Preparation of Water-based Epoxy Resin and Its Application as an Automotive Air Filter Paper Binder

Yuanhuo Ji,[a] Hui Qiao,[a,b] Yun Liang,[a,b] Guilong Xu,[a,b]* Yi Wang,[a,b]* and Jian Hu [a,b]

Water-based epoxy resin emulsion was prepared by emulsifying *o*-cresol formaldehyde epoxy resin with self-emulsified epoxy curing agent synthesized in this study and then used as an environmentally friendly binder for automotive air filter paper. The preparation process of the self-emulsified epoxy curing agent was confirmed by Fourier transform infrared spectroscopy (FTIR). The effects of neutralization degree (Neu) and amount of curing agent on the formation of epoxy resin emulsion were studied. The micro-morphology and size distribution of the epoxy resin latex were characterized by transmission electron microscopy (TEM) and dynamic and static light scattering, respectively. The micro-structure of the air filter paper surface was studied by scanning electron microscope (SEM). The mechanical strength and moisture-resistance properties of air filter strengthened by the prepared water-based epoxy resin emulsion was tested and compared to three commercial binders. The prepared epoxy resin emulsion greatly enhanced the mechanical properties and moisture-resistance properties of the air filter paper while maintaining its filtration properties. Therefore, the epoxy resin emulsion can be used as an environmentally friendly water-based binder for automotive air filter paper with excellent comprehensive properties.

Keywords: Water-based epoxy resin; Automotive air filter paper; Moisture-resistance

Contact information: a: State Key Lab of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China; b: National Engineering Research Center of Papermaking and Pollution Control, South China University of Technology, Guangzhou, 510640, China;
** Corresponding author: feglxu@scut.edu.cn; wangyi@scut.edu.cn*

INTRODUCTION

An automotive air filter paper protects the engine air intake system by removing particle contaminants (Nutter and Sitter 1970; Healey 2003; Storz and Winkel 2005). Automotive air filter paper is normally made of cellulose fibers. However, due to the hydrophilic nature of the cellulose fiber and weak bonds between cellulose fibers, the filter paper has shortcomings such as poor mechanical strength and poor moisture resistance. Therefore, binders are necessary to enhance the properties of air filter paper so that it can meet the requirements of industrial applications (Diehl 1988; Cusick 1999; Yu *et al*. 2014). Latex binders, such as poly-acrylate latex, poly-styrene-acrylate latex, poly-styrene-butadine latex, and polyvinyl acetate latex (Bartley and Yodice 2006; Kern *et al*. 2006; Hutten 2007), are the most commonly used binders for automotive air filter paper due to their excellent adhesive and film formation properties as well as their environmentally friendly nature. However, automotive filter paper treated with latex binders suffer from deformation (or dimensional instability) under high moisture conditions due to the hygroexpansion of cellulose fibers, leading to dimensional instability of the filter core, which can cause engine malfunction (Joseph 1983). These latex binders are thermoplastic resins with a molecular network that is linear. Water vapor molecules penetrate easily into the polymer chain network, leading to hygroexpansion of the cellulose fabric.

To reduce the negative effect of water vapor or humidity on air filter paper, an ideal binder should have excellent mechanical strength and water resistance. Adding a cross-linking agent such as melamine-formaldehyde (MF) resin to the latex binder can improve its moisture resistance to some extent but not enough to meet the requirements of practical applications under high moisture conditions. Phenolic (resol) is a thermoset resin with excellent mechanical and water resistance properties when applied as a binder for cellulose fabric. However, commercial alcohol-based phenolic resins are normally used as a binder for automotive oil filter paper but not for air filter paper (Layte 1954; Jesse *et al.* 2017 Hörl *et al.* 2016). From an environmental perspective, alcohol-based phenolic resin is not a water-based resin, and the poisonous gas formaldehyde is released from the phenolic resin. Therefore, an environmentally friendly thermoset resin as a binder for automotive air filter paper is in great demand. Epoxy resin is another thermoset resin that has excellent mechanical and moisture resistance properties. However, each epoxy resin has its own properties, and it is difficult to know which kind of epoxy resin is suitable for automotive air filter paper. Studies on water-based epoxy resin as the binder for air filter paper are seldom reported. Therefore, an environmentally friendly binder that provides the air filter paper with excellent mechanical and moisture resistance properties is in urgent demand for academic research and industrial applications.

In this study, *o*-cresol formaldehyde epoxy resin was chosen as the binder on account of its unique molecular structure. By using a self-emulsified epoxy curing agent synthesized in as a emulsifier, the water-based epoxy resin emulsion was prepared by a phase-inversed method so that a water-based binder was obtained. The comprehensive properties (including mechanical strength and moisture-resistance property) of the air filter paper strengthened by the prepared water-based epoxy resin emulsion was tested and compared to other commercial binders. It is expected that the large-scale production of this water-based epoxy resin emulsion will enable practical industrial applications.

EXPERIMENTAL

Materials

Bisphenol A epoxy resin E-44 (epoxy equivalent 222.2 g/mol) was provided by Dongfang Resin Co. Ltd. (Foshan, China). Butyl glycidyl ether (BGE), acetic acid, triethylenetetramine, and 1,4-dioxane were purchased from Aladdin Co. Ltd. (Shanghai, China). Pristine air filter paper composed of 97wt.% cellulose fiber and 3 wt.% glass fiber) was provided by Huachuang Chemical Materials Science and Development Co. Ltd. (Guangzhou, China). The *o*-cresol formaldehyde epoxy resin (epoxy equivalent 222.0 g/mol, average molecular weight of 1800) was provided by Weilina Trade Co. Ltd. (Guangzhou, China).

Preparation of Self-emulsified Epoxy Curing Agent

First, 45.6 g of epoxy resin E-44 (0.1 mol), 10.0 g of 1,4-dioxane, and 29.2 g of triethylenetetramine (0.2 mol) were placed in a 250-mL three-necked round bottom flask equipped with a stirrer, a condenser, and an addition funnel. The reaction mixture was heated to 65 °C under stirring for 4 h to form product I. The system was raised to 70 °C, and 26.0 g (0.2 mol) of BGE was added. The reaction was continued for another 3 h to form product II (Li 2016). The solution was cooled to 50 °C and neutralized by various amounts of acetic acid to obtain a self-emulsified epoxy curing agent with various neutralization degrees. The neutralization degree (Neu) was defined as the mole ratio of acetic acid to the secondary amine groups(-NH-) of the curing agent. The preparation of self-emulsified water-based epoxy curing agent is shown in Fig. 1.

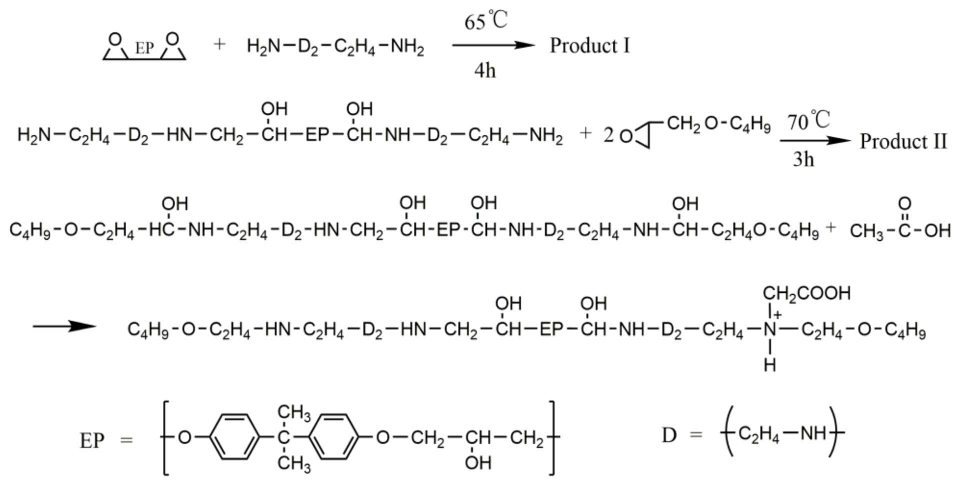


Fig. 1. The schematic of preparing self-emulsified water-based epoxy curing agent

The Neu value of a curing agent has great effect on the hydrophilicity of the curing agent and therefore influence its own emulsify properties. The hydrophilicity of curing agent increased as the Neu increased, which was due to the dissociation of the secondary amine groups on the curing agent chains, and therefore easier to form an emulsion. A higher Neu value has a negative effect on the anti-water properties of the cured resin. The effects of Neu on the water solubility of the curing agent is shown in Table 1. The neutralized curing agent became a transparent liquid when the Neu is 15%, indicating that the neutralized curing agent has excellent hydrophilicity and emulsifying properties when the Neu is above 15%.

Table 1. Effects of Neu on Water Solubility of the Curing Agent

Neu (%)	Result
5.0	Insoluble
7.5	White Emulsion was formed and stable, sediments found in 2months
10.0	Blue Emulsion, stable >3months
12.5	Semi-transparent blue liquid, stable >3months
15.0	Transparent liquid, stable >3months
20.0	Transparent liquid, stable >3months

Formation of Epoxy Emulsion

The *o*-Cresol formaldehyde epoxy resin was dissolved in an appropriate amount of 1,4-dioxane at 80 °C. After cooling to 50 °C, an appropriate amount of prepared self-modified epoxy curing agent was added and mixed for 0.5 h. Emulsification was carried out by dropping deionized water slowly into the mixture solution with the stirring speed at 1000 rpm, until a well-dispersed emulsion was formed. The formation of the epoxy emulsion is shown in Fig. 2.

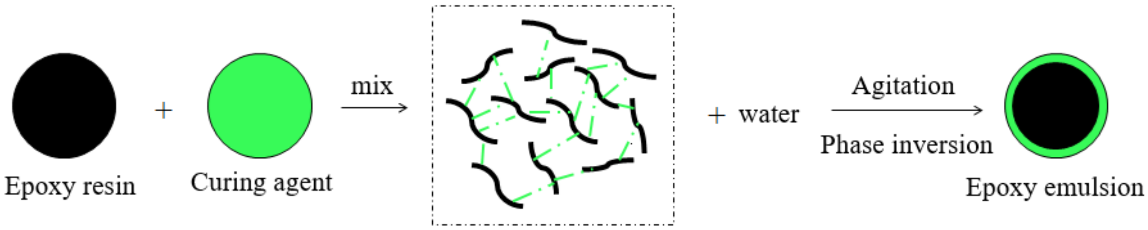


Fig. 2. Formation process of water-based epoxy resin emulation

Impregnation of Air Filter Paper

The prepared water-based epoxy emulsion and other commercial binders were diluted to an appropriate concentration. Then, pristine air filter paper was dipped into the diluted resin solution. After the pristine air filter was completely wetted for 3 min, the wetted air filter paper was removed and dried in an oven at 100 °C for 30 min, and then cured at 130 °C (160 °C for phenolic resin). The impregnated binder accounted for 20 ± 0.5 wt% of the pristine air filter paper.

Characterization

FTIR spectra were acquired on a Fourier transform infrared spectrometer (VERTEX 33, Bruker, Karlsruhe, Germany). The micro-morphology of filter paper was observed by scanning electron microscopy (S-3700N, Tokyo, Japan). A stiffness tester (TMI 79-25-00-0002, New Castle, DE, USA), bursting strength tester (L&W CE-180, Zurich, Sweden), and tensile strength tester (L&W SE-062) were used to measure the stiffness, bursting strength, and tensile strength (average of 10 test values), respectively, of the experimental air filter paper. The wet mechanical properties of the air filter paper were tested by the same method, but the air filter papers were dipped into a 0.1% NP-10 solution for 3 min and then wiped with absorbent cotton before testing. The average particle size of epoxy latex and the particle size distribution (PSD) were measured by a Malvern particle size analyzer (ZS-Nano-S, London, UK). Transmission electron microscope (TEM) measurements were performed by a transmission electron microscope (Model JEM-1400plus, Tokyo, Japan). The moisture-resistance of the filter paper tested by putting a 30 cm × 30 cm air filter paper in a temperature and humidity chamber (under 35 °C, humidity at 98%) for 96 h. The elongation rate (ER) was calculated as follows,

$$\text{ER (\%)} = (L_{\text{aft}} - L_{\text{bef}})/L_{\text{bef}} \times 100 \quad (1)$$

where L_{bef} and L_{aft} represent the length of filter paper before after putting in the temperature and humidity chamber, respectively.

RESULT AND DISCUSSION

FTIR spectra of the prepared self-emulsified epoxy curing agent

Figure 3 shows the FITR spectra of prepared self-emulsified epoxy curing agent. There was a characteristic absorption peak located at 912 cm^{-1}, which is attributed to the asymmetric a stretching vibrations of the epoxy ring group. The curve b shows that epoxy ring was opened after a reaction with triethylenetetramine, and therefore the intensity of epoxy group characteristic peaks disappeared, and a new absorption peak of –NH– group occurred at 3300 cm^{-1}, which indicated that product I has been formed. While in the curve c, the new absorption peak at 722 cm^{-1} was due to the $–C_4H_9$ group of BGE. The FTIR spectra approved that the reactions proceeded as expected.

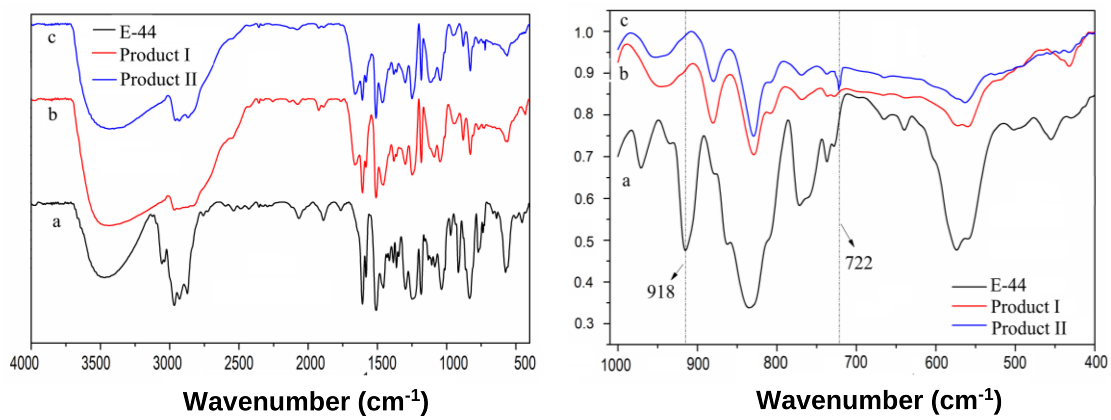


Fig. 3. FTIR spectra of the prepared curing agent

Effects of Neu and Amount of Curing Agent on the Formation of Epoxy Resin Emulsion

The effects of Neu and amount of curing agent on the formation of epoxy resin (*o*-cresol formaldehyde epoxy resin) emulsion are shown in Table 2. An emulsion was not easily formed when the Neu of curing agent was lower than 15%. In fact, an emulsion was not obtained even when the amount of curing agent was 1.2 times the theoretical value. An emulsion was obtained when the Neu value of the curing agent was 17.5% and the amount of curing agent was just the theoretical amount, but the shell life was less than 3 weeks, indicating that the obtained emulsion was still unstable for industrial application. However, a stable emulsion with excellent stability was obtained when the Neu of curing agent was 20%. An emulsion can be obtained when the Neu of curing agent is higher, but a higher degree of neutralization of curing agent has a negative effect on the anti-water properties of the cured resin. Therefore, the optimum Neu of curing agent condition for the formation of epoxy resin emulsion was judged to be 20%, and the amount of curing agent is the theoretical value amount of curing agent.

Table 2. Effect of Neu and Amount of Curing Agent on Formation of Epoxy Resin Emulsion

Neu (%)	15	15	17.5	20	20	22.5
MH: MEp	1.5:1.0	1.2:1.0	1.2:1.0	1.2:1.0	1.0:1.0	0.95:1.0
WC: WEp	1.00:1.00	0.80:1.00	0.82:1.00	0.85:1.00	0.72:1.0	0.78:1.0
result	√	×	√	√	√	√
Shell life	>3month	---	3 week	>3month	3 month	>3 month

Note: MH: MEp, the stoichiometry ratio of active hydrogen equivalent to epoxy group; WC: WEp, the weight ratio of curing agent to epoxy resin; √, emulsion can be formed, ×,emulsion cannot be formed

Micro-morphology and Size Distribution of Epoxy Latex Emulsion

The latex particle morphology and the particle size distribution in the prepared water-based epoxy emulsion were investigated by TEM and a granularity measurement instrument. The results are shown in Fig. 4. It is apparent from the image that the prepared water-based epoxy resin latex particles present as uniformly dispersed nearly-spherical structures in the water phase, indicating that the phase inversion process occurred as depicted in Fig. 2, and a stable emulsion system was successfully obtained. Figure 4(b) illustrates the particle size distribution of the epoxy latex particle. The average particle size of the water-based epoxy resin emulsion was about 120 nm, which is accordance with the TEM observation. In addition, the particle size distributions of water-based epoxy emulsion were narrow. These results demonstrated that a stable water-based epoxy resin emulsion was successfully prepared.

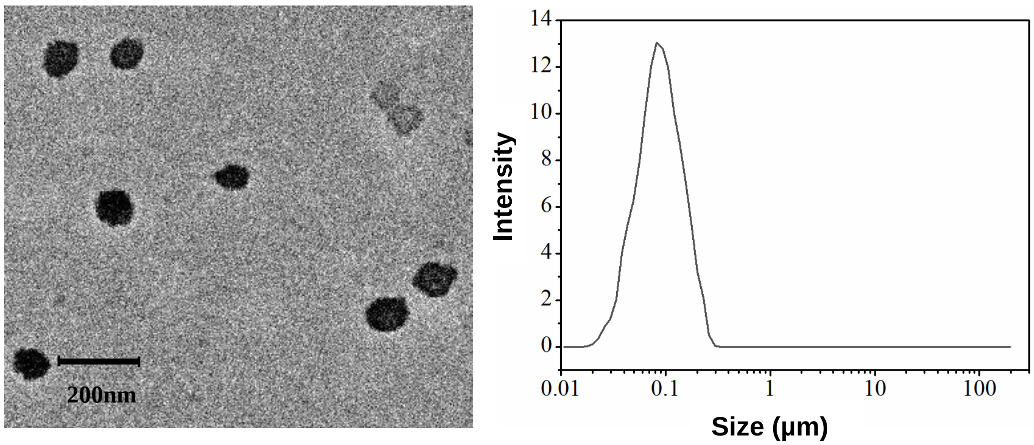
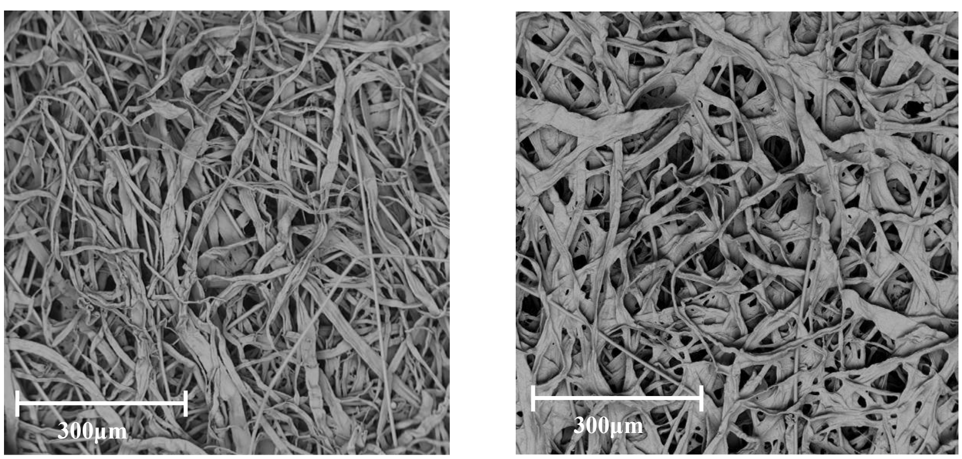


Fig. 4. (a) Micro-morphology of epoxy resin latex; (b) Particle size distribution of epoxy latex



(a) (b)

Fig. 5. Micro-structure of filter paper: (a) pristine filter paper; (b) coated with water-based epoxy resin

Micro-structure of Air Filter Paper

The surface micro-structure of the filter paper before and after being treated by the water-based epoxy resin was observed by SEM, as shown in Fig. 5. Comparing the micro-structure of water-based epoxy resin treated air filter paper (Fig. 5b) with the pristine air filter paper (Fig. 5a), the epoxy resin was mainly coated on the fiber surface and the conjuncture of fibers, which indicated that the pore structure of the filter paper can be well preserved after coating with the water-based epoxy resin. Binders coated on the top of the fiber can greatly change the hydrophilicity of the surface, while binders coated on the conjuncture of fibers act as an adhesive and greatly enhance the binding force between fibers, therefore improving the mechanical strength of the air filter paper and limiting hygroexpansion of cellulose fibers.

Mechanical Strength and Moisture-resistance Properties of Air Filter Paper

The comprehensive mechanical strength and moisture-resistance properties of air filter paper strengthened by the prepared water-based epoxy resin and other binders, including commercial alcohol-soluble phenolic resin (APF, for oil filter paper application), commercial poly-styrene-acrylate emulsion (PSA, for air filter paper application), and E-44 epoxy emulsified by the prepared self-emulsified curing agent(E-44) are shown in Table 3. Air filter paper treated with AFP binder had the best dry and wet mechanical strength and moisture resistance properties. The performances of air filter paper strengthened by the prepared water-based epoxy resin were similar to the commercial AFP binder, while filter paper treated with E44 and PA resin showed the worst mechanical strength and worst moisture resistance properties, respectively. The performance differences of the treated air filter paper were mainly due to the polymer backbone structure and the cross-linking degree of the different binders.

Table 3. Mechanical Strength and Moisture-Resistance Properties of Air Filter Paper

Binders	Bursting Strength (KPa)		Stiffness (mN•m)		Tensile Strength (kN/m)		Moisture Resistance (Elongation)	
	Dry	Wet	Dry	Wet	Dry	Wet	Portrait	Landscape
Pristine filter paper	86	----	0.72	---	0.58	---	4.3%	10.4%
PSA	263	89	1.96	0.87	2.68	0.72	2.2%	3.2%
APF	315	189	2.25	1.25	3.32	1.56	0.6%	0.6%
E-44	235	109	1.68	0.98	2.54	1.02	1.2%	1.6%
Water-based epoxy resin	298	162	2.23	1.36	3.17	1.43	0.8%	1.0%

Note: "---" means that the testing value is less than the instrument test range.

The polymer backbone structure of cured phenolic resin is a highly cross-linked network composed of benzene rings linked by methylene groups. This backbone structure demonstrates not only excellent mechanical strength but can also effectively stop the water molecular form penetrating through the polymer molecular network (Hu *et al*. 2011). Combined with the cellulose fiber, phenolic resin can endow the treated air filter paper with excellent dry mechanical strength, wet mechanical strength, and moisture resistance properties. The *o*-cresol formaldehyde epoxy resin was chosen to prepare the water-based epoxy resin in this study as the binder. The preparation procedure and molecular structure of *o*-cresol formaldehyde epoxy resin (Wang and Liao 1991; Huang *et al*. 2005) is as shown in Fig. 6. According to the reactions depicted in Fig. 6, formaldehyde is expected to be consumed in the reaction and irreversibly converted to a completely different form. The resin structure has about 10 epoxy ring groups. The cured epoxy resin presents a high cross-linking density and therefore shows excellent moisture resistance. However, the main polymer chain of the *o*-cresol formaldehyde epoxy resin is similar to that of the phenolic resin; therefore, the mechanical properties of filter paper strengthened by the prepared water-based epoxy emulsion is similar to that of the phenolic resin. A PSA binder with appropriate glass transition temperature (T_g) presents excellent dry mechanical properties, but due to the fact that PSA resin is a thermoplastic resin, the molecular network of thermoplastic resin is a linear structure, which cannot effectively prevent water molecular form penetrating through its polymer molecular network and consequently deteriorating the strength properties of PSA resin. Therefore, PSA resin treated filter paper presents poor wet mechanical strength and moisture-resistance properties. E-44 is also a thermoset resin and therefore presents relatively good moisture resistance. However, the air filter treated with E-44 presented poor mechanical strength because its polymer backbone structure is quite different from the phenolic resin.

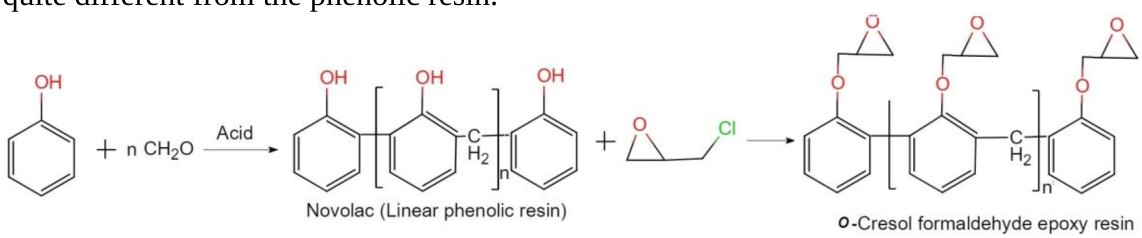


Fig. 6. Preparation procedure and molecular structure of *o*-cresol formaldehyde epoxy resin

CONCLUSIONS

1. A water-based epoxy resin emulsion was successfully prepared by emulsifying *o*-cresol formaldehyde epoxy resin with self-emulsified epoxy curing agent. The prepared water-based epoxy resin emulsion was applied as an environmentally friendly binder for strengthening automotive air filter paper.
2. When the neutralization degree (Neu) of the curing agent is 20% and the amount of curing agent is the theoretical value amount of *o*-cresol formaldehyde epoxy resin, a stable epoxy resin emulsion with a nearly-sphere structure latex particles can be obtained. Air filter paper treated by the prepared water-based epoxy resin emulsion maintains its pore size and filtration properties.
3. The mechanical strength and moisture-resistance properties of air filter paper treated by epoxy resin emulsion is similar to the air filter paper treated by the commercial alcohol soluble phenolic resin and much better than that of the commercial PA latex emulsion and E-44 epoxy emulsion. These results show that the unique molecular structure of the *o*-cresol formaldehyde epoxy resin can replace phenolic resin and act as a water-based binder.

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