

Recent Development of Cardanol Based Polymer Materials-A Review

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Abstract: Polymers from renewable resources are receiving tremendous attention due to the increasing concerns on the depletion of fossil oils and deteriorated environments. Cardanol, as an abundant and renewable chemical raw material, has been widely used for the production of renewable polymer materials via converting into various of chemical monomers with active functional groups. This comprehensive review deals with various aspects of cardanol as a starting material the preparing various polymer and polymer composites such as benzoxazine resins, phenolic resin, polyurethanes, epoxy resin, vinyl ester polymers, polyamide and cyanate ester resins. The assessment of the future prospects for the use of cardanol to synthesise novel and valuable renewable materials is presented.

Keywords: Cardanol; sustainable synthesis; platform chemical; epoxy resin; polyurethane

1 Introduction

Cardanol is one of the most important green industrial raw material refined from natural cashew nut shell oil (CNSL). CNSL is a kind of agricultural by-product produced by pyrolysis or supercritical carbon dioxide extraction of natural cashew shell. CNSL mainly contains cashew acid, cardanol, cardiac phenol and dimethyl cardiac acid, which was firstly reported by Stadeler in 1847 [1-4], as seen from Fig. 1. Cardanol has become a research hotspot in recent years and has been widely used in coatings, adhesives and plasticizers due to its low price, abundant sources, excellent performance and renewability [3-8]. Cardanol presents pale yellow oily liquid. It cannot dissolve in water, but easily dissolve in organic solvent such as ether, petroleum ether and chloroform. Chemical structure of cardanol was determined by Dowson and the results showed that cardanol is a kind of monophenol derivative [9]. Cardanol was identified as 3-alkylphenol via cryogenic fractional crystallization by Paul [10]. The characteristics of side chains in cardanol were investigated by Loev, it contains 0-3 of unsaturated bonds [11]. Based on the above studies, the chemical structure of cardanol is $C_{21}H_{32}O$ and possess a phenol structure and three long carbon chains with double bonds. At the same time, the properties of phenolic compounds, hydroxyl groups and double bonds make it easy to be chemically modified. Cardanol has the characteristics of both aromatic compounds and aliphatic compounds. The special chemical structure makes it high temperature resistance, good flexibility, excellent hydrophobicity and low permeability [12]. Therefore, cardanol can potentially replace phenol in many applications with equivalent or better property. Some reviews have reported the composition, separation, purification chemical reactions and applications of cardanol [13-16]. This comprehensive review deals with various aspects of cardanol as a starting material for preparing various polymer and polymer composites such as benzoxazine resins, phenolic resin, polyurethanes (PUs),

epoxy resin, vinyl ester polymers, polyamide and cyanate ester resins.

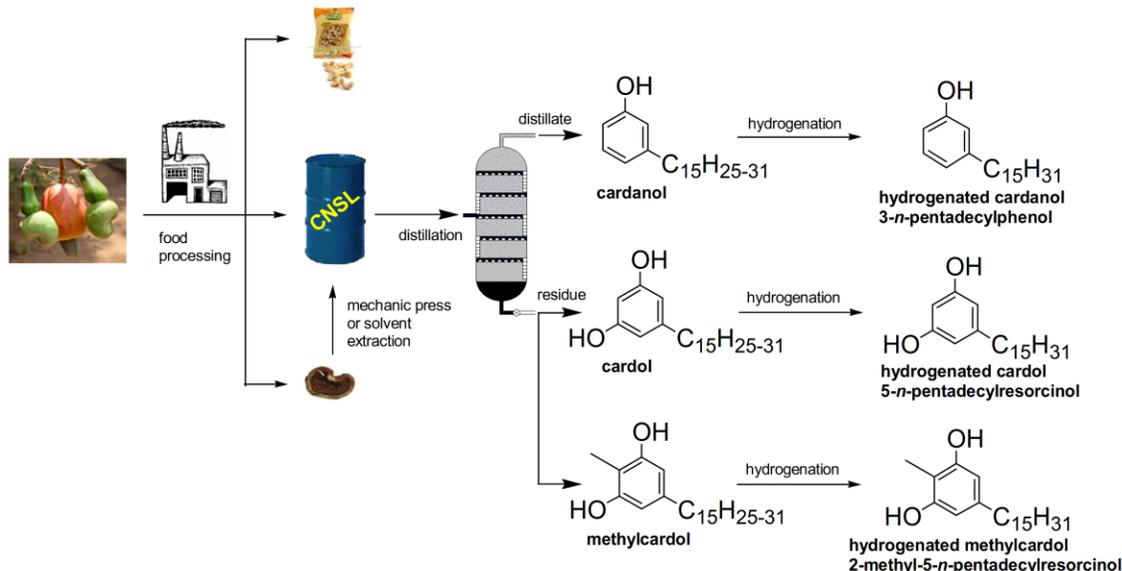


Figure 1: Components and products from CNSL

2 Research Progress of Cardanol Based Polymer Materials

2.1 Cardanol Based Benzoxazine Resins

Benzoxazines are new type high-performance thermosetting resins synthesized from low-cost raw materials, such as phenols, formaldehyde and primary amines [17]. The benzoxazine monomer is a compound containing nitrogen and oxygen hexahydroxy heterocyclic structure generated by the Mannich-like condensation either by employing solution or solventless methods [17-18]. The polymerization of benzoxazine monomers takes place through thermally accelerated ring-opening mechanism without adding initiator or catalyst, near-zero shrinkage, tractability and doesn't release toxic by-products [16-26]. Compared with traditional phenolic resins, polybenzoxazines has drawn a lot attention due to its unique advantages: low dielectric constant, low water absorption, good thermal and chemical stability, high mechanical properties [19-20]. Another advantage for these polymers is the great molecular design flexibility of its monomer. Benzoxazine can be synthesized from a phenolic compound, a primary amine and aldehydes, enabling to vary other properties of the polymer [17-26]. In addition, benzoxazines offer many advantages and unique chemical structures, so they exhibit better flame-resistance and electrical properties than epoxies [21-22]. With these combination of properties, benzoxazines hold great promise for performing in applications such as coatings, adhesives, encapsulants, and others [23-26]. However, similarly to other thermosets, the major shortcomings of polybenzoxazines are their brittleness [27-28], high curing temperature, and low degree of polymerization. Brittle nature of the benzoxazine resin have limited their applicability especially when it was processed into thin films. Preparation of benzoxazine monomers with the constituents of cardanol is a way to enhance ductility and processability [29-30].

Calò E and co-workers developed the first batch of cardanol-based benzoxazine and polybenzoxazine [18]. Since then, cardanol was used as a fine bio-chemical for synthesis of other novel polybenzoxazines, proving that the phenolic compound is promising for this class of polymers [30-33]. The types of benzoxazine monomer and their synthetic methods are summarized from the aspects of monofunctional, bifunctional and multifunctional. Fig. 2 shows some monofunctional cardanol based benzoxazine resins. A cardanol-based benzoxazine (CA-b-1 of Fig. 2) was synthesised from cardanol, ammonia, and formaldehyde, and successively polymerized to produce different polybenzoxazines depending on the polymerization method [18]. Polybenzoxazines (PBzs) may be low or high viscosity

liquids or solids. In the low viscosity resin, it is possible to achieve good wettability, processability and ease in applicability without the use of high temperature and pressure. In high viscosity resin, generally a reactive diluent is blended with neat base resins to reduce viscosity, extend pot life and improve cure. Minigher et al. [34] described a solvent-less process, based on a Mannich reaction involving a primary amine and an aldehyde, for the preparation of new benzoxazines deriving from cardanol. Three kinds of liquid benzoxazines named CA-b-1, CA-b-3, CA-b-4 are showed in Fig. 2 [34]. A monofunctional liquid cardanol-based benzoxazine (named CA-b-2; Fig. 2) was prepared and used as a reactive diluent and toughening agent for a bisphenol A-based benzoxazine [21,26,35]. Kotzebue et al. synthesized new cardanol-based benzoxazines (named C-a, C-ch, C-cy, C-thf; Fig. 2), described their complete polymerization under mild conditions using magnesium chloride as a catalyst, obtained soluble polybenzoxazines [23]. All the soluble polybenzoxazines can be used as solution-processed polymers, because they are completely soluble in toluene, chloroform, and dichloromethane, widening its application range [23].

Compared to other thermosets, one of the main drawbacks of polybenzoxazine resins is their relatively low crosslink density, which can be improved by proper benzoxazine functionalization. Mono-benzoxazine monomers based polybenzoxazines suffer from a lower crosslink density and char yield that especially is further diluted by the presence of longer alkylene chain in cardanol. In order to improve the crosslink density, char yield and to understand the role of higher aromatic content vs functionality, a series of cardanol-based benzoxazine monomers (C-a, C-ta and C-tapm of Fig. 2; Bnz-1 to Bnz-4 of Fig. 3) were synthesized [17,24,36-37]. Ambrožič et al. synthesized a novel bio-based benzoxazine from epoxidized cardanol, polyether monoamine and paraformaldehyde, which contained epoxy groups and at the same time possessed surfactant [17]. It was found that the introduction of furan groups could enhance the char yield and thermal stability, the introduction of additional polymerizable groups (oxazine, epoxy or furan ring) into benzoxazine molecule increased the crosslink density, activation energy and reaction enthalpy of curing. The incorporation of higher aromatic ring in benzoxazine monomers is another route in enhancing the crosslink density besides higher functionality to modulate their properties [17,24,36-37].

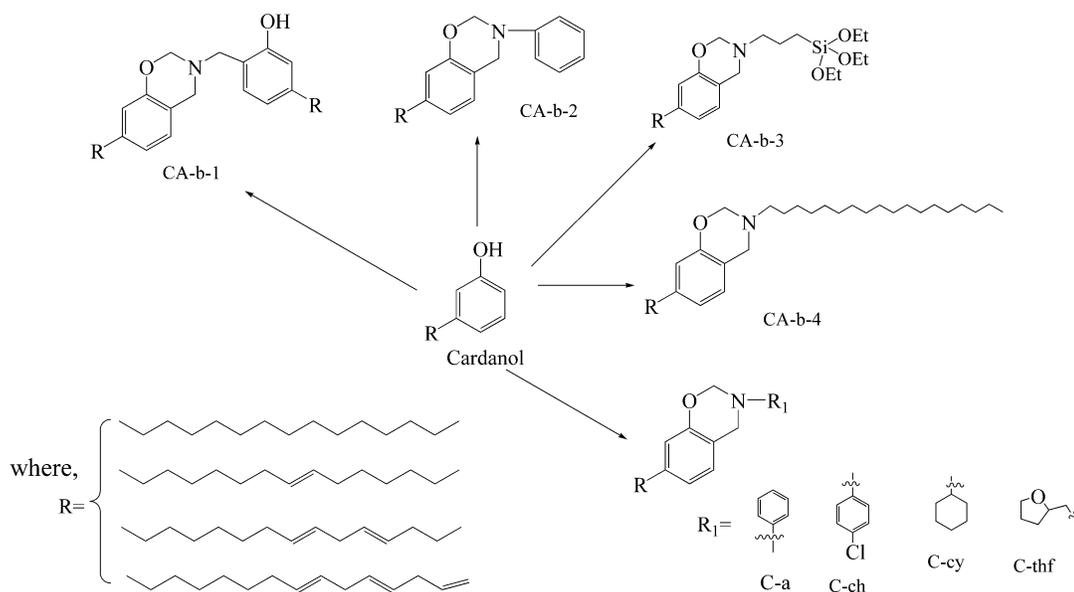


Figure 2: Some monofunctional Cardanol based benzoxazine resins

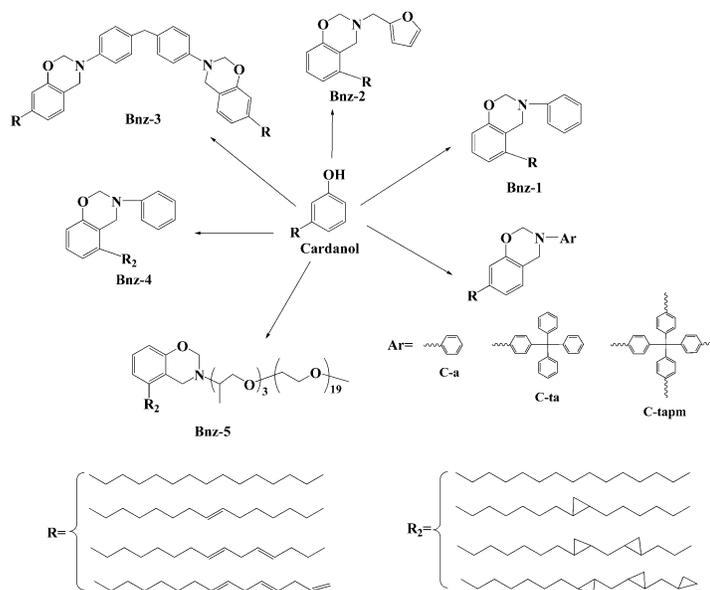


Figure 3: Structures of monofunctional Cardanol based benzoxazine resins

Monobenzoxazines are cured by ring-opening polymerization (ROP) to yield a linear polymer. In order to prepare cross-linked polymer and improve the crosslink density, it is desirable to have bifunctional monomer, i.e., bisbenzoxazine, which can be achieved by using either a difunctional phenol such as bisphenol-A or a diamine. The synthetic strategy of bisbenzoxazines includes reaction of aromatic/aliphatic diamines [25,33,38-39]. A solventless synthesis of bisbenzoxazine monomers (abbreviated as Bzc-HP, Bzc-HM, Bzc-DDS and Bzc-BA, showed in Fig. 4) based on cardanol with diamines namely bis-(4-(4-aminophenoxy)phenyl)ether (HP), bis-(3-(4-aminophenoxy)phenyl)ether (HM), 4,4-diaminodiphenylsulphone(DDS) and 2,2-bis(4-(4-aminophenoxy)phenyl)propane(BA) was carried out [38]. Bisbenzoxazine monomers based on bisphenol-A (b) and aniline was abbreviated as Bzb-A. The decomposition temperature for 5% mass loss ($T_{5\%}$) of resins followed the order PBzb-A < PBzc-DDS < PBzc-BA < PBzc-HM ~ PBzc-HP. Lap shear strength on steel plates followed the trend PBzc-DDS < PBzc-HM < PBzc-BA < PBzc-HP. The materials showed their potential as adhesives. Adhesive strength was found to be higher for the polymers containing flexibilizing group (-O-) between the benzene ring than the rigid group (-SO₂-). The higher adhesion of HP over HM polymer isomer could be accounted due to the difference in position of -O- linkage for probably better wettability of the adhering surfaces. Even though, DDS unit-based PBz resin had polar group but it showed poor adhesion, which might be outweighed by the structural rigidity. Introduction of functional groups into the oxazine ring can alter the properties of the resin appreciably [39]. Ambrožič et al. prepared a new type of bisbenzoxazine using caproamine with cardanol (CBZ, Fig. 4), and made an attempt to develop hybrid composite materials with excellent thermo-mechanical and dielectric properties based on industrially potential and commercially competitive resin i.e., epoxy and benzoxazine with graphene reinforcement [17]. Sharma et al. synthesized a bis-benzoxazine monomer containing amide linkages (BZC-AOET, Fig. 4), and the presence of amide linkages and the polar group formed during the ring opening of benzoxazines led to the improvement strength in adhesive [25].

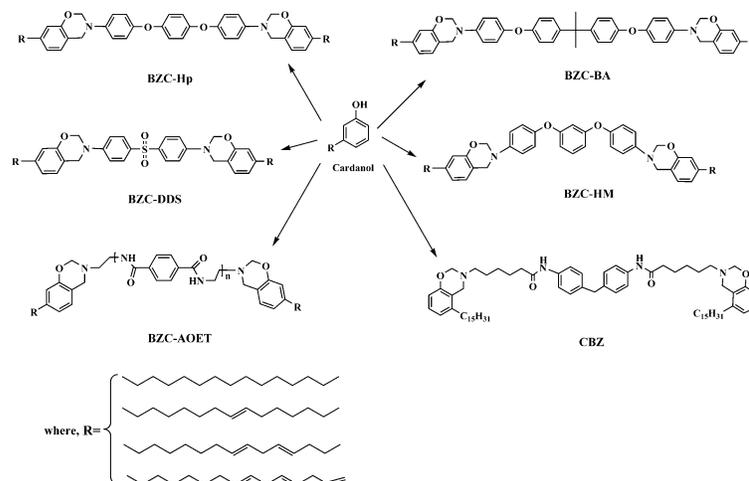


Figure 4: Some difunctional cardanol based benzoxazine resins

The Bnz coating is well known for having excellent mechanical, electrical, and thermal properties as well as lower water absorption [40]. However, Bnz resin is not favorable for coating applications due to the high curing temperature and brittleness. To overcome the negative aspects, the additional functional group such as amino, amine, cyano, and hydroxyl can be incorporated into the Bnz resin structure. The Mannich-like condensation reaction of a cardanol, paraformaldehyde, and *N,N'*-bis(2-aminoethyl)ethane-1,2-diamine were carried out to synthesize the amine functional benzoxazine (Bnz, Fig. 5) resin [41-42]. To enhance the coating performance, amine functional Bnz resin was successfully copolymerized with various epoxy resins. Poly(Benzoxazine-co-Epoxy) coatings display well corrosion resistance, high chemical and solvent resistance properties compared to the polybenzoxazinecoating and this could be due to the dual cross-linked network. Poly (Benzoxazine-co-Epoxy) coatings were observed to be suitable for high performance anticorrosive metal surface coating [41]. In order to improve the mechanical properties and anticorrosive performance, the Bnz resin structure was modified by glycidoxypropyltrimethoxysilane (GPTMS) in various proportions (Fig. 5) [42]. The highly crosslinked structure of the GPTMS-modified Bnz coatings enhanced the barrier protection to corrosive species and improved mechanical, chemical, and solvent resistance properties compared to the neat Bnz coating [42].

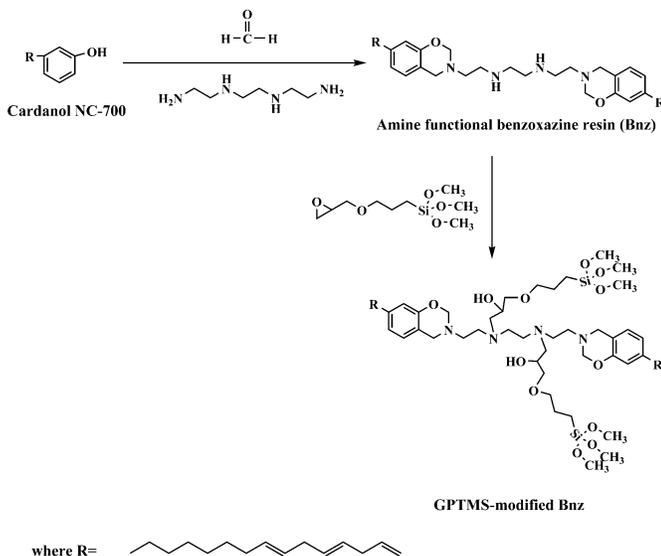


Figure 5: Synthesis reaction of Bnz and GPTMS-modified Bnz

Thermosets prepared by main-chain benzoxazine polymers (MCBP) can address the brittleness, but their high viscosity and reactivity for preparation are drawbacks [43-45]. Main-chain benzoxazine oligomer (MCBO) has been purposed to overcome the challenges [46]. However, without using diluents, the viscosity of the resin remains large. To address the above difficulties, Zhang L et al reported the synthesis of three phenol-capped MCBO [29]. Among them, two oligomers completely or partially capped by cardanol show very large processing window as well as low viscosity. Attractively, without adding diluents, they can satisfy the viscosity requirement of resin transfer molding RTM. In sum, cardanol-based benzoxazine resins could be considered as very attractive thermoset resins to produce novel bio-composite materials.

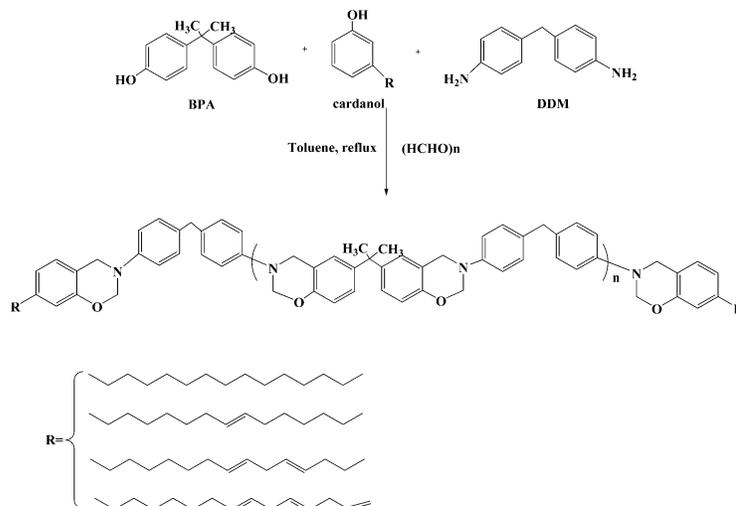


Figure 6: Synthesis of MCBO(BPA-ddm)C, MCBO(BPA-ddm)C-P and MCBO(BPA-ddm)P based on BPA, DDM, phenol and cardanol

2.2 Cardanol Based Phenolic Resin

Phenolic resin (PR) is the earliest synthetic resin to realize industrialization in the world and has been in existence for nearly a hundred years [47-49]. PR possesses excellent corrosion resistance, mechanical properties, electrical insulation, moulding processability, flame retardancy, dimensional stability and low toxic haze, moreover its low cost, simple production process and equipment [50-52]. Therefore, PR is not only widely used in high-end aerospace, military equipment, etc., but also in wood bonding, friction materials, construction, coatings, inks, moldings, castings, insulation products and microelectronics [53-54]. The aromatic nucleus of the PR is only connected by a methylene group, and under the action of an external force, the methylene group is easily broken, resulting in embrittlement of the PR. Meanwhile, the methylene group of the PR is also broken due to easily oxidation at the high temperature, which limits its application [55-56]. Hence, it is an important research direction to improve the toughness and heat resistance of the PR. Cardanol is the main component of CNSL that is byproduct of the cashew agribusiness. Two types of active group that phenol and polyunsaturated flexible long chain (15 carbon atoms) were emerged in cardanol [57]. Therefore, cardanol not only has the reaction characteristics of a phenolic compound, but also has the chemical properties of an unsaturated olefin. The novolac prepared with cardanol has excellent gloss and fullness, high hardness and good mechanical properties [54]. The overall thermal stability of cardanol modified phenolic resin was better than that of pure phenolic resin by Liu Y et al. [58].

An irreversible non-spontaneous second-order reaction using cardanol with formaldehyde in the presence of organic weak acids such as p-toluenesulfonic acid, ethanedioic acid, amber acid and citric acid as the catalyst was carried out [59-61]. In all the systems, the value of step rate constant k_1

were found to be lower than k_2 , thus the condensation reaction may be considered as the rate-determining stage of the whole reaction. The results showed that increasing temperature and mole ratios of formaldehyde-to-cardanol was beneficial to the reaction. Cardona et al observed that CPR and PR could be completely miscibility to form a homogeneous system by mixing CPR/PR in different proportions [62]. The flexural strength and fracture toughness of cured CPR/PR resin proportionally increased with the increase of cardanol content, while the flexural modulus decreased. This is attributed to the plasticization and toughening effect of CPR imparted by the “internal plasticization” of C_{15} side chain [63], which was further proved via the blending of CPR with propanediol. Recently, a novel fully bio-sourced flexible phenolic thermosets was synthesized from cardanol and nonyl aldehyde. The material possessed tunable mechanical properties due to the plasticizing effect of the alkyl chains [64]. Novolac resin based on cardanol and furfural has also been prepared under the catalysis of oxalic acid. Compared with PR, the cured cardanol-furfural based films exhibit better mechanical properties, heat resistance and chemical stability (alkali solution, organic solvent and water) [65].

Due to the steric hindrance and plasticizing effect of C_{15} side chains, the CPR often exhibits lower crosslinking density than that of PR, which caused that tensile strength of CPR was inferior to that of PR. Composites made of the intensive CPR via adding exogenous substances (natural fibers and reactive small molecules, etc.) is an effective method [54]. Green coconut shell particles (CSP)/CPR composites were prepared by doping different quality CSP as fillers. The micro-morphology of the composite showed that the fine CSP (75 μm) particles were closely bound to the CPR, thus improved the tensile strength, water absorption, the rigidity and hardness of the composite [66]. It is noteworthy that the composites with 5% NaOH processed CSP particles had better thermal stability, because the processed particles existed better interfacial adhesion, and thereby assisted to disperse evenly in the matrix. Similarly, the smaller CPS particles (25 μm) exhibit higher thermal stability regardless of whether they had been processed or not [67]. From the perspectives of sustainability and environmental protection, the combination of CPR matrix composites with biodegradable biomass is a good alternative. Natural fibers have remarkable physical properties, and alkaline or organosilicon treatment can further optimize the physical properties of fibers. The effect of different concentrations of NaOH and silane treated kenaf single fiber on the interfacial shear strength of CPR was investigated. The results showed that the kenaf single fiber treated with 2% NaOH for 4 hours can significantly increase the tensile strength of the composite, while the high concentration of chemical treatment would damage the fiber by removing impurities and lignin [68]. Long fibers are capable of effectively transferring large loads such that the composite has enhanced mechanical properties. Dashtizadeh Z et al. used untreated kenaf fibers to obtain composites with tensile strength and impact strength that were 91.9% and 43.4% stronger than CPR [69]. The research displayed that the treated kenaf fiber showed a negative effect on the toughness of composite materials due to short kenaf fiber allow stress concentration and high temperatures damage fiber. However, the compatibility of natural fibers with resins is slightly insufficient, agglomeration and sedimentation, thus the increase in strength is limited. The reinforcing mechanism of boric acid compounds in phenolic resins has been fully demonstrated [70]. The residual carbon content of the modified CPR was as high as 69% even if a small amount of boric acid (1.27 wt%) was added, indicating that the modified CPR had excellent thermal stability [71]. Other researchers have studied the enhancement effect of Mo salt on phenolic resin [72]. The T_g of Mo-modified CPR increased by 72°C, probably due to the condensation reaction of hydroxyl groups in the CPR with Mo salts to form -Mo-O bonds with higher bond energies. Under this action, the tensile strength and limiting oxygen index of Mo-modified CPR increased from 123.7 MPa and 19.2 to 167.7 MPa and 23.0, respectively. Recently, a functional polymer based on in-situ mixing of CPR with polyaniline (PAni) has been reported [73]. Because of the presence of PAni, the conductivity of the polymer was imparted and the conductivity was sensitive to pressure changes. Only a small amount of PAni allowed the polymer to show a conductivity variation of ~340%. The result of increasing the PAni concentration cause a decrease in conductivity variation due to an increase in the number of contact points between the PAni chains. The polymer was potential pressure sensing material. Sang et al. synthesized a carbon fiber paper-based composite (GCPR)

by impregnation using graphene and CPR as a solution [74]. The incorporation of CPR optimized the porosity and mechanical properties of the GCPR. When the CPR content is 20%, the tensile strength was up to 38.17 MPa from the 30.13 MPa of the pure carbon fiber composite.

2.3 Cardanol Based Curing Agent and Epoxy Resin

Cardanol is a naturally occurring substituted phenol which can take part in a variety of reactions for fine chemical products and polymer preparation. It is a cheap and renewable substance and can replace phenol in many applications with equivalent or better results. As a commercial epoxy curing agent, cashew phenolic amine is a mannich base which was obtained by the reaction of cashew phenol, aldehydes and polyamine. Cashew phenol amine is a good curing agent for epoxy resin at room temperature or low temperature. And due to cashew phenol amine's low temperature and rapid curing properties, which allows it to solidify on wet or even water surfaces. However, its application range is limited, because the phenolic hydroxyl of cashew phenol is easy to be oxidized and the color of curing agent is generally deeper [75].

Cardanol-based curing agent with light color (MBCBE) was synthesized and used to compare with phenalkamine, as seen from Fig. 7, MBCBE showed relatively lower reactivity than phenalkamine. Epoxy resin materials modified with MBCBE consisted of cavities dispersed within a continuous epoxy matrix due to a decrease in solubility of MBCBE, the addition of MBCBE did not change the storage modulus and T_g of epoxy resin materials. However, the toughness and shear strength of epoxy resin materials modified with MBCBE were obviously improved [76].

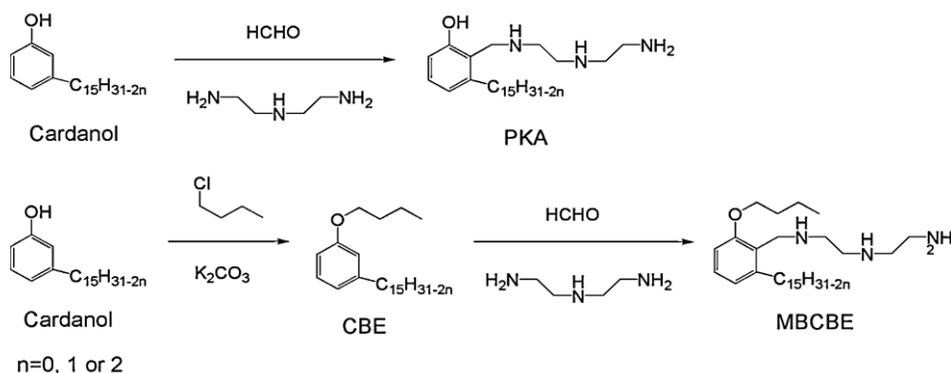


Figure 7: Synthesis of MBCBE

Cardanol based curing agents not only improve the physical properties but also modify the chemical resistance. Aggarwal et al. produced cardanol based epoxy resin materials using cardanol based curing agents from epichlorohydrin, bisphenol-A and cardanol. The chemical resistance behaviour of the obtained epoxy resin materials was carried out by an immersion test and humidity cabinet test. And the epoxy-cardanol resin based paints showed superior to that of paints formulated using the unmodified epoxy resin, irrespective of the pigments, fillers and the additives used. The further research shows that the anticorrosive behaviour of the paints has some relation to their strength and permeability properties [77]. Epoxidized cardanol is a kind of commercial curing agent deriving from phenolation of aliphatic chain and reaction of phenol hydroxyl groups with epichlorohydrin. Biobased aromatic epoxy materials from epoxidized cardanol NC-514 were synthesized by Caillol et al. A likely chemical structure of commercial NC-514 cardanol supplied by Cardolite was proposed. The results showed that thermal stability of synthesized NC-514 cardanol based epoxy resin materials was slightly lower than DGEBA modified epoxy resin materials due to the likely presence of noncross-linked chains [78].

Kanehashi et al. synthesized the cardanol-based epoxy coating by the thermal polymerization reaction between amine compounds and epoxy cardanol prepolymer (ECP).ECP coating required less

time (about 2.5 h) than that of the commercial cashew coating (8 h) to harden dry, and it was rubbery state at room temperature owing to the flexible side chains of ECP. Moreover, the color indices of ECP coatings immersed in H_2SO_4 and NaOH solution were almost the same, which indicated that it has better chemical stability [79].

The effects of diepoxidized cardanol (DEC) as diluent, epoxy fortifier, and anhydride as curing agent on the curing behavior of DGEBA were investigated by Patel et al. Compared with their 1988's work, mono epoxidized cardanol (MEC) was used as diluent in the curing reaction, and the E_a was 80-115 kJ/mol, which was lower than DEC. Three different ratios of DGEBA/DEC such as 90/10, 80/20, and 70/30, respectively were used to investigate the effects of diluent, and when the diluent content increased, the onset temperature of the exotherm increased accordingly [80].

Two amines, isophorone diamine (IPDA) and Jeffamine T403, were used to formulate epoxy-amine resins by Darroman et al. The gel time with BADGE, as seen from Fig. 8, was 3.5 h and 15 h respectively, which indicates an improved reactivity. Two kinds of sucrose epoxy derivative compounds, sorbitol (cardanol/sorbitol = 50/50) and isosorbide (cardanol/isosorbide = 25/75), in place of bisphenol A, was used to enhance the properties of cardanol epoxy resins. With the increase of epoxy sorbitol or isosorbide content, the degradation temperature decreased, and T_g values increased. The brightness, hardness, and the stability of polymer regarding ethyl acetate treatment also showed a slightly increase. In 2015's work, their team worked on the blends of epoxy cardanol with three different epoxy reactants: either diglycidyl ether of resorcinol, hBADGE and triglycidyl ether of TMP. The epoxy cardanol blended with either the incorporation of resorcinol or hBADGE led to higher T_g (105°C at 75% of epoxidized resorcinol and 64°C at 75% of hBADGE) and hardness (from 86 at 0% to 98 and 96 at 75% respectively). With the incorporation of TMP, the thermal stability of poly-epoxide blends was improved [81].

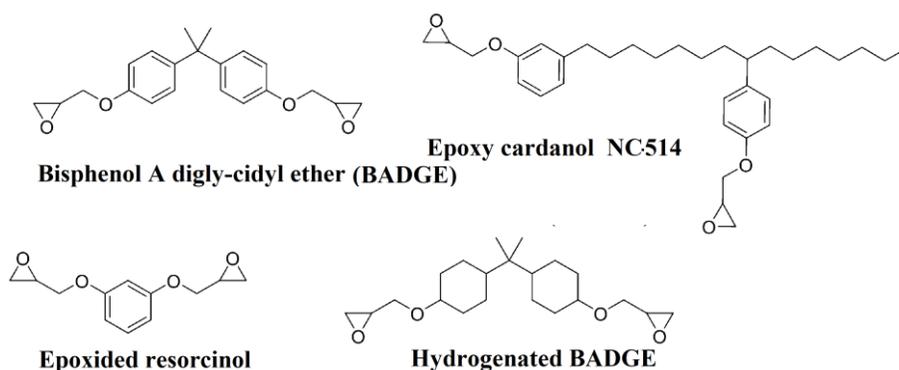


Figure 8: Chemical structure of epoxidized cardanol based curing agents

Based on mannich reaction, three novel cardanol-based phenalkamines: phenalkamine 1 (PAA1), phenalkamine 2 (PAA2) and phenalkamine 3 (PAA3), were synthesized using poly-condensing phenolic compounds with paraformaldehyde and hexamethylenediamine (HDA) by Liu et al. Two different chemical structure was inferred in associated with the mechanism of this reaction and different ratios of materials. The results showed that the reactivity of three phenalkamines decreased from DGEBA/PAA3, DGEBA/PAA2 to DGEBA/PAA1. There is an increase about the toughness of the cured epoxy resins. The impact strength of the composite DGEBA/PAA1 increased by 81% due to the long alkylside chains [82].

Cardanol was mixed with epichlorohydrin under the catalysis of caustic soda to synthesize mono functional cardanol-based epoxy resin systems, which was performed by Unnikrishnan et al. The epoxide equivalent reached the maximum at 61% in 9 h, which was lower than that of phenol due to its incapability of forming a cure network. However, these epoxy compounds blended with commercial DGEBA were effective in synthesizing flexible system with less brittleness. Co-epoxides of bisphenol A

and 20 mol% cardanol led to a less viscous, tensile and compressive strength and a remarkable increase of elongation at break [83].

Wang et al. performed a control-experiment of cardanol-BS modified layered double hydroxide (m-LDH) incorporated into epoxy resins (EP), namely m-LDH/EP, and LDH/EP by combining three-roll mill and ultra-sonication technique. Among which the cardanol-BS was synthesized by the effect of 1, 4-butane sultone (BS) ring-opening reaction on cardanol. According to the results, m-LDH/EP was well-dispersed. With the loading of 6 wt% m-LDH, LOI of the blends reached 29.2%, UL-94 V0 rating. Therefore, homogeneous-dispersed m-LDH nanofillers can improve flame retardant of epoxy resins [84].

The use of polyepoxide cardanol glycidyl ether (PECGE) as diluent to synthesize epoxy resin showed better characteristic. The viscosity of epoxy resin reduced with the increasing content of PECGE. When adding no more than 20 wt% of PECGE reactive diluent, the mechanical properties including tensile strength, elongation at break, and heat-resistant property of cured resins enhanced more than that of cardanol glycidyl ether [85]. The lignin and cardanol based novolac epoxy resin, triglycidyl cardanol resin (TGC) and NC-514 based epoxy resin were also investigated. The obtained epoxy resins showed excellent mechanical, thermal and flame retardant performances [86-92].

2.4 Cardanol Based Polyols and Polyurethanes

Polyurethane (PU) is a new synthetic material, which has the advantages of wear resistance, corrosion resistance and impact resistance, and good shock absorption effects. It has been widely used in automotive, electronics, machinery and medical fields [93-94]. However, the urethane structure contains a large amount of hydrogen bonds leads to the poor compatibility of resin with a certain degree of microphase separation phenomenon. The compatibility can be improved by changing the soft segment. Recently, bio-based PUs have become the research hotspots. These bio-based PUs are derived from vegetable oil based polyols. The vegetable oil mainly includes palm oil, castor oil, linseed oil, rapeseed oil and so on [95-97].

Rigid PU foams are usually with excellent physical and mechanical properties. Shrestha M L et al prepared new cardanol-based polyols through thermally initiated thiolene reaction. It is a known fact that the phenolic group possesses a strong inhibitory effect on thiol-ene radical reaction. And in this study, alkoxylation with propylene oxide is used to block it. Then rigid PU foams are synthesized with a mixture of cardanol polyols (50%) and a sucrose polyol Voranol 490 (50%). However, the rigid PU foams derived from cardanol polyols have the same appearance and cellular structure as the foams prepared from petrochemical polyols. Indeed, such rigid PU foams possess great physical-mechanical properties and modulus retention, which may result from the presence of aromatic rings in their structure [98]. While in Huo's work, these green cardanol-based PU foams show better performance than petroleum-based (PEG) PU foams. Different from Shrestha's team, the ring opening reaction of epoxy group with diethanolamine (DEA) was chosen to synthesize PU foams. The cardanol-based polyols were synthesized through ring-opened reaction by diethanolamine (DEA) and epoxidized cardanols. Even though the viscosity of the obtained cardanol-based polyols exceeds that of cardanols, it is still lower than the commonly accepted upper limit. When it comes to mechanical property, cardanol-based PU foams show better performance due to the presence of C15 side chain, which helps avoid the situation of being too rigid. Besides, higher crosslinking matrix along with the higher hydroxyl value are the reasons for higher decomposition temperature [99]. Cardanol-based mannich polyols could be prepared by reaction with N-(2-hydroxyethyl)-1,3-oxazolidine, then used in obtaining rigid PU foams with good physico-mechanical and fire retardant properties [100-101]. In Zhang's study, melamine added into mannich polyols could increase the flame retardancy. In fact, compare with no-filled cases, such rigid PU foams show better compressive strength, thermal stabilities, char residue, heat release and smoke emission [102].

Actually, differences exist in various kinds of cardanol-based PUs. For example, PUs based on diol (PUD) and glycard (PUG) were stable above 300°C except the triol-based one (PUT) [103]. Even the rigid PU is proved to have higher hardness than the tough PU, which shows the higher applicability in

chemical reagents [104]. P-Containing cardanol polyol (PCP) and S-Containing cardanol polyol show higher mass residual and superior corrosion resistance than their counterparts respectively [105-106].

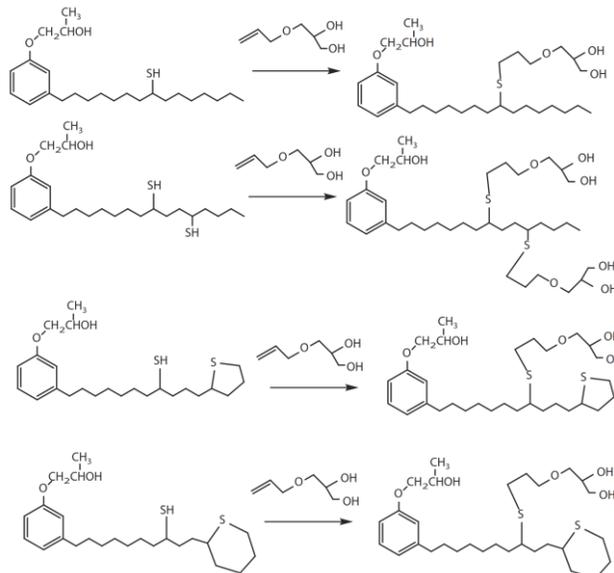


Figure 9: Synthesis of polyols from photochemical thiol-ene reactions of cardanol based derivatives

Other than rigid PU foams, there are still various kinds of cardanol derivatives with potential application. Free PU films prepared by cardanol derivatives show better flexibility, thermal stability, hydrophobicity, and film-forming tendency with excellent elongation, and moderate hardness [107]. The cross-linking in the film also improve the film properties such as hardness, solvent resistance and water resistance [108]. Additionally, the crosslink density relies on the content of cardanol during the process, and enhances the flexibility, the tensile strength and the glass transition temperature [109]. PUs prepared from linear hydroxyalkylated cardanol formaldehyde and hydroxyalkylated dimerised cardanol formaldehyde resins have better thermal stability and mechanical properties than that from branched hydroxyalkylated resins [110]. Moreover, PU elastomers can be applied on biomedical field [111]. PU coatings is available for metal substrates, protective wood coatings and 2K aqueous PU coatings [112-114].

Shrestha et al. reported that a series of cardanol based polyols containing polyhydroxyl functional groups were prepared from cardanol by the thiol-ene addition reactions of thiol groups and the C=C bonds, as seen from Fig. 9 and Fig. 10. Then these products were used as raw material to prepare PU with improved physical and chemical properties, such as mechanical, chemical, optical, anticorrosive and thermal properties. These phenomena were caused by the presence of cardanol with aromatic ring, sulphur atom in the structure, hydrophobic long aliphatic chain and the urethane linkages in the coatings. This provides a technical method for chemical modification of PU with cardanol [115].

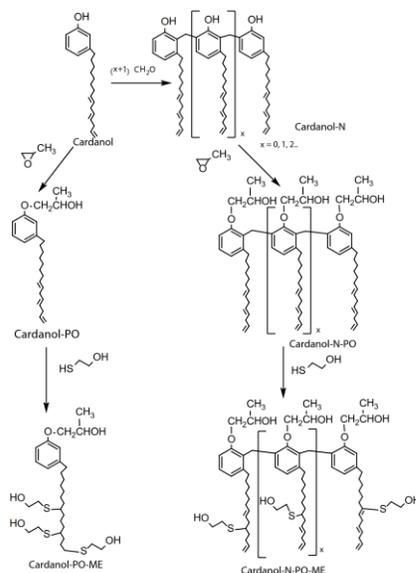


Figure 10: Synthesis of cardanol-based polyols by using thiol-ene reaction

2.5 Cardanol Based Vinyl Ester Polymers

Vinyl ester resin is a kind of denatured epoxy resin obtained by reacting bisphenol or novolac epoxy resin with methacrylic acid, commonly known as vinyl ester resin (VE), alias epoxy acrylic resin, thermosetting resin. Vinyl ester resins possess the excellent properties of epoxy resins, excellent in curability and formability, soluble in styrene and acrylic monomers. Due to the advantages of both epoxy and unsaturated, its application field is expanding [116].

Cardanol-based vinyl ester resin (CVER) is synthesized from cardanol-based epoxidized novolac resin (CENR) and methacrylic acid (MA). GMA decreased the tensile strength and enhanced the elongation-at-break and impact strength of CVER. Moreover, the cured films of vinyl ester resin (VER) possess good impact and acids resistance [117]. The VER from cardanol would be a better choice and may be used for the development of reinforced plastics, eco-friendly coating systems [118]. Researches about kinetic models show that the esterification of CENR with MA follow first-order reaction kinetics and is spontaneous as well as irreversible [119]. Based on such model, the esterification reaction was optimized through adjusting the molar ratio of CENR and MA to 1:0.9, which results in the maximum extent of conversion (95.3%) [120]. Besides, CVER could also mix with carboxyl terminated butadiene acrylonitrile (CTBN) to prepare cured films. These products also show better acids, deionised water and synthetic water resistance [121]. Aside from mixtures above, VE mixed with acrylic acid and NC514, a bio-based product coming from CNSL, can both enhance the elongation at break and gloss [122-123].

2.6 Cardanol Based Polyamide

Due to its excellent mechanical properties, heat resistance and oxidation resistance, polyamide resin has been widely used in many fields such as industry and home appliances. However, its molecular arrangement is orderly, interaction force is strong and it has some disadvantages like being difficult to dissolve in organic solvents or insufficient toughness. Modification of the polyamide resin through cardanol could improve the miscibility.

Cardanol is usually functionalized by maleic anhydride and then condensed with diethylenetriamine (DETA). Polyamides with different molecular weights were prepared by varying the mole ratios of acid and amine components in the formulation. Some are used as crosslinker in conventional epoxy zinc-rich primer and then compared with commercial polyamide. The cumulative effect of increased crosslinking densities resulted from sacrificial protection due to galvanic action of zinc pigments. These will lead to enhanced

chemical, solvent and corrosive resistance [124]. Moreover, the optimum balance arise from aliphatic moieties also show that the coatings is suitable for conventional epoxy resin and metal substrates [125].

2.7 Cardanol Based Cyanate Ester Resins

Cyanate ester resin is a new type of thermosetting resin with two or more cyanate functional groups (-OCN) in the molecular structure developed in the 1960s. Its molecular structure is: NCO-R-OCN, cyanate ester resin is also called Triazine A resin or TA resin, abbreviated as CE. There are many types of cyanate ester resins, and different structures have different properties. However, they are net-like polymers mainly composed of triazine ring structures after curing polymerization. So they have common characteristics: the average molecular weight of CE is 2000. It is solid or semi-solid at normal temperature, and some varieties are liquid and it can be softened in the temperature range of 50-60°C. The most common type of cyanate ester resin is bisphenol A type cyanate ester resin with a simple synthesis process and cheap raw materials. However, since the triazine ring structure in the molecule is highly symmetrical, the crystallinity is high, the brittleness of the resin cured product is large, lead to poor paving property of the prepared composite. And the crosslinking density of the monomer after polymerization is large, so toughening modification is necessary. Copolymerization is a good way for cardanol to enter phenol-formaldehyde resin, which then gets transformed into cyanate esters resin. While the increase of content of cardanol and decrease the thermal stability of cured polymers, it may lead to better toughening modification [126].

3 Conclusions

With the rising price of petrochemical raw materials and the gradual decrease of natural mineral resources, cardanol, as a cheap, abundant and renewable resource, has become a hot spot in polymer materials. However, the application of cardanol is limited to a few industries such as coatings. The main reasons are: (1) The composition of cardanol is complex, and the separation and purification methods are not suitable for large-scale industrial production. (2) The mixture of 1-3 unsaturated olefins in the side chain of cardanol is more active, unsuitable for storage and difficult to control the reaction. The side-chain hydrogenation product m-pentadecyl phenol has low reaction activity, so the substitution and condensation of cardanol and its hydrogenation products are difficult to break through, which restricts its industrialization process. How to make full use of the long chain molecular structure of cardanol side chain to improve the compatibility and flexibility of polymer materials will be the focus of research in this field. It is believed that with the deepening of research and the emergence of advanced methods, the research and application of cardanol based polymer materials will be deeper and extensive.

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