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Liquid crystal bio-based epoxy coating with enhanced performance

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ABSTRACT

Tetrafunctional rosin based epoxy was synthesized and cured with either rosin based hardener or conventional phenylene diamine to study the feasibility of producing high performance thermosetting polymer from renewable resource. The chemical structure of the prepared epoxy was confirmed by elemental analysis, FTIR, ^{1}HNMR, UV, total acid number and epoxy equivalent weight. Dynamic mechanical (DMA) and thermogravimetric (TGA) analyses results indicate that fully biobased epoxy system possesses high glass transition temperature (T_g), high modulus (G`) and improved thermal stability.

Keywords **–** DMA, high performance epoxy coating, liquid crystal crosslinker, rosin, thermal stability

I. INTRODUCTION

Epoxy has a wide range of applications, including metal coatings, use in electronic and electrical components, high tension electrical insulators, fiber reinforced plastic materials, and structural adhesives. On the other hand, regarding increasing petroleum prices, hazardous effects and environmental legislations, potential efforts are directed toward replacing petroleum based materials with bio-based resources. Rosin as a natural renewable source containing tricyclic hydrophenanthrene structure is a good candidate for synthesizing coating materials with enhanced performance. Moreover, a very interesting reaction, involving the double bonds of resin acid, as diene permits their coupling with unsaturated carboxylic substances as dienophiles and transformation into organic poly-basic acids in accordance to Diels-Alder mechanism. In this context, many investigations have been done on developing polyesters [1-3], unsaturated polyesters [4], polyamides [5], polyamideimide [6], epoxies [7-12] and epoxy curatives [13-15].

Bicu et al. reported synthesis of ketone type derivatives of acrylopimaric and maleopimaric acid adducts in presence of sulfonic catalyst for preparing polyamides or polyimides i.e. Diels Alder cycloaddition followed by dehydrocarboxylation [16, 17]. The latter reaction depends mainly on the difference in behavior of acrylic acid or maleic acid carboxylic groups and that of pimaric acid toward dehydrocarboxylation.

In a previous article [18], the ketone type derivative of levopimaric acid was performed using the same catalyst system. The produced bis-diene was then adducted with dimaleimide i.e. de-hydrocarboxylation followed by Diels Alder cycloaddition. In fact the sequence of reactions followed in these studies attracts attention.

The objective of this research was to make use of the rigidity of the tricyclic hydrophenanthrene structure of rosin acids to prepare fully bio-based epoxy system with enhanced performance. In this context, N,N`-diglycidyl-N,N`-diundecylglycidyl ester diacrylodipimaryl ketone (TGDMP) was prepared and cured with a rosin acid based hardener (dirosin-maleic anhydride imidodicarboxylic acid (D-RMID) previously prepared by Liu et al. 2010 [14] or traditional p-phenylene diamine hardener (pPhDA) for comparison.

II. EXPERIMENTAL

2.1. Materials

Abietic acid (ABA) (75%), acrylic acid, zinc acetate, 11-aminoundecanoic acid and epichlorohydrin were purchased from Sigma-Aldrich. Sodium hydride was obtained from Loba chemical company – India and p-phenylene diamine (pPhDA) were obtained from CDH chemical company – India. Tetrabutyl ammonium bromide was delivered from Acros Organics chemical company, Belguim.

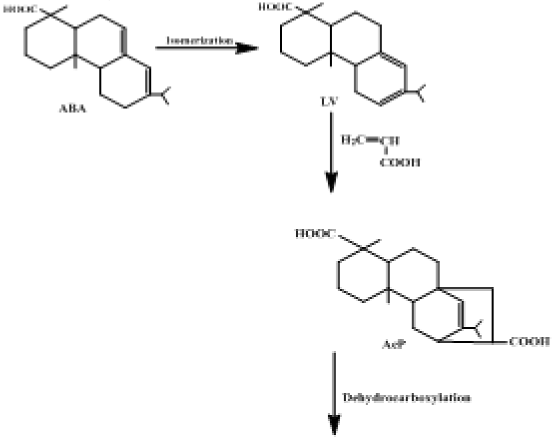
2.2. Measurements and characterization

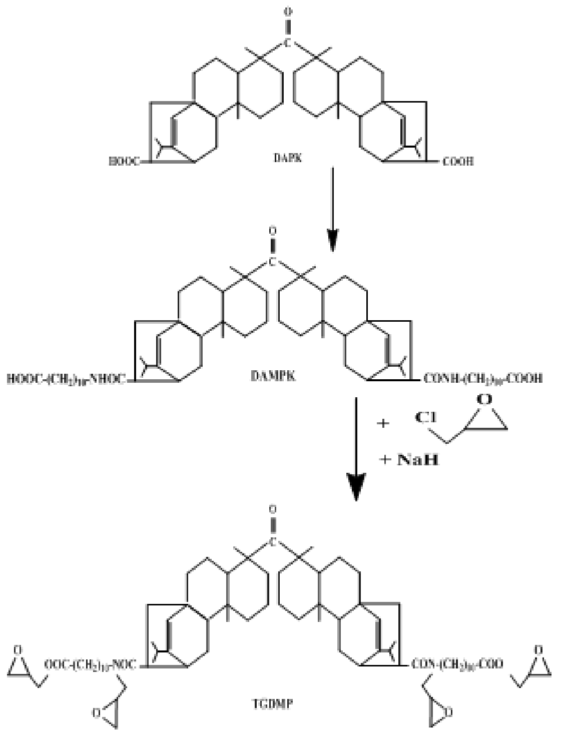
Spectroscopic techniques were used for elucidating the chemical structure, ^{1}HNMR analysis was recorded on Varian NMR 300 MHz spectrometer, FTIR spectra were recorded on Mattson-infinity series bench tab 961, Perkin Elmer Spectrum GX and UV spectra were recorded on Shimadzu UV-1600 series. Elemental analyses were performed on Shimadzu Qp-

2010 plus while total acid number was evaluated according to ASTM D- 664 on MATi 02 Automated TAN/TBN analyzer - Metrhom and epoxy equivalent weight was investigated according to ASTM D-1652. DMA was carried out on Triton Technology DMA using a three point bending mode. Samples were tested from 30 – 350 °C at a heating rate 10 °C min^{-1} and frequency of 1 Hz. Thermogravimetric analyses were conducted using Simultaneous DSC-TGA, Q 600 SDT (USA) thermogravimetric analyzer. Cured epoxy samples were scanned at a heating rate of 10 ºC min^{-1} under nitrogen atmosphere from room temperature to 600 °C.

2.3. Synthesis of N,N`-diglycidyl-N,N`-diundecylglycidyl ester diacrylodipimaryl ketone (TGDMP) Scheme 1

Isomerization of abietic acid (ABA) into levopimaric acid (LV) was performed under high temperature and inert gas conditions. Such conditions were conventionally used by many authors [14, 19]. Isomerization was followed up through UV spectroscopy. Acrylodipimic acid (AcP) was prepared following Diels-Alder cycloaddition protocol using zinc acetate as catalyst and acetic acid where reflux was continued for 12 h. The product was purified by double recrystallization from acetic acid and washing with sodium carbonate solution and water (yield 85%). Diels Alder cycloaddition of acrylic acid into LV was confirmed using ^{1}HNMR. Detailed procedures for preparing diacrylopimaryl ketone (DAPK) is described by Bicu et al. [20]. Amidation of DAPK was performed by refluxing 178.5 g (0.25 mol) of DAPK with 100 g (0.5 mol) of 11-aminoundecanoic acid in xylene for 4h to get diacrylamide dipimaryl ketone (DAMPK). The produced water was azeotrpically collected in a trap. In a 500 ml four neck flask, 108 g (0.1 mol) of DAMPK was dissolved in excess dimethyl formamide (DMF) and treated with 6 g of purified sodium hydride. After this mixture was stirred at 130 °C for 3h, 370 ml (4 mol.) of epichlorohydrin was dropwisely added while the temperature was gradually raised to reflux temperature. The reaction was refluxed for 6 h then an extra amount of sodium hydride was added. By cooling the reaction to room temperature, the product was washed by isopropanol and the precipitate was filtered under vacuum and the filtrate was concentrated under reduced pressure. LV, AcP, DAPK, DAMPK and TGDMP chemical structures were confirmed by elemental analysis, melting point (MP), total acid number (TAN) and FTIR.

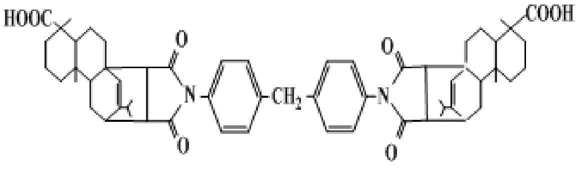




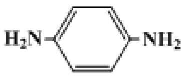
Scheme 1: Synthetic route for N,N`-diglycidyl-N,N`-diundecylglycidyl ester diacrylodipimaryl ketone (TGDMP)

2.4. Preparation of dirosin- maleic anhydride imidodicarboxylic acid (D-RMID)

D-RMID hardener was prepared and purified as described by Liu et al. [14]. Structures of either crosslinkers (D-RMID and pPhDA) are presented in Fig. 1.



D-RMID



pPhDA

Figure 1: Structures of D-RMID and pPhDA

2.5. Epoxy curing

N,N`-diglycidyl-N,N`-diundecylglycidyl ester diacrylodipimaryl ketone (TGDMP) was cured by dirosin- maleic anhydride imidodicarboxylic acid (D-RMID) with 1:1 stoichiometric ratio and 1% by weight 2-ethyl-4-methylimidazole as catalyst. After good mixing using DMF, the solvent was evaporated under vacuum and the mixture was poured in tin food can mold with dimensions: 25 mm x 20 mm x 2 mm. Curing was completed at 80 °C under vacuum for 8h. Cured sample was left to cool to room temperature before demolding for TGA and DMA analysis.

The same procedures for curing were followed using TGDMP and p-phenylene diamine (pPhDA) but with 1:0.5 stoichiometric ratio.

III. RESULTS AND DISCUSSION

Renewable sources including carbohydrates, proteins, amino acids, lactic acid, steroids, monoterpenes, rosin acids, fatty acids and long chain alkyl groups, as well as aromatic compounds attract attention of recent research. The principal components of rosin are rosin acids, which are monocarboxylic acids of hydrophenanthrene. Such structure can be used for the synthesis of coating materials with improved properties.

3.1. Synthesis and characterization

Elemental analyses, MP and TAN of LV, AcP, DAPK and TGDMP data are shown in Table 1. In isomerization step, the formation of levopimaric acid with characteristic homoannular double bonds was confirmed by UV spectroscopy (not represented here). Levopimaric acid show absorption at λ_{max} 247 mµ indicating efficient isomerization into pimaric structure whereas abietic acid absorption is at λ_{max} 233 and 240 nm. AcP formation was confirmed through ^{1}HNMR, a characteristic peak appears at 5.4 ppm assigned for the new proton attached to the unsaturated carbon formed after Diels Alder cycloaddition (see Fig. 2). In addition, an evident increase of TAN compared to those of ABA and LV (Table 1) gives a further confirmation of cycloaddition.

Dehydrocarboxylation of AcP was performed at high temperatures regime. This regime was selected by Bicu et al. [16] shows, on one hand, that only the more labile carboxylic groups were involved in the reaction, namely that belonging to the levopimaric segment, and, on the other hand, the two carboxylic groups of AcP present different chemical reactivities. This last observation was also mentioned on other occasion **[**19]. FTIR spectrum of DAPK (Fig. 3), shows C=O vibration of ketone appears at 1729 cm^{-1} whereas that of –COOH appears at 1697 cm^{-1} indicating successful dehydrocarboxylation.

FTIR spectrum of DAMPK (Fig. 3) shows characteristic amide absorption band at 1652 cm^{-1}, absorption band for carboxylic group OH at 3308 cm^{-1}, strong band at 3429 cm^{-1} for N-H stretching of secondary amide group.

A drop in TAN value of TGDMP compared to DAMPK can be observed confirming consumption of carboxylic acid group though epoxidation. FTIR of TGDMP (Fig. 3) shows absorption bands at 1722 cm^{-1} for stretching vibration of the new ester carbonyl group while epoxide rings give bands at 1245 cm^{-1} and 974 cm^{-1} and 746 cm^{-1} for symmetric and asymmetric C-O stretching vibration. Moreover, experimentally determined epoxy equivalent is 303.5 g/eq assisting epoxy formation and on the other hand used to calculate the required amount of hardener.

FTIR spectrum for D-RMID shows characteristic bands (Fig. 3) at 3441 cm^{-1} assigned to carboxylic acid O-H and an intense band at 1704 cm^{-1} for C=O group of carboxylic acid and maleimide moieties. ^{1}HNMR would be more

Table 1: Elemental analysis, total acid number (TAN), epoxy equivalent weight (EEW) and melting point (MP) data for prepared compounds

Sample	C%		H%		N%		TAN (mg KOH.g^{-1})	EEW (g/eq)	MP (°C)
	Calcd	Found	Calcd	Found	Calcd	Found			
AbA	79.4	78.54	9.9	7.47	---	---	183.98	---	160
LV	79.4	79.71	9.9	6.54	---	---	184.37	---	158
AcP	73.9	74.35	8.8	8.95	---	---	282.90	---	102
DAPK	78.9	79.28	9.35	9.53	---	---	156.20	---	---
DAMPK	76.8	76.92	9.7	9.84	2.7	2.67	110.56	---	---
TGDMP	74.1	74.35	9.0	9.21	2.3	2.35	7.31	303	---
D-RMID	76.1	74.24	7.7	7.26	2.9	2.87	112.65	---	300

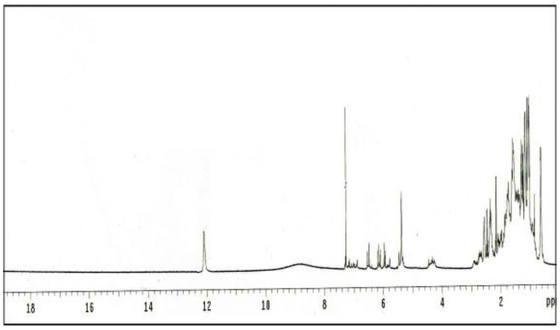


FIGURE 2: ^{1}HNMR OF ACP

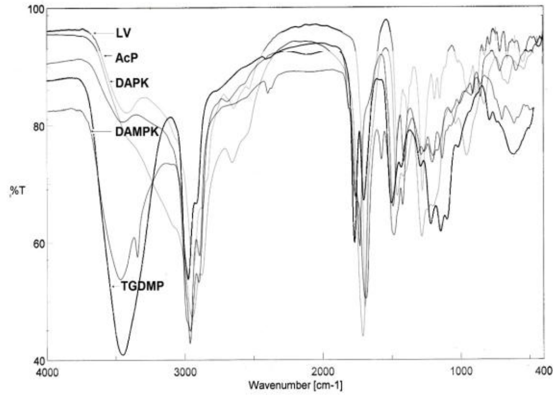


Figure 3: FTIR spectra for LV, AcP, DAPK, DAMPK and TGDMP

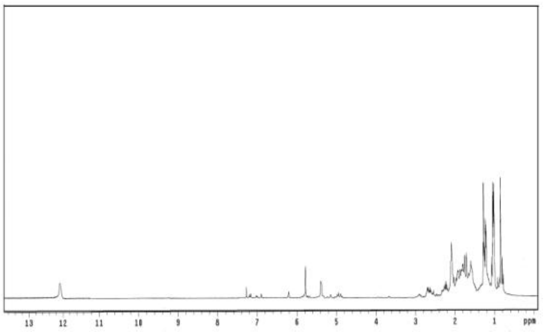


Figure 4: ^{1}HNMR of D-RMID

helpful in confirming the structure. New formed bonds after Diels Alder cycloaddition are: succinimide protons that appears at 2.7 ppm and the new formed unsaturation appears at 5.4 ppm (see Fig. 4) besides the disappearance of C-H peak at 6.8 ppm attributed to double bond of maleimide moiety that are good evidences for D-RMID chemical structure.

3.2. Mesomorphic transition of D-RMID

A polarized light Olympus BX51 microscope was used to detect the formation of the liquid crystal (LC) structure of D-RMID while heating, as previously mentioned in our former study [21]. The transition from crystallization to liquid crystalline phase for D-RMID revealed cholesteric texture when the temperature reaches 247 C. Upon increasing the temperature to 350 C, there is an isotropic transition for D-RMID from liquid crystalline phase. Mesomorphic properties of liquid crystalline curing agent (D-RMID) was also determined by DSC [21]. Heat capacity data are presented as a function of temperature. Samples were separately heated from room temperature to 350 °C with heating rate 10 °C/min under nitrogen atmosphere. From these measurements, enthalpy changes for phase transitions can easily be determined. Two main endothermic transitions were observed for D-RMID. The first transition is for crystal to liquid crystal phase and the second one is for liquid crystal to isotropic phase. The first transition of D-RMID for solid crystal to liquid crystal phase occurs at a range of 250 - 300 °C while the isotropization temperature was T = 347 °C. This broad range of the first transition gives an indication of the wide range that the liquid crystal phase can withstand. It can observed that these transformation temperatures correspond with the transition phenomena observed in the POM with little shift.

Regular epoxy resins are one of the most vital thermosetting engineering plastics that are widely used for important applications because of their characteristic properties. Liquid crystalline epoxies in comparison can show superior properties with regard to their thermal stability, toughness and low thermal expansion coefficient as a result of restricted motion of the cured network through liquid crystal domains formation of many LC domains in the cured networks. Over the past few decades, various LC thermosets have been synthesized, and their curing behaviors, thermal properties, and phase behaviors have also been studied by many research groups [21-23]. Osada et al. reported LC epoxy resin cured by the mesogenic hardening compound, 4,4`-bis(ω-carboxydecanoxy) azoxybenzene [24]. Two commercial diepoxides (EPON 925 and XY400 from Showa-Shell Co.,), showed mesophase upon curing with such mesogenic hardener. Treated EPON 925 with LC curing agent shows a smectic-like mesophase before gelation but no mesophase was observed upon reaching T_g while XY4000 show a smectic-like mesophase before gelation and a nematic-like mesophase after T_g.

The importance of the prepared curing agents comes from the economic benefit through using low cost bio-based materials and processes, an advantage that will helps in justification for development and wider use of these types of materials.

3.3. Evaluation of cured epoxy resins

Epoxy curing reaction proceeds through cleavage of the oxirane ring through a nucleophillic addition reaction. Due to the involvement of an addition reaction, no volatile byproducts are formed during the curing of epoxy resins. Because the reactions of the epoxy monomers with the respective hardener are sometimes not fast enough for a specific application, accelerators are often added to the resin formulations. Lewis acids are used for accelerating the reaction between an epoxy and an alcohol. Similarly, alcohols, phenols or carboxylic acids are used as accelerators in amine-cured epoxies, and tertiary amines (e.g., benzyl dimethylamine) are usually used in anhydride-cured epoxy systems. Generally, tertiary amine, was added in a small amount (1% w/w), catalyzed the anionic polymerization through the ring opening of oxirane rings. This method of curing liquid-crystalline epoxides was analyzed by Ribera's group [25]. In this respect, we used 1% by total weight of 2-ethyl-4-methylimidazole containing a tertiary amine and a secondary amine as an accelerator.

Samples were placed in special molds for dynamic mechanical analysis or used as coatings for iron steel panels for conventional coating testing and thermal stability evaluation. Samples were cured at room temperature for 24 h and postcured at 80 □C for 4 h.

3.3.1. Dynamic mechanical analysis (DMA) of cured epoxy resins

Dynamic mechanical properties are determined in all branches of material science. A great interest in evaluating such properties is integrated with coating research and development. By using structure/property information, one can design and optimize chemical structure of binder components of coatings. In fact determination of dynamic mechanical properties requires the use of free films. This requirement is a serious limitation because many, if not most, of the performance properties of coatings are influenced by coating-substrate interactions. Therefore, tests of coatings intact on their end-use substrates must be thoughtfully coupled with free film determinations. Thus dynamic mechanical analysis (DMA) would be useful when interpreted coupled with results of adhesion, abrasion, hardness and others. Since DMA analysis requires preparation of free films, special molds were prepared according to dimensions provided by DMA instrument manufacturer for three point bending mode. Typical storage modulus curves for DAMPK cured with D-RMID or pPhDA were obtained (see Fig. 5). TGDMP/D-RMID show higher modulus value (G`) reaching 200.9 MPa than that of TGDMP/PPhDA which gives 54.2 MPa. This may be attributed to more compact and rigid structure that would be obtained using D-RMID rather than pPhDA. This is also can be ascribed to mesogen structure of D-RMID as early discussed while observing mesomorphic structure of D-RMID by POM and DSC [21]. In addition, TGDMP/D-RMID system exhibited higher Tg (157 °C) compared to TGDMP/ pPhDA system (131 °C). This can be attributed to more restricted chain segment movement through large hydrophenanthrene ring rich system (TGDMP/D-RMID).

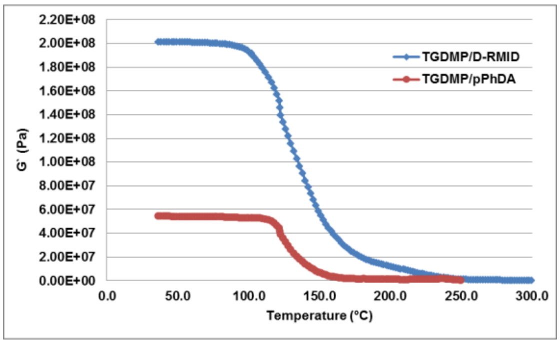


Figure 5: Storage modulus curve for TGDMP/ D-RMID and TGDMP/pPhDA

3.3.2. Thermal stability of cured epoxy resins

The study of the degradation of a thermoset system, namely the derivatives of epoxy resins, has been an object of constant research [26-29]. The information obtained by the controlled degradation of polymer can be used to decide whether a given system will be useful for high temperature application or not.

Su and coworkers [30, 31] and Ren et al. [32] cured liquid crystal epoxy resin (LCER) contained biphenyl (BP) and 4,4`-dihydroxyl-3,3` ,5,5` –tetramethylbiphenyl (TMBP) rigid-rod mesogenic units, with diaminodiphenylsulfone (DDS) and other curing agents. Such resin exhibits excellent thermal properties by retaining the liquid-crystalline (LC) structure during the curing process.

Castell et al. [33] reported a novel LCER combining azine type and BP-type mesogens. Because of the high aspect ratio of the mesogen, the novel LCER, once cured, possessed excellent thermal stability. However, it had to be cured at a higher temperature.

In this section, thermal stability of cured epoxy resins was investigated as a function of curative structure. TG traces were obtained by plotting percent residual weight against temperature and following characteristic temperatures from TG/DTG traces.

Cured samples were scanned from room temperature to 600 °C under nitrogen atmosphere using heating rate of 20 °C/min. Fig. 6 and 7 present TGA thermograms together with differential thermogram (DTG) of TGDMP/D-RMID and TGDMP/pPhDA, respectively. It can be seen that TGDMP/D-RMID experiences 5% degradation at 161.46 °C which may be attributed to moisture, the major loss was observed at 352.52 °C with total loss of 40%. TGDMP/pPhDA shows 5% weight loss while the major loss occurs at 312.17 °C with total 35% loss in weight. This observation reveals the higher thermal stability of TGDMP/D-RMID than TGDMP/pPhDA. It is obvious that the thermal stability was improved by the introduction of D-RMID capable of forming liquid crystal phase. In addition, resemblance in structure of both TGDMP and D-RMID can pose more compact and well packed structures and additional intermolecular interactions.

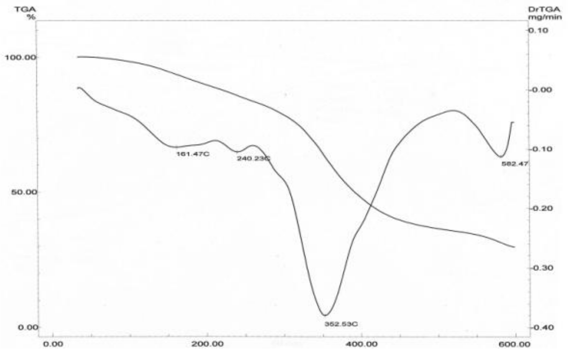


Figure 6: TGA and DTG of cured TGDMP/D-RMID

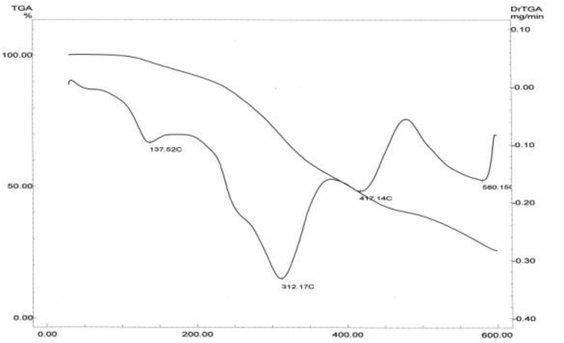


Figure 7: TGA and DTG of cured TGDMP/pPhDA

IV. CONCLUSION

Fully bio-based epoxy resins were synthesized and used to prepare thermoset resins suitable for coating applications. Rosin based crosslinker shows better performance with regard to thermal stability, storage modulus and glass transition temperature. Such behavior is attributed to liquid crystal morphology attained by the bio-based epoxy crosslinker.

V. ACKNOWLEDGEMENT

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