoxies are generally inferior in thermal resistance and shear strength due to their reduction in crosslink density and lose their structural strength rapidly with increasing temperatures.<sup>24</sup>

The polyamidoamine curatives are amides having amine functionality and lower viscosity.<sup>25</sup> They are the products of a monomeric fatty acid such as tall oil fatty acid (TOFA) and a polyethyleneamine.<sup>26</sup> They cure relatively quickly at room temperature and develop tougher bonds than do the amine cured system. Their properties are very similar to the polyamide cured epoxy systems. Compared to other curing agents, polyamides and polyamidoamines offer the following unique feature: they can be used over a broad range of non-critical concentrations including one-to-one.<sup>25</sup>

Commercial polyamides are available with different viscosities from 10,000 to 500,000 cP, whereas polyamidoamine viscosities are generally ranged from 100 to 700 cP. This is clearly found an advantage over polyamide when it is tried to formulate coatings and related products with no solvent or minimum amount of solvent.<sup>26</sup>

Little has been reported within the literature with regards to the investigation over the usage of polyamides and polyamidoamines as epoxy curing agents. Lin et al. have synthesized the condensation products of alkyl-substituted aromatic dicarboxylic acid and polyoxyalkylene polyamines and used them as epoxy curing agents. They have found that the functionalities of alkyl and less hindered amines in the amidoamine structures affect the epoxy curing rate and material flexibility.<sup>27</sup> Hong et al. have studied the adsorption and curing behaviors of the epoxy/amidoamine system in the presence of metal oxides.<sup>28</sup>

Parzuchowski et al. have found that an epoxy resin modified with Carbonated soybean oil (CSO) when cured with a polyamine hardener at room temperature indicates phase separation. The phase separated networks exhibit higher impact strength as well as tensile strength than those of unmodified epoxy. Thus the samples containing CSO exhibit increased toughness.<sup>29</sup>

Saleh et al. have studied the mechanical properties of epoxy resin cured at constant curing time and temperature with different hardeners. They have found that the stoichiometry ratio formulations give the best mechanical properties, while the diglycidyl ether of bisphenol A (DGEBA)/diaminodiphenylmethane (DDM) system showed better mechanical properties than the DGEBA/triethylenetetramine (TETA) system.<sup>30</sup>

In the present study, we synthesized two series of polyamidoamines from TETA, castor oil, salicylic acid, and dimethyl formamide (DMF). They were used as curing agents for curing of DGEBA epoxy resins and the characteristics of these samples were compared with those of polyamine cured samples.

## EXPERIMENTAL

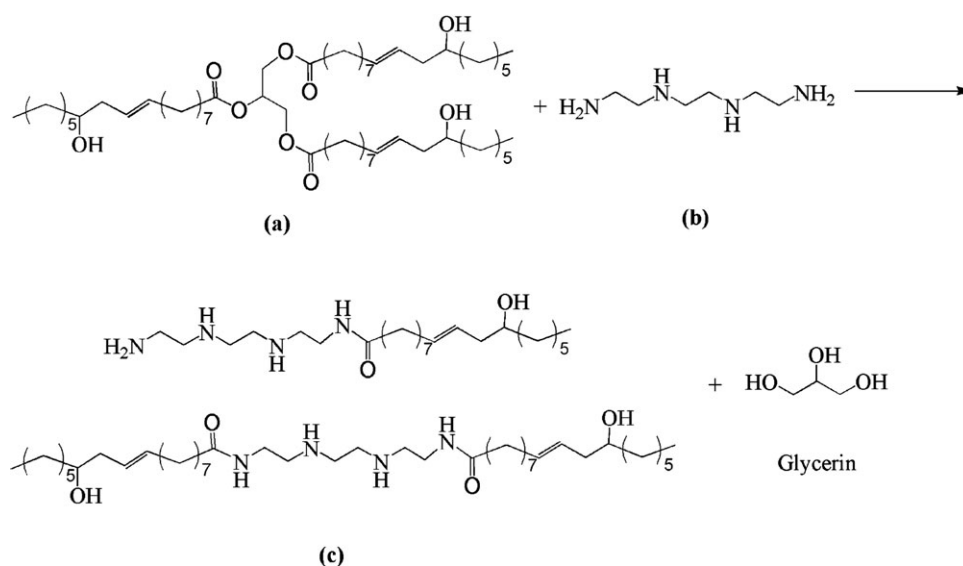
### Materials

The matrix used in the present study was Epikote 828, a three-component DGEBA epoxy resin system from Shell Chemical Co. TETA was prepared from Akzo Nobel (Sweden) and commercial castor oil (hydroxyl value = 168–172 mg KOH/g) was from Shiva agro process Pvt (India). DMF was purchased from Samsung Corporation (Korea) and salicylic acid was from Merck (Germany). All materials were used as received without further purification.

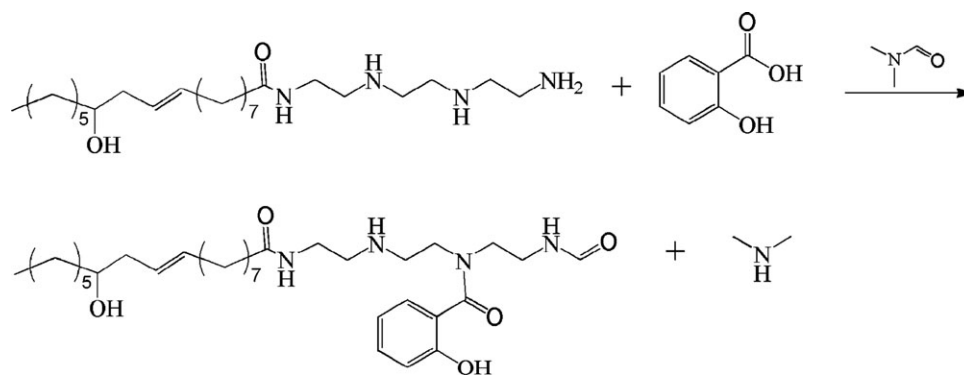
Moreover, the substrates utilized for adhesion and hot water immersion experiments were mild steel plates and for the impact experiments were aluminum plates. All the test substrates were initially degreased with DMF according to SSPC-SP1. Also, the mild steel plates were polished by using power tools according to SSPC-SP3 and were then washed with solvent prior to coating application.

### Test Methods and Characterization

The hydroxyl equivalent weight was measured according to ASTM D4274-05. The viscosities of raw materials or products were measured at 30°C by Viscomaster VM2 from Sheen Co. (Redhill, Surrey/England). Mechanical properties of the cured



**Scheme 1.** Structures of the major component of castor oil (a); TETA (b); plausible structures of the first series of polyamidoamines (TRA) (c).



**Scheme 2.** Formation and structures of the second series of polyamidoamines (TRSF).

samples were studied at 23°C by an Instron 4501 testing machine at a crosshead speed of 5 mm min<sup>-1</sup>, according to ASTM D638-08. The glass transition temperatures ( $T_g$ ) were determined by Bahr thermo analyze DSC 302 under N<sub>2</sub> (g) atmosphere at a heating rate of 5°C min<sup>-1</sup>. Water uptakes were measured according to ASTM D570. Adhesion measurements were done on the mild steel plates, according to the ASTM D4541-02 by Elcometer 106 pull off adhesion tester from Sheen Co.

Rapid deformation (impact) tests were made on the aluminum plates by tubular impact tester 807 from Sheen Co according to the ASTM D2794-93. Thicknesses of the coatings were 650–800 microns and the temperature was 23°C. The tests were made on the coated side (face impact).

Hot water immersion tests were done according to ASTM D870-02. In these tests, coated mild steel plates were immersed in hot water and were evaluated sequentially. Thicknesses of coatings were 650–800 microns and temperature of water in the course of the tests was (80 ± 2)°C. Results of these tests were represented according to ASTM D714-02.

Product's structures were characterized by using Fourier transfer infrared spectroscopy (recorded on a PerkinElmer FTIR spectrum One B spectrometer).

GC-Mass examination was done using a gas chromatograph/mass spectrometer model GCMS-QP5050 from SHIMADZU.

<sup>1</sup>H-NMR spectra of the products were recorded on a Bruker AC500 (500.133 MHz) nuclear magnetic resonance (NMR) instrument using CDCl<sub>3</sub> solvent as an internal standard.

### Preparation of Polyamidoamine Curing Agents

**Synthesis of TETA-Ricinolamide.** As shown in Scheme 1(a), the major component of castor oil is ricinoleic acid (approximately 90 wt %),<sup>31</sup> so it was used directly in TETA-ricinolamide (TRA) synthesis.

Plant oils are triglycerides that participate slowly in a nucleophilic acyl substitution reaction with linear polyamine such as TETA [Scheme 1(b)] at room temperature or faster at elevated temperatures. The obtained product is a mixture of polyamidoamines and glycerin [Scheme 1(c)]. The viscosity of the product depends on the weight ratio of raw materials. The weight ratios of castor oil/TETA can range from about 0 to 6.

In this study, castor oil was initially heated for several hours at 50°C to remove absorbed water. The dried castor oil was mixed with TETA at three different weight ratios of castor oil/TETA equal to 1, 2, and 3. The reaction mixtures were stirred at 75°C for 12 h.

**Synthesis of TETA-Ricinolamide-Salicylamide-Formamide (TRSF).** Scheme 2 depicts the synthesis of TETA-ricinolamide-salicylamide-formamide (TRSF). Salicylic acid was dissolved in DMF (weights ratio was equal to 1) and produced polyamidoamines from previous section were added to the solutions, while stirring. The reaction of dissolved salicylic acid with polyamidoamines took place rapidly, in an exothermal reaction, and new series of polyamidoamines, dissolved in DMF, were obtained. Then, the mixture was cooled to 50°C and stirred for 12 h.

Weight ratio of salicylic acid/ aliphatic polyamine was determined based on the weight ratio of castor oil/ aliphatic polyamine (i.e., remained active NH) and can ranges from 0 to 6.

In this study, weight ratio of salicylic acid/TETA was equal to 0.75.

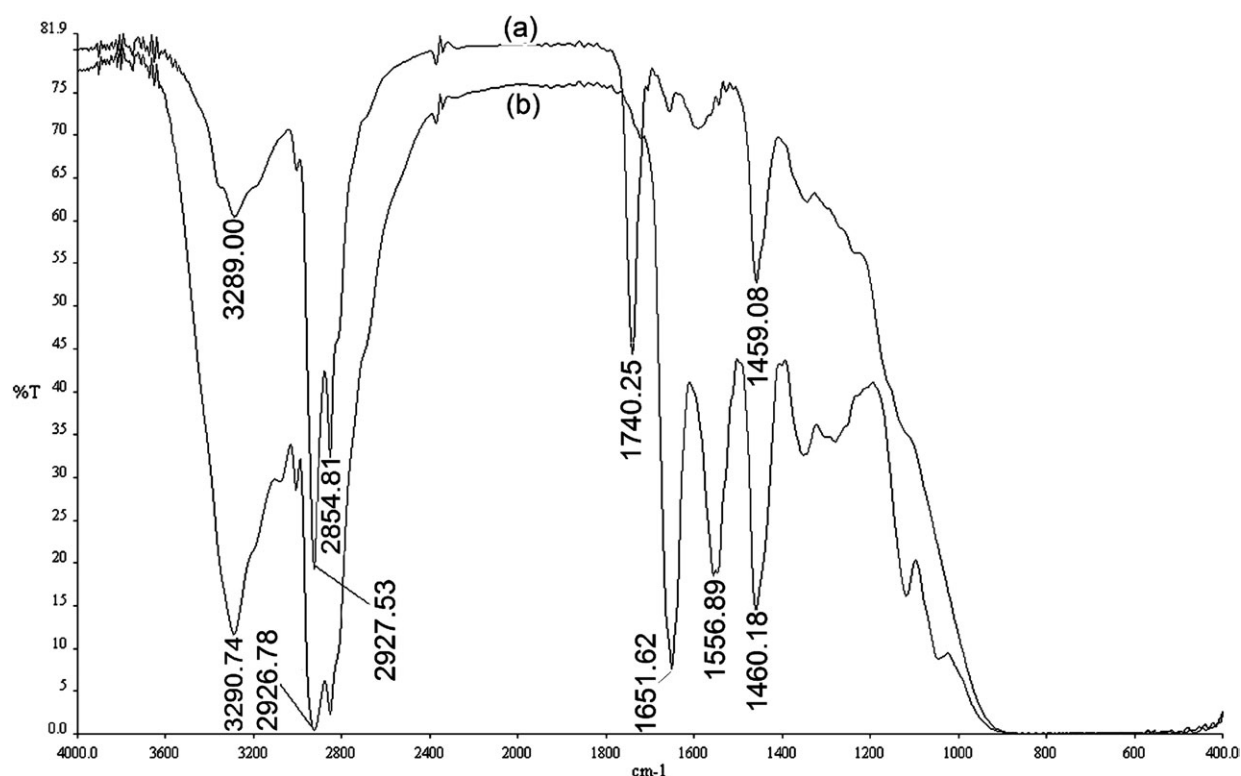
### Preparation of Cured Samples

Cured samples were prepared by mechanically mixing of epoxy resin and curing agents for about 20–30 min, as induction time, to prevent blushing. Then, the blends were cast into the molds or applied on the plates, and cured for 7–10 days at room temperature.

Produced TRAs and TRSFs as curing agents were used for preparation of cured samples with different weight ratios of curing agents to resin as shown in Table I. Regardless of castor oil weight, the weight ratio of TETA/ resin for all samples was equal to 0.15.

**Table I.** Weight Ratios of Curing Agents/Resin

Weight ratio of castor oil/TETA	Weight ratio of TRA/Epoxy	Weight ratio of TRSF/Epoxy
1	0.3	0.5
2	0.45	0.65
3	0.6	0.8



**Figure 1.** FTIR spectra of TETA/castor oil mixtures (a) immediately after mixing, (b) after 12 h mixing at 75°C (TRA).

In order to compare the results, another series of cured samples was prepared with the following compositions: (1) TETA cured epoxy with hardener/resin weight ratio equal to 0.15 and (2) TSF cured epoxy with weight ratio equal to 0.35.

## RESULTS AND DISCUSSION

### Synthesis of TRA and TRSF

**FTIR Spectroscopy.** FTIR spectra of castor oil/TETA mixtures are shown in Figure 1 in different reaction times: (a) immediately after mixing and (b) after 72 h (i.e., TRA).

The replacement of the band at 1740.25  $\text{cm}^{-1}$  associated with the carbonyl group of castor oil [Figure 1(a)] by a band at 1651.62  $\text{cm}^{-1}$  in polyamidoamine spectrum [Figure 1(b)],

which is according to the carbonyl group of the amides, demonstrates the formation of TRA.

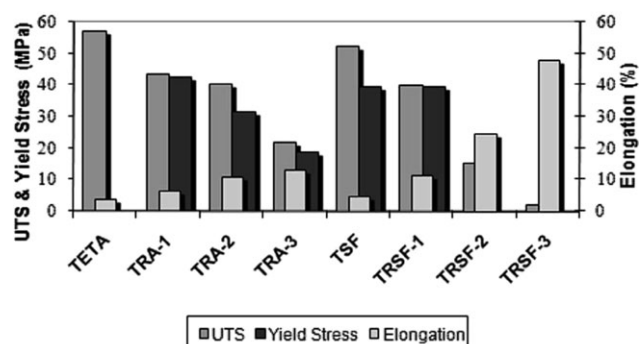
**GC-Mass Spectroscopy.** Dongsik and Heung showed that DMF participates in N-formylation reaction in the presence of a promoter (e.g., methyl benzoate) and produces new formamide.<sup>32</sup>

The mixture of reactants for synthesizing TRSF was placed in a vessel and purged by nitrogen gas. The reaction continued for two days and the produced gas on the top of the vessel was sampled several times during the reaction time and was analyzed by GC-Mass. The result showed that the major component of the produced gas is dimethyl amine that resulted from the decomposition of DMF (Scheme 2). So, as expected, the participation of DMF in N-formylation reaction was observed.

**Table II.** Viscosities of Polyamine and Polyamidoamines

Curing agent	Viscosity (cP)
TETA	24
Castor oil	551
TRA-1 <sup>a</sup>	787
TRA-2 <sup>a</sup>	Semi-solid
TRA-3 <sup>a</sup>	Semi-solid
TSF	147
TRSF-1 <sup>a</sup>	544
TRSF-2 <sup>a</sup>	1007
TRSF-3 <sup>a</sup>	1313

<sup>a</sup> Weight ratios of castor oil/TETA.



**Figure 2.** Mechanical properties of the cured samples.

**Table III.** Mechanical Properties of Cured Samples

Curing agent	Ultimate tensile strength (MPa)					Elongation at break (%)					Yield strength (MPa)				
	1	2	3	Mean	STDEV	1	2	3	Mean	STDEV	1	2	3	Mean	STDEV
TETA	57.5	58.9	55.8	57.4	1.552	3.5	4.1	3.8	3.8	0.305	-	-	-	-	-
TRA-1 <sup>a</sup>	45.7	42.4	43.6	43.9	1.67	6.9	6.7	5.9	6.5	0.529	45.6	40.2	41.8	42.5	2.774
TRA-2 <sup>a</sup>	39.2	41.9	40.9	40.6	1.365	11.2	12.3	9.5	11	1.419	34.7	27.9	32.1	31.6	3.431
TRA-3 <sup>a</sup>	22.8	21.4	22.4	22.2	0.721	13.1	14.5	12.2	13.3	1.159	16.2	21.1	19.3	18.9	2.479
TSF	52.7	51.2	53.9	52.6	1.353	4.2	4.6	5.1	4.6	0.451	38.4	40.3	40.1	39.6	1.044
TRSF-1 <sup>a</sup>	38.3	42.1	40.2	40.2	1.9	12.2	10.5	11.1	11.3	0.862	37.6	42.1	39.6	39.8	2.255
TRSF-2 <sup>a</sup>	14.2	16.1	15.6	15.3	0.985	21.5	27.7	24.6	24.6	3.1	-	-	-	-	-
TRSF-3 <sup>a</sup>	18.9	21.5	19.8	2.1	1.32	44.9	50.2	49.1	48	2.797	-	-	-	-	-

<sup>a</sup> Weight ratios of castor oil/TETA.

**<sup>1</sup>H NMR Spectroscopy of TRSF.** One of the synthesized products was placed in a vacuum oven over night at 60–70°C under 0.1 bar vacuum to purify it from low molecular weight components such as unreacted DMF. The purified product was analyzed by <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>-d<sub>6</sub>). In the represented spectrum, the characteristic peaks of TRSF are clearly seen at δ: 0.8349 (—CH<sub>3</sub> group of ricinoleic acid), 1.1615–1.4041 (—CH<sub>2</sub>— groups of ricinoleic acid), 2.7600–2.9004 (—CH<sub>2</sub>— groups of TETA), 3.2932–3.7005 (—NH— groups of TETA), 5.3520–5.4593 (—CH=CH— of ricinoleic acid and —OH of salicylic acid), 6.6895–7.7663 (—H atoms of benzene rings), and 7.9454–8.0477 (—NHCO— and —NCHO groups), respectively.

Therefore, the results of GC-Mass and <sup>1</sup>H-NMR characterizations indicated the successful synthesis of TRSF.

**Viscosity Measurements.** The viscosity of a coating formulation is considered as one of the most important parameters because it affects the processability and the final properties of the cured film. The viscosities of TETA and obtained polyamidoamines are represented in Table II. It can be seen that viscosities of polyamidoamines are much higher than those of polyamine or castor oil because polyamidoamines contain hydroxy-ester and amide groups, which induce hydrogen bonding and also they have higher molecular weight. Furthermore, increasing weight ratio of castor oil caused more enhancements

of polyamidoamines viscosities, to the extent that TRA-2 and TRA-3 are semi-solids. On the other hand, using salicylic acid and DMF caused decreasing of polyamidoamines viscosities due to the role of unreacted DMF as solvent, decrease in active NH that leads to hydrogen bond decrement, and also substitution of benzene rings on the chains that causes decrease in packing factor and prevention of crystallization. It is apparent from the results that TRSFs have so low viscosities that can be used solvent-free.

**Mechanical Properties.** Tensile test is one of the most important tests of mechanical properties of a material, which determines the behavior under axial stretch loading. The resulted data are usually presented as a strain–stress curve and are used to determine elastic limit, elongation, modulus of elasticity, proportional limit, reduction in area, tensile strength, and yield point and other tensile properties.<sup>33</sup>

The results of application of tensile tests are listed in Table III, and shown in Figure 2. The results revealed that polyamidoamines curing agents had dramatic effects on the mechanical properties of the coatings. Therefore, it can be concluded that polyamine curing agents make relatively brittle coatings to the extent that TETA cured sample didn't show yielding strength, whereas polyamidoamines curing agents produce more elastic coatings. The results shows that polyamidoamines cured

**Table IV.** Adhesion, Impact Resistance, and Water Absorption of Cured Samples

Curing agent	Adhesion (MPa)					Impact resistance (kg cm)					Water absorption (%)				
	1	2	3	Mean	STDEV	1	2	3	Mean	STDEV	1	2	3	Mean	STDEV
TETA	1.2	1.7	1.1	1.33	0.321	5	5	5	5	0	0.358	0.377	0.487	0.41	0.0696
TRA-1 <sup>a</sup>	1.6	1.3	2	1.63	0.351	7.5	7.5	7.5	7.5	0	0.727	0.696	0.747	0.72	0.0254
TRA-2 <sup>a</sup>	3	2.8	2.2	2.67	0.416	12.5	10	15	12.5	2.5	0.969	0.825	0.977	0.92	0.0858
TRA-3 <sup>a</sup>	4.5	3.55	3.8	3.95	0.492	30	37.5	30	32.5	4.330	1.640	1.578	1.541	1.59	0.0500
TSF	1.75	1.5	2.1	1.78	0.301	5	5	7.5	6	1.443	1.299	1.411	1.507	1.41	0.1040
TRSF-1 <sup>a</sup>	3.3	2.5	3	2.93	0.404	27.5	32.5	32.5	30	2.886	1.697	1.406	1.324	1.48	0.1959
TRSF-2 <sup>a</sup>	4.1	3.4	2.95	3.48	0.579	37.5	47.5	42.5	42.5	5	1.356	1.990	2.027	1.79	0.3771
TRSF-3 <sup>a</sup>	5.65	6.1	4.5	5.41	0.825	75	72.5	80	75	3.818	2.173	2.228	2.217	2.21	0.0292

<sup>a</sup> Weight ratios of castor oil/TETA.

**Table V.**  $T_g$  of Cured Samples

Curing agent	TETA	TRA-1 <sup>a</sup>	TRA-2 <sup>a</sup>	TRA-3 <sup>a</sup>	TSF	TRSF-1 <sup>a</sup>	TRSF-2 <sup>a</sup>	TRSF-3 <sup>a</sup>
$T_g$ (°C)	131	87	63	38	89	56	34	19

<sup>a</sup> Weight ratios of castor oil/TETA.

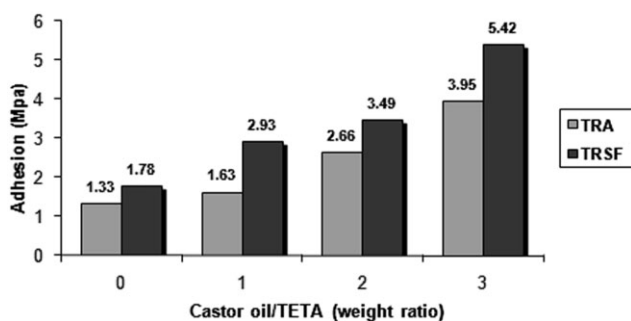
samples have higher elongation at break and lower yielding strength due to decrease in crosslink density (Table IV). Crosslink density decreases because of decrease in active NH/g vs. increase in molecular weight in the obtained polyamidoamines. Crosslink density decrement leads to increase in free volumes between chains and as a result  $T_g$  decreases (Table V).<sup>34</sup> Also, increasing castor oil weight ratio and using salicylic acid and DMF, alone or together, causes more enhancements in elongation at break and more decrement in yielding strength due to more decrement in crosslink density. Lower yielding strength usually means better toughness.<sup>34</sup> Furthermore, the TRSF cured samples with weight ratios of castor oil/TETA equal to 2 and 3 (i.e., TRSF-2 and TRSF-3) didn't show yielding stress and they behave as rubber-like.

**Adhesion.** The extent of corrosion resistance of metals strongly depends on the adhesion of the coating to the metal surface. Figure 3 and Table IV show the results of adhesion measurements of the polyamine and polyamidoamines cured samples.

The reported data are the average of several repeated experiment results on each kind of sample. The polyamidoamines cured samples showed higher adhesion to the substrates than do the polyamine cured samples. In addition, increasing weight ratio of castor oil led to more adhesion enhancement, which is related to the increment of hydroxyl content.

As it was resulted, the existence of salicylic acid and DMF in curing agents increased hydroxyl content and decreased viscosity of polyamidoamines. The latter effect reduced the viscosity of their coating systems that led to better wetting and diffusion in surface roughness and higher mechanical interlocking. Consequently, adhesion was greatly enhanced by using salicylic acid and DMF.

**Impact Resistance.** Toughness can be defined as the ability of a coating to withstand against impact force without cracking or breaking. The results of rapid deformation test on samples are shown in Figure 4 and Table IV.



**Figure 3.** Pull off adhesion tests results.

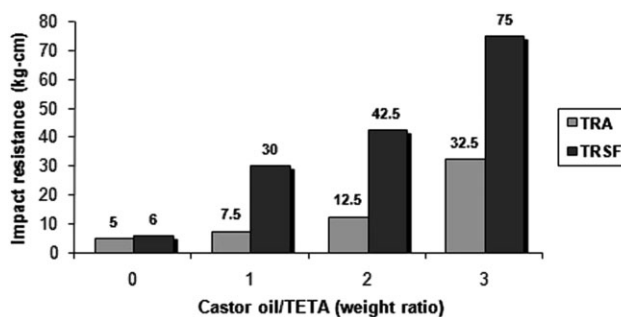
It is apparent from the aforementioned figure that impact resistance of polyamidoamines cured samples was much higher than those of polyamine cured samples. In addition, impact resistance was enhanced with the increasing weight ratio of castor oil. This phenomenon is due to reduction in crosslink density, increase in free end points, and therefore decrement of  $T_g$ .

Also, the samples which were prepared by TRSFs showed very great enhancement in impact resistance. The existence of salicylic acid and DMF as members of cured coating systems causes more reduction in crosslink density. In addition, viscosity reduction of TRSFs compared to TRAs causes increase in pot life and curing time that leads to reduction in residual stresses.

**Hot Water Immersion.** Degradation and surface protection capability of different coating systems are evaluated by hot water immersion test. The obtained results are summarized in Table VI.

It was observed that polyamidoamines cured samples showed less degradation, longer times for blistering and smaller blisters size and range compared to polyamine cured samples. Furthermore, increasing of castor oil weight ratio, and/or using salicylic acid and DMF caused enhancement of time for blistering and decrement of blisters size and range. These phenomena are due to higher adhesion and toughness of polyamidoamines cured samples. Higher adhesion means less water permeation and so less separation of coats from substrates. Also, higher toughness means that coats can release thermal stresses and so less degradation. In addition, increasing of castor oil weight ratio leads to increment of fatty acid content of coats. As a result of fatty acid's hydrophobicity, they can act as filming amines that prevent water permeation.

Finally, it can be observed from rows 1–5 that growth of blisters size and range on the coated surfaces led to total loss of adhesion and separation of coatings from substrates.



**Figure 4.** Impact resistance of polyamine or polyamidoamine cured samples.

**Table VI.** Hot Water Effects on Polyamine or Polyamidoamines Cured Samples

Curing agent	Time (h)	Effect(s)	Time (h)	Effect(s)
TETA	3	Blistering No.2, "few"	3.5	Separating from substrate
TSF	12	Blistering No.2, "few"	13	Separating from substrate
TRA-1 <sup>a</sup>	14	Blistering No.2, "few"	17	Separating from substrate
TRSF-1 <sup>a</sup>	20	Blistering No.4, "few"	48	Blistering No.2, "few, " Separation from substrate 24 h after removing
TRA-2 <sup>a</sup>	17	Blistering No.2, "few"	19	Separating from substrate
TRSF-2 <sup>a</sup>	24	Blistering No.4, "few"	48	Blistering No.4, "medium dense, " No Separation
TRA-3 <sup>a</sup>	20	Blistering No.4, "few"	48	Blistering No.4, "medium dense, " No Separation
TRSF-3 <sup>a</sup>	24	Blistering No.6, "few"	48	Blistering No.6, "medium, " No Separation

<sup>a</sup> Weight ratios of castor oil/TETA.

## CONCLUSIONS

In this study, it was shown by FTIR, GC-Mass, and <sup>1</sup>H-NMR spectroscopy that castor oil-based polyamidoamines can be easily synthesized using TETA, castor oil, salicylic acid, and DMF. The viscosity of produced polyamidoamines is low enough that they can be used solvent-free. It was concluded, based on obtained results, that using castor oil-based polyamidoamines as curing agents for epoxy systems caused significant improvement in toughness and adhesion compared to polyamine cured systems. Furthermore, the polyamidoamines cured samples showed higher water resistance and less degradation than polyamine cured samples in hot water immersion tests and their protection capability was better. Also, it was found that either increasing castor oil weight ratio, or using salicylic acid and DMF, or both made great improvement in the mentioned parameters. It was observed that in castor oil/TETA weight ratios of 2 and 3 (i.e., TRSF-2 and TRSF-3) cured samples behave as rubber-like and have particular toughness and adhesion.

## ACKNOWLEDGMENTS

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## REFERENCES

- Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw-Hill: New York, **1967**.
- Lee, H.; Neville, K. *Epoxy Resins; Their Applications and Technology*; McGraw-Hill: New York, **1957**.
- May, C. A.; Tanka, G. Y. *Epoxy Resin; Chemistry and Technology*; Marcel & Deckker: New York, **1973**.
- Bascom, W. D.; Hunston, D. L. *Am. Chem. Soc.* **1989**, *222*, 193.
- Manfred, M. M.; Claus, G. K.; Uwe, N. B. S. U.S. Pat. 5,847,027 (**1998**).
- Bashir, A.; Saleh, A. B. Ph.D Thesis, University of Science, Malaysia, **2005**.
- Ji, W. G.; Hu, J. M.; Liu, L.; Zhang, J. Q.; Cao, C. A. *Surf. Coat. Technol.* **2007**, *201*, 4789.
- Raetzke, S.; Ohki, Y.; Imai, T.; Tanaka, T.; Kindersberger, J. *IEEE Trans. Dielec. Electr. Insul.* **2009**, *16*, 1473.
- Zhou, G.; Movva, S.; Lee, L. J. *J. Appl. Polym. Sci.* **2008**, *108*, 3721.
- Abacha, N.; Kubouchi, M.; Sakai, T.; Tsuda, K. *J. Appl. Polym. Sci.* **2009**, *112*, 1021.
- Salinas-Ruiz, M. D. M.; Skordos, A. A.; Partridge, I. K. *J. Mater. Sci.* **2010**, *45*, 2633.
- Pereira Soares, V. L.; Ramos, V. D.; Rangel, G. W. M.; Nascimento, R. S. V. *Adv. Polym. Technol.* **2002**, *21*, 25.
- Saadati, P.; Baharvand, H.; Rahimi, A.; Morshedian, J. *Iran. Polym. J.* **2005**, *14*, 637.
- Barcia, F. L.; Amaral, T. P.; Soares, B. G. *Polymer* **2003**, *44*, 5811.
- Chikhi, N.; Fellahi, S.; Bakar, M. *Eur. Polym. J.* **2002**, *38*, 251.
- Levita, G.; Marchetti, A.; Butta, E. *Polymer* **1985**, *26*, 1110.
- Verchere, D.; Sautereau, H.; Pascault, J.; Moschiar, S.; Iaccardi, C.; Williams, R. *Polymer* **1989**, *30*, 107.
- Sankaran, S. *J. Appl. Polym. Sci.* **1990**, *39*, 1635.
- Verchere, D.; Pascault, J. P.; Sautereau, H.; Moschiar, S. M.; Riccardi, C. C.; Williams, R. J. *J. Appl. Polym. Sci.* **1991**, *43*, 293.
- Pearson, R.; Yee, A. *Polymer* **1993**, *34*, 3658.
- Lu, S.; Ban, J.; Yu, C.; Deng, W. *Iran. Polym. J.* **2010**, *19*, 669.
- Wang, H.; Chen, J. *Polym. Eng. Sci.* **1995**, *35*, 1468.
- Harani, H.; Fellahi, S.; Bakar, M. *J. Appl. Polym. Sci.* **1999**, *71*, 29.
- Petrie, E. M. *Epoxy Adhesive Formulations*; McGraw-Hill: New York, **2006**; p 85.
- Petrie, E. M. *Handbook of Adhesives and Sealants*, 2nd ed.; McGraw-Hill: New York, **2007**; p 376.

26. William, E. S. N.; David, A. D. K.; Frederik, H. W. A. U.S.Pat.6,258,920 (2001).
27. Lin, J.; Speranza, G. P.; Waddill, H. G. *J. Polym. Res.* **1996**, 3, 97.
28. Hong, S. G.; Tsai, S. J. *Therm. Anal. Calorim.* **2001**, 63, 31.
29. Parzuchowski, P. G.; Jurczyk-Kowalska, M.; Ryszkowska, J.; Rokicki, G. *J. Appl. Polym. Sci.* **2006**, 102, 2904.
30. Saleh, N. J.; Abdul Razak, A. A.; Tooma, M. A.; Aziz, M. E. *Eng. Technol. J.* **2011**, 29, 1804.
31. Wikipedia, *Castor oil*, [http://en.wikipedia.org/wiki/Castor\\_oil#cite\\_note-1](http://en.wikipedia.org/wiki/Castor_oil#cite_note-1), accessed on November 2, 2011.
32. Dongsik, Y.; Heung, B. J. *Bull. Korean Chem. Soc.* **2010**, 31, 1424.
33. Nielsen, L. E. *Mechanical Properties of Polymers and Composites*; Marcel & Dekker: New York, **1994**; p 233.
34. Ratna, D. *Handbook of Thermoset Resins*; Lighting Source: UK, **2009**; p 155.