



## Synthesis and Characterization of Novel Dual UV/Thermal Curable Epoxy Rosinate

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### ABSTRACT

Rosin is used in adhesives, printing inks, protective coatings, rubbers and pharmaceutical applications. In this research, novel dual UV/thermal curable epoxy rosin was synthesized by esterification of epoxy resin and purified rosin. Synthesized product was characterized by FT-IR spectroscopy techniques and acid value. UV curable resin was formulated by benzophenone as photoinitiator, dimethyl-p-toluidine (DMPT) as catalyst, trimethylolpropane triacrylate (TMPTA) and hydroxyethyl methacrylate (HEMA) as reactive diluents. Ingredients in formulation of UV/thermal curable epoxy rosin have been balanced for achieving the best properties. Thermal behaviors of cured film were characterized by TGA and DSC. Film properties such as hardness, impact resistance, adhesion, gloss, flexibility, solvent resistance and gel fraction have also been evaluated after UV/ Thermal dual curing. Prog. Color Colorants Coat. 7(2014), 121-128. © Institute for Color Science and Technology.

### 1. Introduction

Gum Rosin or colophony is a light to dark yellow amber, thermoplastic brittle solid resin (glass transition temperature of about 30 °C) obtained from the exudation trees of Pines species (Family–Pinaceae). Rosin is composed of mono carboxylic acids (abietic and pimaric) having the typical molecular formula  $C_{20}H_{30}O_2$  (They are mono carboxylic acids of alkylated hydro-phenanthrene), which contains approximately 90% abietic acid and its isomers that also contain a small amount of non acidic components. It contains a conjugated diene and a tertiary

carboxylic acid group that are present as free acids or dimers or as anhydride formats [1-4]. The unsaturated bond in the resinic acids make it oxidizable by air explosion, causing brittleness increasing. The carboxyl group also involves a weak resistant to alkalis (e.g. sea water) via saponification of the carboxyl group. For commercial purposes, rosin is usually classified according to its color from A, the darkest, to N, extra pale, superior to W, window glass, and WW, water white varieties, the latter having a significantly higher price

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than the ones with usual qualities. This variation in color depends mainly on the age of the tree and the amount of heat applied in distillation. The rosin is used widely in the manufacture of paints and varnishes, adhesives, prints ink, synthetic rubber, cosmetics, dental materials and pharmaceutical due to its low cost and based biomaterials. It was used to obtain new polymers such as polyester imides and polyamid-imide and incorporated in some formulations of unsaturated polyester. Rosin and its derivatives with low percentage are used as an important part in antifouling paint formulations [5-12].

However, it does not possess good properties such as water, alkali and acid resistance which are expected from a surface coating material. Therefore, rosin acids are chemically modified to increase their coating applications but a low amount in formulation. The most modified rosins are limed rosin, ester gum, maleic modified rosin, and rosin modified phenolic resins, obtained by hydrogenation, polymerization and disproportionation of rosin acids [13-17]. In the past, resin acids, specially abietic acid, have been extensively used as raw materials for new polymers with specific chemical structures and valuable properties owing to their three-cyclic structure, resin acids ought to present high enough chemical and thermal stability, but the unsaturated groups from the hydrophenthrene moiety make them vulnerable and give them characteristic chemical reactivity [18, 19] and with this ability we have designed novel UV/thermal cure epoxy rosinates in this respect.

Radiation curing of coatings is a new technology that has advantages including having 100% solid, low energy consumption, low emission, low capital investment, low space consumption, excellent surface properties and marginal substrate heating. On the other hand it has disadvantages such as higher raw material cost, low adhesion to some substrates, curing shrinkage, difficult surface cure in the presence of oxygen, difficult cure of pigmented paint and shadow areas. The dual cure coatings discussed here combine the fast curing mechanism of the UV-curing reaction with thermal, moisture or air drying cure. The dual cure improved scratch resistant and a good adhesion to substrate [20, 21]. The aim of this work was to use the rosin as potential raw material for the production of UV/thermal curable resins as coatings due to its low price, good thermal properties and ability to modify its chemical structures for radiation and thermal curing.

## 2. Experimental

### 2.1. Materials

Rosin (isomers mixture) with acid value of 230 mg KOH/g was supplied from LURESA. Liquid epoxy resin (EPIRAN Resin 828) with  $M_w=376$  g/mol and EEW =188 g was purchased from KZPC (Iran). Para methoxy phenol (PMP), tetrabutylammonium bromide (TBABr), methyl ethyl ketone (MEK) and benzophenone were supplied from Merck Company. Hexandiol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA), hydroxy ethyl methacrylate (HEMA), dimethyl-p-toluiden (DMPT) were purchased from Aldrich Company. All the chemicals were used as received without any purification.

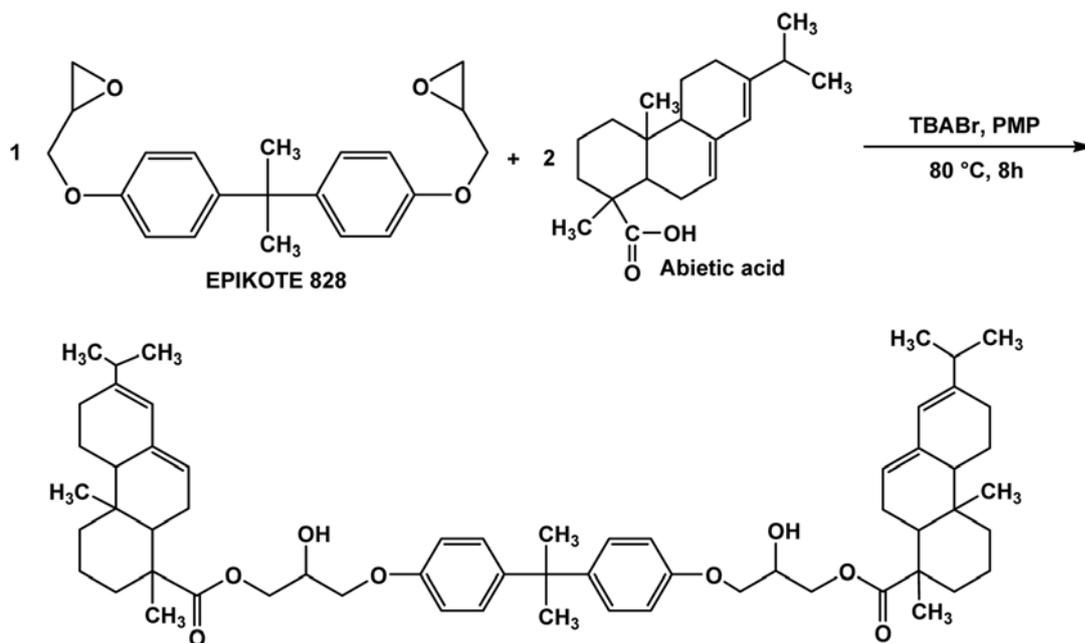
### 2.2. Synthesis of epoxy rosinate and formulation

Epoxy resin (37.6 g, 0.1 mol), Rosin (49 g, 0.2 mol) and 30 ml MEK as solvent was added to a 250 ml three-neck flask, which was equipped with condenser and thermometer. The mixture was stirred for 2 hours at 40 °C with magnetic stirrer until obtaining a homogenous solution. Then, 0.5% w/w PMP as inhibitor and 0.2% w/w TBABr as reaction catalyst were added to the solution, the temperature was raised to 80 °C and the reaction was continued for 10 hours (Scheme 1). Reaction growth (esterification of acid groups in rosin and oxirane groups in epoxy resin) was monitored by controlling acid value. Acid value in the end of the reaction was decreased by 70 mg of KOH. Solvent was evaporated from synthesized resin on vacuum oven condition and was readied for next formulation steps. The synthesized epoxy rosinate was diluted with 7% w/w TMPTA and 15% w/w HEMA and then mixed with 3% w/w photoinitiator and accelerator. The total mixture was stirred for 30 min.

All samples which coated on glass and metal plates (90 microns film) were preheated in oven for 5 min at 40 °C and then were irradiated under UV exposure for 1 min. In the last step all the plates were heated in oven for 30 min at 100 °C.

### 2.3. Characterization and measurements

Perkin Elmer (Spectra 1 model) spectrophotometer was used to obtain the Fourier transformed infrared spectra (FT-IR).



**Scheme 1:** The synthesis reactions of epoxy rosinate.

The analyses were done in wave number range of 400-4000 $\text{cm}^{-1}$  with 1 $\text{cm}^{-1}$  resolution and 40 scans in ambient temperature (25 °C).

The thermal stability of the cured epoxy rosinate (Eprose) sample was studied in nitrogen environment using a thermogravimetric analyzer (Perkin Elmer Company, Pyris Diamond TG/DTA). The measurements were carried out from 30 to 600 °C at a heating rate of 10 °C/min. Differential Scanning Calorimetry (DSC) of the cured epoxy rosinate (Eprose) sample and glass transition temperature ( $T_g$ ) was studied using a (Perkin Elmer company, Pyris Diamond DSC). The measurements were carried out from 30 to 400 °C at a heating rate of 10 °C/min.

UV-curing machine from Run Wing M&E Company (China), RW-UV 2BP model, equipped with high pressure mercury lamp (2kw 365 nm) with 0.5-10 m/min speed.

#### 2.4. Mechanical properties

Physical and mechanical properties (hardness, gloss, impact resistance and adhesion) of resulting product were determinates according to ASTM test methods.

Synthesized resin after formulation was coated on prepared mild steel panels and glass plate (10×15 cm) with 90 microns thickness by applicator. König pendulum hardness of cured films determined with a BYK-Gardner pendulum hardness tester and the values are reported in seconds (ASTM D4366). The adhesion performance of the enamel was tested with commercial cello tape according to the cross-cut adhesion test method (ASTM D3359). The results are presented using a rating of 0B for a poor adhering coating through 5B for a very good adhering coating. The gloss characteristics of the films were determined according to ASTM D523, with an Erichsen gloss master Model 507, over a resin-coated mild steel panel at an angle incidence of 20° and 60°. The ability of coating to withstand extension without cracking when the deformation is applied rapidly (Impact resistance) was evaluated by ASTM D 2794-23. Mandrel bend test of coatings was performed according to ASTM D522-93. The average of ten measurements was reported for all the results.

#### 2.5. Chemical properties

The Acid value of the synthesized resins was determined

by the conventional method according to ASTM D639-90. For this case samples were taken during the reactions and solved in mixture of MEK/acetone (70/30 w/w) and was titrated. Solvent resistance of organic coating material (xylene, MEK rub test) was evaluated according to ASTM D-5402-93 and in this research the most common test of solvent resistance which is important, was the MEK double rub test measuring.

Gel fraction is an important property of any coating. This parameters is indicate the cross linking density of coating. The gel fraction of cured samples were evaluated with thermal, UV and dual curing (UV/thermal) technique. For this reason the samples were weighed after curing and immersed in MEK and soxhelted for 4 hr at 80°C. Then samples were dried at 80°C in vacuum to reach a constant weight. The gel fraction of the samples was calculated using equation 1:

$$\text{Gel fraction (\%)} = [\text{Weight after extraction} / \text{Initial weight}] \times 100 \quad (1)$$

### 3. Results and discussion

#### 3.1. FT-IR analysis

The characteristic peaks in the FT-IR spectra of rosin are observed as wide strong peak at 3300-3400  $\text{cm}^{-1}$  for O-H stretching vibration of COOH groups, sharp strong peak at 3075  $\text{cm}^{-1}$  for C-H ( $\text{sp}^2$ ) stretching vibration of hydrophenanthrene moiety. The C-H ( $\text{sp}^3$ ) stretching vibration peaks are at 2953, 2996 and 2869  $\text{cm}^{-1}$  and strong carbonyl peak at 1697  $\text{cm}^{-1}$  relates to COOH groups. The  $\text{CH}_2$  bending vibration and  $\text{CH}_3$  bending vibration can be seen at 1470  $\text{cm}^{-1}$  and 1385  $\text{cm}^{-1}$ , respectively (Figure 1(a)).

The characteristic peak in the FT-IR spectra of Eprose was observed at 3476  $\text{cm}^{-1}$  as sharp medium O-H (alcohol) stretching vibration from opened oxiran ring which show that acid group is consumed and hydroxyl is generated in the reaction. The sharp strong C-H ( $\text{sp}^3$ ) stretching vibration is indicated at 2953, 2936, 2873  $\text{cm}^{-1}$ . The C-H ( $\text{sp}^2$ ) stretching vibration in aromatic ring (Epoxy) and saturated/unsaturated band of rosin was at 3075  $\text{cm}^{-1}$ . The sharp strong band at 1727  $\text{cm}^{-1}$  corresponds to carbonyl in ester groups. The  $\text{CH}_2$  bending vibration was at 1470  $\text{cm}^{-1}$  and  $\text{CH}_3$  bending vibration was at 1385  $\text{cm}^{-1}$ . At 1052  $\text{cm}^{-1}$  a strong sharp peak can be seen which belongs to single C-O band stretching in ester linkage (Figure 1(b)).

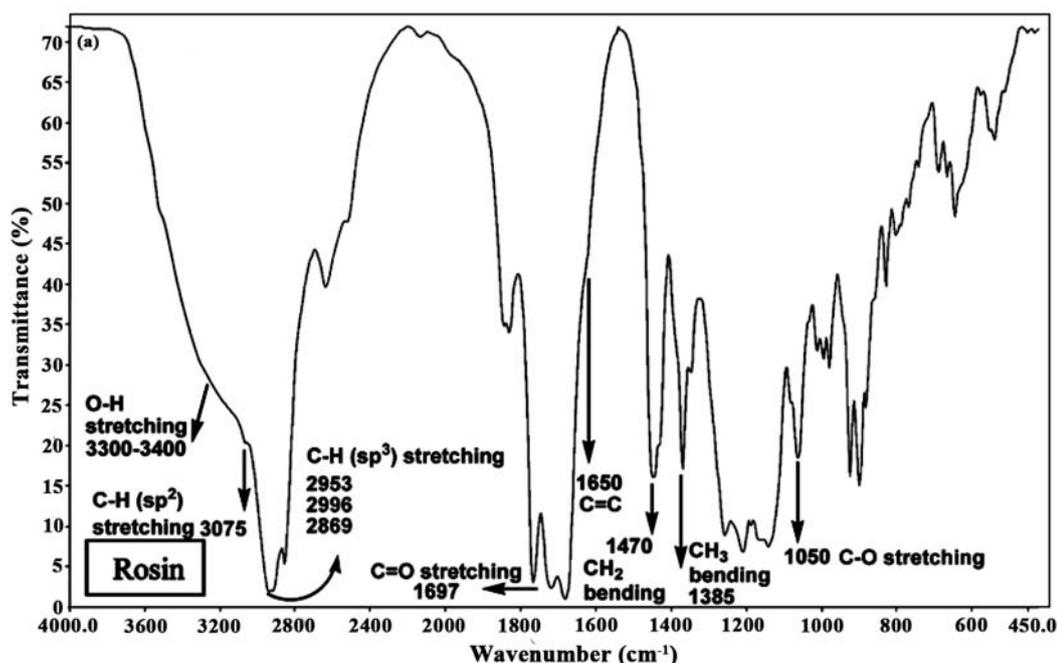


Figure 1: The FT-IR spectra of (a) rosin and (b) eprose.

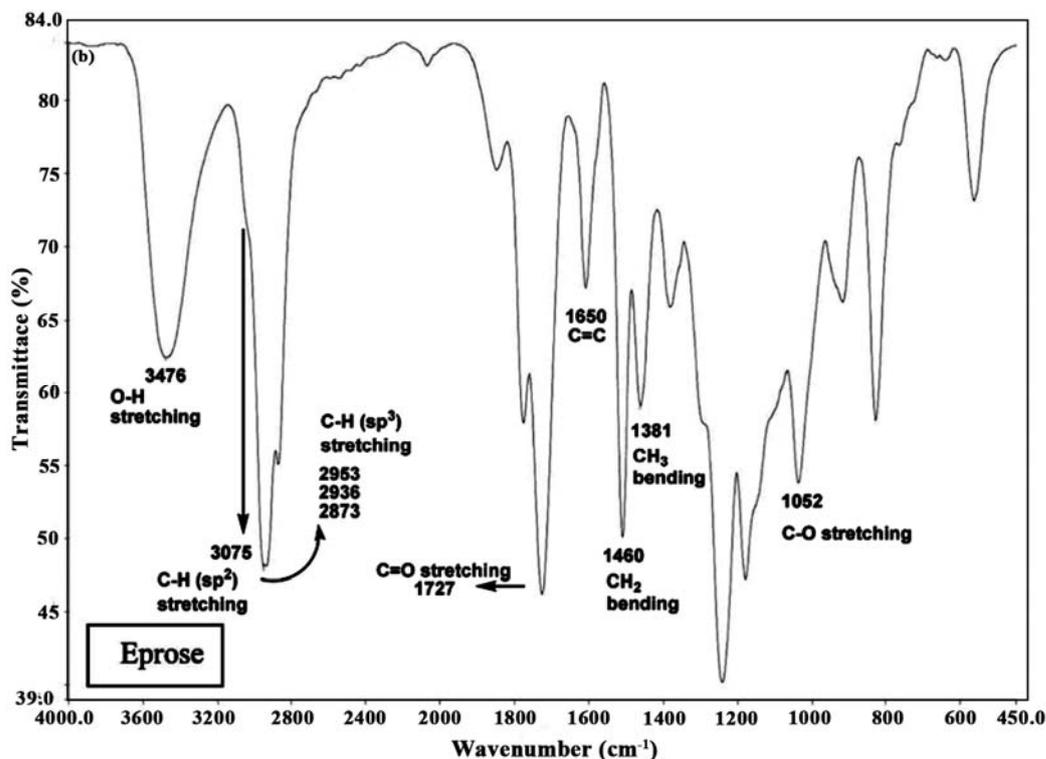


Figure 1: Continued.

### 3.2. Thermal analysis

The thermal behavior of Eprose was evaluated by DSC and TG-DTA. The DSC thermogram is shown in Figure

2 and the glass transition temperature ( $T_g$ ) was found to be 25°C. In this case,  $T_g$  can be at ambient temperature for coating application to form a flexible film.

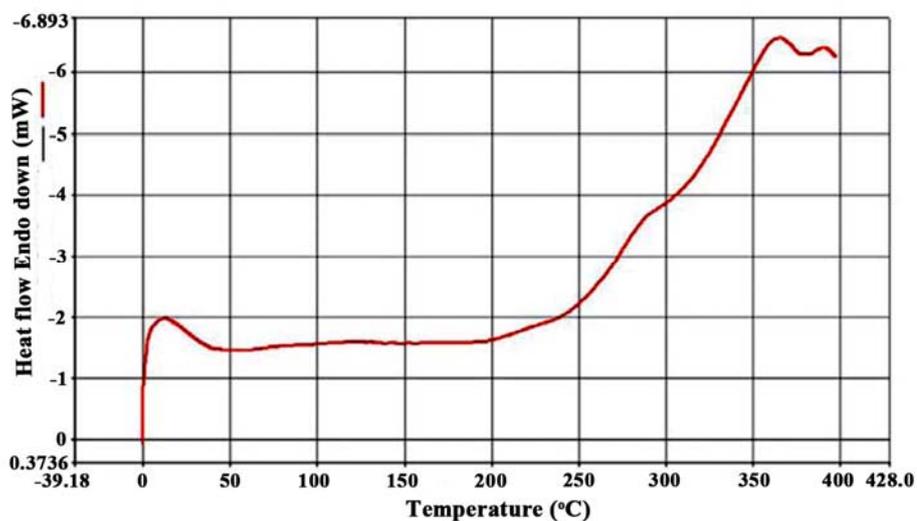


Figure 2: DSC thermogram of epoxy rosinat.

As shown in Figure 3, the initial decomposition temperature (Td) was around 360°C. It is indicated that the coating composition begins to decompose at this temperature and this point in DSC thermogram shows subsidiary endothermic decomposition of coating. The high values of Td of Eprose synthesis are attributed to the thermally stable cyclic structure of the rosin base and this partial composition in the coating formulation.

### 3.3. Film properties

Epoxy-rosinate in optimum formulation was cured with dual UV/thermal curing. Flexibility of coatings was tested by conical mandrel. The results shown that with increasing the cross link density the flexibility is decrease. The other properties of the coatings such as adhesion, solvent rub resistance and hardness were not acceptable (Table 1). In the formulation for steel protective coating, acceptable mechanical and chemical properties along with a good cross link density are necessary.

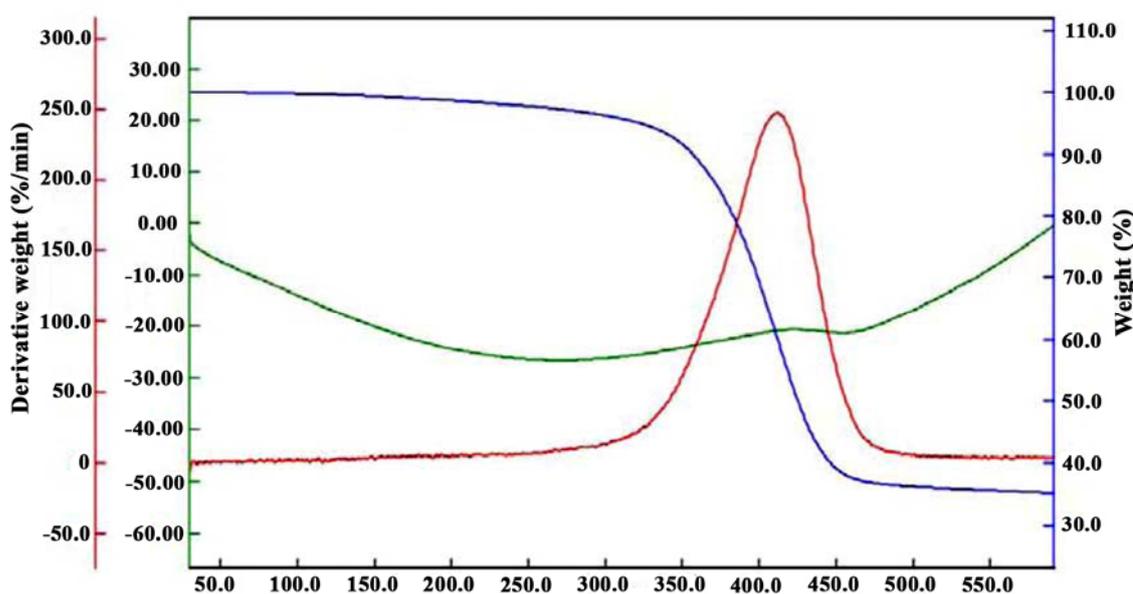


Figure 3: TGA thermogram of epoxy rosinate.

Table 1: Properties of the film.

Test/standard	Conditions	Results (Unit)
Hardness/ASTM D4366	90 $\mu$ /glass plate	180 (sec.)
Specular gloss/ASTM D523-89	90 $\mu$ /glass plate	Gloss at 20°: 140 Gloss at 60°: 130
Rapid deformation (Impact)/ASTM D2794-93	90 $\mu$ /metal panel	>40 direct >80 indirect
Conical mandrel- ASTM D522-93	90 $\mu$ /metal panel	No crack
Adhesion (cross – cut)/ASTM D3359-02	90 $\mu$ /metal panel	5B
Solvent rub/ASTM D5402-93	90 $\mu$ /metal panel	>100

**Table 2:** Gel fraction and chemical properties of coatings.

Method	Properties	
	Gel fraction	MEK-Rub
Thermal curing*	75%	Pass
UV curing**	60%	Failed
Dual UV/thermal curing***	95%	Pass

\*1hr in 110 °C, \*\* 3 min in UV cabinet, \*\*\* First 3min UV a then 30 min in 100 °C.

### 3.4. Chemical properties

The results of gel fraction and chemical resistance of coatings are presented in Table 2. In thermal curing the efficiency of the initiator for polymerization is low and only the unsaturated part of the rosin will convert to dimers. While in UV curing the unsaturated part of acrylate/metacrylate, diluents and rosin polymerized without any contact to form uni-polymer network. In the dual UV/thermal curing technique first photo initiator completely convert to radical and started the radical polymerization then after increasing the viscosity under growth of temperature curing will be complete via convert to three dimension network.

### 4. Conclusion

The high rates of polymerization, in UV curing process

caused the shrinkage and then generally observed poor adhesion to smooth metal surfaces for this coating group. UV/thermal curing process is one of the techniques that is suitable for pigmented coatings. In this technique at first the coatings were cured under the UV irradiation and complete curing were achieved by thermal energy. Heating after UV curing relaxes the cross-link network and often improves adhesion. The screening study leads to the conclusion that all formulation parameters affect the coating properties such as adhesion, hardness, gloss, impact and curing process time and temperature. This formulation can be suitable for printing inks and graver specially.

This study also confirms the modification of rosin with epoxy resin for UV-curable application. In future research by changing in molar rate of materials we can synthesize a new product for UV curing systems.

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