December 2007 Volume 3 Issue 4

Trade Science Inc.

Macromolecules

An Indian Journal

Microreview

MMAIJ, 3(4), 2007 [176-200]

Synthesis and characterization of resoles and their blends with epoxy resin : a review

Kavita Srivastava[1]*, Chandra Kumar[2], Deepak Srivastava[2], Santosh Kumar Tripathi[1]

[1]Department of Chemistry, V.S.S.D. College, Kanpur, (INDIA)

[2]Deparment of Plastic Technology, H.B.T.I., Kanpur, (INDIA)

E-mail : rashmi_sri97@rediffmail.com

Received: 27th November, 2007 ; Accepted: 2nd November, 2007

ABSTRACT

In view of outstanding properties of epoxy resins and their uses in many hi-tech applications, such as aerospace, marine coating, satellite communication, etc., the modification of various resoles with such resin will definitely provide better performance, including high temperature performance, improved toughness and flexibility and better electrical insulation resistance, and hence would lead to the development of number of new application areas. Therefore, in the present paper, the synthesis and characterization of resole-type phenolic resins based on phenol and different alkyl phenols, viz., o-, p-, and m-cresoles, separately, with formaldehyde and blended these resoles, separately, with diglycidyl ether bisphenol A (DGEBA) epoxy resin have been reviewed along with the effect of orientation of various phenols on various physico-chemical, -thermal and -mechanical characteristics of the blend systems.

INTRODUCTION

Phenolic resins[1,2] encompass a wide variety of polymeric substances; each polymer is composed of a multitude of structure and a variety of raw materials and catalysts are used. Phenolic resins are employed in a wide range of applications from commodity construction materials to high technology applications in electronics and aerospace. Generally, but certainly not exclusively, thermosetting in nature, phenolic resins provide numerous challenges in the areas of synthesis, characterization, production, product development, and quality control. These are mainly derived from condensation products of formaldehyde and phenol or among others, alkyl-substituted phenols, furfural, furfural alcohol, etc.

Phenolic resins are of two major types : novolac and resole. Novolac resins are prepared by reacting a molar excess of phenol and formaldehyde under acidic conditions. Formaldehyde adds to the ortho- or para-position of phenol, forming methylene bridges. Resoles are synthesized by alkaline reaction of phenol and formaldehyde, whereby the formaldehyde is used in excess. Formaldehyde to phenol(F/P) molar ratios between 1:1.0 to 3:1.0 is customary in technical resoles. These are mono- or polynuclear hydroxymethyl phenols(HMP) which are stable at room temperature and, by application of heat, seldom of acids, are transformed into three-dimensionally cross-linked insoluble and infusible polymers (resits) over different intermediate stages(resitols). However, the limited storage stability of resoles at ambient temperature must be taken into consideration. The resole resins are usually neutralized with an acid before isolation and so the molecular structure of resoles depends on the formaldehyde to phenol ratio, temperature, pH, catalyst used and other less important variables[1-3].

The methylene bridge in resole is thermodynamically the most stable cross-linkage. It is prevalent in completely cured phenolic resins. Theoretically, 1.5mole of formaldehyde is needed for the complete three-dimensional crosslinking of 1mol of phenol. A higher proportion of formaldehyde is used in technical resins. On an average, considering all fields of applications, approximately 1.6 mol of formaldehyde is used. This excess is necessary to meet distinct technical requirements, for example, resin efficiency or free phenol content[4].

The storage stability of the resoles has been found to be maximum at the neutral point of the resole[1]. This might be due to the weakly acidic character of phenol which might suggest that the neutral point of phenolic resole would be at a pH value lower than 7. The hydroxymethylation of phenol, in the pH range of 1 to 11, was found to be bimolecular[1,5]. The rate of reaction was found to be lowest for pH values in the range of 3.6 to 5.0. For pH values below 3.6 or above 5.0, the rate of reaction increases linearly[1-4]. The shelf life[4] of the resole was found to be longest with pH around 5.

The viscosity of resoles is time dependent, and the viscosity may increase of an order of magnitude even at room temperature over a period of few months. The resoles are, therefore, stored at sub ambient temperature where the reaction is relatively slow. The magnitude of changes in reaction depends on the storage temperature as well as other important variables already mentioned above[6,7]. The uncontrolled increase in the viscosity of the resole and the associated molecular changes lead to variability among different batches of the resins and result in aggravation to the end users. In the worst situations, the increase in viscosity might even prohibit the use of resins for applications such as pultrusion and filament winding. The resole polymerization[1] proceeds in three stages, viz. addition, condensation and curing.

The addition of formaldehyde to phenol corresponds to an electrophilic aromatic substitution in acidic as well as in alkaline environments. It is generally assumed that this reaction type involves the rate determining formation of a π-complex followed by rapid loss of proton. The actual pathway of reaction, however, is much more complicated with phenols because of solvent interaction and inter- and intra- molecular hydrogen bond formation, the abnormal and wide variation in ortho/para ratio supports this. The reaction between formaldehyde and phenol in the alkaline pH-range[8,9] and pH above 5, bis-and tris-alcohols are formed as well as monoalcohols and other compounds[10]. The simplest product is this reaction is 2-dydroxy benzyl alcohol. Sodium hydroxide, ammonia, and hexamethylene tetramine (HMTA), sodium carbonate, calcium, magnesium and barium hydroxide and tertiary amines are used as catalysts in the alkaline hydroxymethylation reaction[11-16].

Heat curing, by for the most important hardening process for resoles, is performed at temperature between 130°C and 150°C. Since this is a polycondensation reaction, the molecular weight increase depending on conversion shows a different course in comparison to a polymerization reaction[1-3,17]. The heat curing of resoles results in the formation of quinone methides intermediates. In chemical structure, quinone methides are similar to quinines, but differ in their -election charge distribution. Thus, they show a high reactivity towards electrophiles as well as towards nucleophiles. The quinone methides play an essential role at temperatures below 180^0C. This applies especially in the case of prepolymer formation in aqueous medium. At higher temperatures and appropriate conditions(solvent and water free etc.), the formation of quinone methides may result, and this could explain the presence of some linking groups identified in cured resins[5,18].

Epoxy resins[19,20] are a class of thermoset materials used extensively in the formulation of adhesives and protective coatings due to their excellent attributes such as chemical resistance, dielectric and insulation properties, low shrinkage on cure, dimensional stability and fatigue resistance. They are also used in structural and specialty composite applications because they offer a unique combination of properties that are unattainable with other thermoset resins. Available in a wide variety of physical forms from low-viscosity liquid to high-melting solids, they are amenable to a wide range of processes and applications. In general epoxies offer high strength, low shrinkage, excellent adhesion to various substrates, effective electrical insulation, chemical and solvent resistance, low cost, and low toxicity. They are easily cured without evolution of volatiles or by-products by a broad range of chemical specie. Epoxy resins are also chemically compatible with most substrates and tend to wet surfaces easily, making them especially well suited to composites applications. Epoxy resins[19-25] are characterized by a three membered ring known as the epoxy, epoxide, oxirane or ethoxyline group. Commercial epoxy resins contain aliphatic, cycloaliphatic, or aromatic backbones. The capability of the epoxy ring to react with a variety of substrates imparts versatility to the resins. Treatment with curing agents gives insoluble and intractable thermoset polymers. In order to facilitate processing and modify cured resin properties other constituents may be included in the composition : fillers, solvents, diluents, plasticizers, and accelerators.

The commercial possibilities for epoxy resins[20-23] were first recognized simultaneously in Europe and in the United States in the late 1930s and early 1940s. Credit is most often attributed to Pierre Castan of Switzerland and S. O. Greenlee of the United States who investigated the reaction of bisphenol-A with epichlorohydrin. The families of epoxy resins that they commercialized were first used as casting compounds and coatings. The same resins are now commodity materials that provide the basis for most epoxy formulations. About 45% of the epoxy resin production are used in protective coatings, and the remainder in structural applications such as laminates and composites, tooling, molding, casting, construction, bonding and adhesives, and others[20-22]. High chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, flexibility, good electrical properties, and ability to be processed under a variety of conditions are characteristics of epoxy resins[23].

The outstanding performance characteristics of the epoxy resins are conveyed by the bisphenol-A moiety (toughness, rigidity), and elevated temperature performance, the carbon-carbon and ether linkages(chemical resistance), and the high polar hydroxyl and epoxy groups(adhesive agents). Optimum performance properties are obtained by cross-linking the epoxy resins into a three-dimensional insoluble and insoluble network. The resin is treated with a curing agent or hardener, its choice depends on processing methods, curing conditions, and the physical and chemical properties desired.

Curing agents are either catalytic or coreactive. A catalytic curing agent function as an initiator for epoxy resin homopolymerization, where as the coreactive curing agent acts as a monomer in the polymerization process. The curing agent can react with the epoxy and pendent hydroxyl group on the resin backbone by way of either an anionic or cationic mechanism[21,25-28]. The functional groups surrounding the epoxide resin also affect the curing process[24]. Steric factors can influence ease of cure. Electron-withdrawing group adjacent to the epoxide ring often enhance the reactivity of the epoxy resin to nucleophilic reagents, retarding its reactivity toward electrophilic reagents[21,29]. The epoxide ring is susceptible to attack from chemicals with different structures. However, the most important group of coreactive curing agents are those with active hydrogen atoms, e.g. phenols, alcohols, thiols, primary and secondary amines, and carboxylic acids. Catalytic cures are initiated by Lewis acids, e.g. boron trihalides, and Lewis bases, e.g., tertiary amines[20-23].

The chemical compatibility of epoxy resins with a rather wide variety of polymers is also of great significance. A number of systems result from the blending of epoxy resins and polymeric modifiers such as nylon, phenolic resins and nitrile rubbers. The variety of chemical, thermal and mechanical properties that can be obtained from the combination of currently avaibale epoxy resins and polymeric modifiers enables formulating epoxy-based adhesives and coatings to meet a wide range of specifications and usage criteria.

The blending of epoxy with phenolic novolac resins has opened to recommend these resins for use in high temperature structural and electrical laminates, moulding and sealing compounds for electronic packaging, coating and encapsulation for elevated service temperature applications[1,24,25,30-32]. The low pressure molding compounds with selected silicone treated inorganic fillers has been developed by these blends for the micro electronic fields. They are superior to pure epoxies with diamino diphenyl or hexamethylene tetrachlorohydrin, when dimensional stability, physico-chemical behaviour are considered. These systems posses the electrical properties required by an insulating material and could function satisfactorily under atmospheric conditions without surface failure. These resins are clear materials that must be considered as they posses good electrical properties coupled with high mechanical strength, when used in conjunction with glass fibers. However, some improvements must be made in the weathering characteristics and tracking properties of these system. It can be seriously considered for outdoor insulation. The main advantage of using these modified systems is the high weight ratio together with good electrical performance that enables equipment to be redesigned so as to obtain weight and cost savings.

The epoxidized resole resins[33-36] show excellent performances, such as rapid curing behaviour, high heat resistance, good adhesive properties, outstanding strength, solvent & chemical resistance and good thermal stability. The resins are used in paints which could able to withstand solvent attack because of their outstanding chemical resistance, physical properties, and may, therefore, be used in order to reduce maintenance and repairing cost to minimum in comparison to vinyls. These resins are also used as flooring to cover or topping on top of a sub floor. They are classified in number of ways for wearing surfaces. These floorings are most commonly used for domestic purposes because of low levels of sound insulation and lack of pleasing appearance. Many efforts have been made to improve the appearance of such flooring such as incorporation of color aggregates or spattering color on the floor surfaces and incorporating rubber crumbs as extenders to improve flexibility and also useful to reduce impact noise. The blend system based on epoxy resin and resole-type phenolic resins is studied[37-39] for their thermal characteristics. However, the relationship between the blending conditions, the structure and mechanical properties has not been yet complete clarified. In view of outstanding properties of epoxy resins and their uses in many hi-tech applications, such as aerospace, marine coating, satellite communication, etc., the modification of various resoles with such resin will definitely provide better performance, including high temperature performance, improved toughness and flexibility and better electrical insulation resistance, and hence would lead to the development of number of new application areas. Therefore, in the present paper, resole – type phenolic resins based on phenol and different alkyl phenols with formaldehyde and blended these resoles, separately, with diglycidyl ether bisphenol A (DGEBA) epoxy resin have been reviewed along with the studies on the effect of orientation of various phenols on various physico-chemical, -thermal and -mechanical characteristics of the prepared blend systems.

Synthesis and characterization of resoles and their blends with epoxy resin

In 1872, von Bayer[40] obtained a colourless noncrystallizing resinous product from the reaction of phenol with formaldehyde, while he was investigating phenol-based dyes. The occurrence of similar intractible materials in an acidic medium was also reported by ter Mer[41], Claus and Trainer[42], Claisen [43] and others. The reaction between formaldehyde and phenol in the alkaline pH range was first recorded in 1894 by Lederer[8] and Manasse[9]. This reaction was generally referred to as the Lederer-Manasse reaction. These early investigators did not perceive any practical use for the ill-defined products. Speier [44] and Luft[45] were the first to recognize the technical significance and practical use of curable phenolic resins.

In 1907, Baekeland developed an economical method to convert these resins into moldable compositions which could be transformed by heat and pressure to hard and heat-resistant molded products[46]. Recognizing the commercial importance of his invention, he concurrently disclosed in numerous patents an extensive number of applications[47] for this new composition. The first commercial phenolic resin plant, Bakelite GmbH, was started on May 25, 1910 by Rutgerswerke AG at Erkner near Berlin. Excellent review articles and books by Hultzsch[48], Martin[5], Megson[49] and others have provided a summary of chemical research and existing phenolics technology from that time to the mid-eighties.

Klatil et al.[50] prepared resoles from phenols, bisphenols, and formaldehyde by successive alkaline and acid condensation, where 0.01-0.5 molecular dm^{-3} organic and inorganic acids with pKa 1.2-4.9 were added after the alkaline stage to adjust pH to 1-4 because a part of alkaline phenolates was acidified slowly. Thus, after condensation of p-tert-butylphenol 300, bisphenol A 32, 37% aqueous formaldehyde 373, and 15% aqueous sodium hydroxide 121.2 g, the mixture was stepwise acidified with 15% sulphuric acid 127, 10% sulphuric acid 50, and 10% sulphuric acid 100mL to the final pH 1.05.

Waitkus and Lepeska[51] prepared resoles with efficient use of equipment by filling a reactor to 60-80%

of its volume with phenols, heating at 60-100°C/11-26 inch of Hg, and adding 35-60 aqueous formaldehyde at such a rate that the amount of water added was approximately equal to that removed, maintaining the volume of reaction mixture at 60-90% of that of the reactor. A 4-litre stainless steel reactor was charged with phenol 1504, tolune 150, and 45% sodium hydroxide 31.2g and heated at 85°C/24.3 inch of Hg while 1955g 51.4% formaldehyde was added over 4h and then at 90, 70, and 65°C until the bubble viscosity was 12, 25, and 60 s, especially, to give 2625 g resole with viscosity 55 P at 25ºC, solids 72.16%, and weight-average molecular weight 1383.

Iyer and Shah[52] prepared phenolic resole resins for use as binders for refractories or foundry molds and cores. The phenol feed (optionally including cresols) was reacted with molar excess of an aldehyde (especially formaldehyde) in the presence of an alkaline catalyst (especially at 60-90°C), until 10-90% of free aldehyde was left. The mixture was then acidified to pH<7, and heated (especially to 80-95°C) together with a catalyst to promote formation of *o-o* benzylic ether bridges until free aldehyde was <2%. Phenolic resins were suitable for cold hardening by an organic acid catalyst for manufacture of sand molds and cores.

Shadbolt[53] developed a binder for foundry molds and cores was based on: (a) an alkaline phenol-aldehyde resole resin having a phenol:aldehyde mol ratio of 1:(2-3), and phenol:alkali mol ratio of 1:(0.5-1.2); and (b) an alkaline phenol-aldehyde resole resin having phenol:aldehyde mol ratio 1:(1.5-1.30), and phenol:alkali mol ratio 1:(0.5-1.2). Sodium hydroxide was optionally used as an alkaline component, and a silane (especially γ-aminopropyltriethoxysilane) was added at 0.05-3% to improve strength. The hardener for the binder is an ester of C_{1-10} carboxylic acid, a lactone, or propylene carbonate. The resins were prepared by mixing phenol and sodium hydroxide solution to mol ratio 1:1, cooling to 50°C, and adding 34% formalin for phenol-formaldehyde ratios of 1:2.6 or 1:2. The water was distilled off until viscosity of the resin mixtures at 20°C reached 130 and 2160 cP, respectively. The resins were mixed at a weight ratio 8:2. Two portions of Chelford 60 sand 1500g each were mixed for 1 min with 45g of the resulting resin mixture and with 13.5 g glycerol triacetate, respectively. Both mixtures were combined for molding. Compression strength of resulting cores after 24 h was 4800-5200 kPa.

Abdel-Mohsen and Helaly[54] prepared resole resins from formaldehyde-phenol with high molar ratio which had low solid content. To prepare a resole with high solid content and low viscosity it was desirable to use 1-1.1mol formaldehyde/1mol phenol. Shorter reflux time was preferred, followed by dehydration under vacuum and finishing the reaction as quickly as possible at a much lower temperature to prevent overreaction. The reaction was followed by measuring the refractive index.

Kozutsumi[55] prepared phenolic resin compositions which are curable at temperature ≤100°C, resistant to discoloration, and useful as coating material for fiber-reinforced phenolic resin plastics, contain (A) resole-type phenolic resins prepared by polymerising 1-8mol formaldehyde with 1mol bisphenol A or its mixture with other phenols in the presence of a basic catalyst and (B) acidic phosphates and/or phosphites. Thus, 1 mol bisphenol A and 4 mol 37% formaldehyde were reacted at 100°C for 1 h to obtain a resole phenolic resin; a composition containing 100 parts of the resin and 15 parts triphenyl phosphate was applied on a film and heated at 60°C for 2h, and peeled from the film to give a cured resin coating showing transparency, Y-value 87.5, x-value 0.317, and y-value 0.325, which changed to 85.9, 0.325, and 0.341, especially, after 30 days. Then the resulted coating was adhered with a fiber-reinforced phenolic resin plastic to show 38kg/cm^2 adhesion strength.

Hesse and Rauhut[56] prepared resole resins with less than 5% free phenol content, useful as binders with low shrinkage with formaldehyde having trifunctional phenols and alkylidenepolyphenols with the phenolic OH in the trifunctional phenols to that in the alkylidene polyphenols being (3-9):(1-7) and OH-formaldehyde mol ratio being 1:(1.2-2.0). Thus, adding 121.5 parts 37% aqueous formaldehyde solution and 173.3 parts paraformaldehyde in 1 h to 282 parts phenol and 30.3 parts 33% aqueous sodium hydroxide at 60°C with stirring, continuing the stirring for 2h, adding 228 parts 2,2-diphenylolpropane, and stirring for an additional 150 min gave a product with free phenol content 3.8%.

Santana et al.[57] took an alternative to phenol, a petroleum-based nonrenewable resource, in phenol-formaldehyde resins to support the wood-based panel industry. Tannins were the best substitute for phenol in this case. Tannin from black wattle, *Acacia mearnsii*, could be liquefied with phenol in the presence of an acid catalyst. In this study, tannin replaced 33% of the phenol in the preparation of resole-type plywood adhesives. Globally pine (*Pinus Taeda*) plywood bonded with the liquefied tannin resin had strengths and wood failures that were comparable to com. phenol-formaldehyde adhesives and significantly better than unmodified tannin-formaldehyde adhesives when used to bond southern pine under bonding conditions commonly employed with phenol-formaldehyde resins.

Majchrzak et al.[58] obtained reactive phenolic resin for chemically hardening core and molding compounds by polymerizing phenol with formaldehyde in the presence of sodium hydroxide catalyst at phenol-formaldehyde-sodium hydroxide ratio 1:1.8:0.042 at 80 ± 1°C for 110 min, followed by neutralization with p-toluenesulfonic acid and a mixture of adipic, glutaric, and succinic acid. The resin was subsequently mixed with 0.5% aminosilane A 1100 coupling agent.

Ootani and Nakamura[59] prepared resole phenolic resins with metal content 0.05% (based on solid content of resins) and fixed carbon content ≥40% (based on solid content of resins) by using ≥1 catalyst selected from ammonia, primary amines, secondary amines, and tertiary amines. Thus, phenol 700, bisphenol A 300, 37% formaldehyde 1080, and 25% ammonium hydroxide 10 parts were reacted at 80±1°C for 150 min, neutralized with AcOH, and dehydrated to give a 70%-nonvolatile phenolic resole (fixed carbon 51.9%, metal 0.02%). Carbon fibers were impregnated with the resole and the resulting prepregs were hot pressed to give a test piece showing bending strength 1.2×10^{3} kg/cm^{2} and flexural modulus 0.9×10^{5} kg/cm^{2}.

Ogiwara and Takada[60] manufactured resole phenolic resin foams, useful for for building walls and ceilings, by expanding and curing resole phenolic resins in the presence of blowing agents, foam stabilizers, and 2-60 phr mixtures of acidic curing agents containing naphthalenesulfonic acid formalin condensates (I) and arylsulfonic acid acidic curing agents $RR'C_6H_3SO_3H$[II; R, R'=$(CH_2)_mH$, H, OH; m=1-3] with I/II(weight ratio) (9/1)-(5/5). Thus, 2kg Phenol and 2.93kg 37% aqueous formaldehyde were treated at 80^{0}C for 3h in the presence of sodium hydroxide to obtain a resole phenolic resin. A mixture(X) containing the thus obtained resin 100, Tween 40 4, and CH_2Cl_2 6 parts was blended with a mixture(Y) containing 60 parts I(d.p.=4-5) and 40 parts xylenesulfonic acid with X:Y(weight ratio) 100:20, expanded, and cured at ambient temperature in a mold to give a phenolic resin foam with density 24.0kg/m^{3}.

Majchrzak et al.[61] manufactured formaldehyde-phenol-urea resole resins with good viscosity stability during storage by heating 1 mol phenol with 1.4-1.8mol formaldehyde 150-240 min at 62-67°C in the presence of 0.15-0.25mol sodium hydroxide, adding formaldehyde at formaldehyde-phenol overall ratio (2.4-2.6):1 and 0.4-0.5 mol sodium hydroxide/mol phenol, heating at 72-77°C until the viscosity was 90-130mPa s, adding 1-4% urea based on reaction mixture and sodium hydroxide at sodium hydroxide-phenol overall mol ratio (0.7-0.9):1, heating at 77-83°C until the viscosity was 250-800mPa s, adding 6-14% urea based on reaction mixture in 80min, and continuing the reaction until the viscosity was 250-600 mPa s. The viscosity stability in storage was improved by dividing the amount of sodium hydroxide in the third step into 2 portions at a 1:(0.4-0.6) ratio, with the 1st portion added at the beginning of step 3 and the 2nd adding after the viscosity of the product is 250-450 mPa s.

Uragami et al.[62] prepared thermosetting solid resole resins, solvent-solution, storage-stable, and forming heat- and water-resistant cured moldings, by condensing phenol with RCH_2-p-$C_6H_4CH_2R$(R=halo, OH, C_{1-4} alkoxy) to give $HOC_6H_4(CH_2$-p-$C_6H_4CH_2Z)_n$ CH_2-p-$C_6H_4CH_2C_6H_4OH$(I; Z=hydroxyphenylene; n = 0-100) followed by base-catalyzed reaction with an aldehyde. Reacting 4.5mol phenol with 3 mol CH_3OCH_2-p-$C_6H_4CH_2OCH_3$ in the presence of CH_3SO_3H to give I (n≈34) followed by reaction with formaldehyde gave a resole resin which showed gel time 125 s at 150°C and was press-cured at 170-230°C to give a molding having 5% weight loss temperature 423°C and acetone-solution content <0.2%. A mixture of the resin 30, glass fibers 40, and wollastonite 30 parts was press-molded at 220°C and 2.3 ton/cm^{2} to give a molding with flexural strength 15.7 kg/mm^{2} at 23°C and 8.1kg/mm^{2} after 312h at 270°C, flexural modulus 1710kg/mm^{2} at 23°C and 1300 kg/mm^{2} after heating, and boil-ing water absorption 0.11%.

Gryta et al.**[63]** manufactured water-solution resole resins with low content of precipitates and free phenol, useful as binders for production of products from mineral and glass wool, by heating a (3.7-4):1(mol ratio) formaldehyde-phenol mixture containing 0.3-0.8% alkali catalyst based on mixtures of oxides and(or) hydroxides of Ca and Mg at 60^{0}C until 60-75% of the phenol was converted to hydroxymethyl derivatives and then heated the mixture at 61-66?C until the content of free phenol was <1%, with the nonactive and(or) insoluble impurities of the catalysts being removed from the reaction mixture in each step by continuously passing the reaction mixture through an external heat exchanger having an even numbers of channels, which acted as a decantation system.

Majchrzak et al.[64] manufactured phenol-formaldehyde resole resin containing phenol, formaldehyde, and sodium hydroxide in a 1:(1.6-2):(0.01-0.02)mol ratio were heated 55-65 min at 79-82°C, and the product with n 1.459-1.469 was mixed with 0.023-0.04 mol sodium hydroxide/mol phenol and heated at 40-130min at 79-82°C. The product with n 1.472-1.482 was cooled to 70-75°C and mixed 0.5-1.5h with 45 g p-toluenesulfonic acid (I)/1kg phenol, and the product was dewatered in vacuo to #4 Ford cup viscosity 90-180s. The dewatered resin was optionally mixed with 40g urea/1 kg phenol, cooled to 40-50°C, mixed with 15-30 g 1:1:1 adipic acid-succinic acid-glutaric acid mixture/1 kg phenol to adjust the pH to 6-7.9, and modified with aminosilanes. Optionally, I was not added, and the resin was dewatered in vacuum to #4 Ford cup viscosity 280-450 s before adjusting the pH. The resulting resin had low concentrations of free formaldehyde and phenol and was useful for moldings and foams.

Sun et al.[65] prepared water-soluble resole phenolic resin adhesives by polymerization of a 1:1.4 phenol-formaldehyde molar mixture in the presence of sodium hydroxide as catalyst at 90-92°C for 1.5h. The adhesive had good water resistance, weatherability, and chemical resistance. The viscosity of the adhesive was 5×10^4 mPa.s.

Sikorski and Amin[66] manufactured phenolic resole bismaleimide useful for heat-resistant products, from phenolic resole bis(maleic anhydride), using ammonium hydroxide and isolating a phenolic resole bis(malonic acid) intermediate.

Wang et al.[67] polymerized tert-butylphenol (I) with formaldehyde in the presence of sodium hydroxide catalyst. Suitable reaction conditions were: I-formaldehyde molar ratio 2.5, sodium hydroxide concentration 6%, adding formaldehyde at 65°C, and reaction time 4h. The resole with the main structure of a methylene bridge between two hydromethylphenol had apparent viscosity of 1200MPa.s(25°C), number-average molecular weight 365. The resole modified with rosin has high viscosity and mineral oil tolerance, and could be used as advanced offset ink vehicles.

Ueda et al.[68] prepared resole phenolic resin molding materials using no solvents by polycondensing 1.2-2.5mol formaldehyde with 1mol phenol in the presence of alkalies to form liquid polycondensates (A) having number-average molecular weight (M_n) 300-3000, storing Liquid A at 50-120°C, dispersing A in fillers, and particularizing the mixtures liquid formaldehyde-phenol copolymer (I) with M_n 700 was prepared and stored at 80^{0}C and 5000g I was mixed with 3400 g wood powder, 2100g calcium carbonate, 8000 g cotton powder, 370 g $Ca(OH)_2$, and 144g zinc stearate in a Henschel mixer at 70^{0}C to give a molding material.

Maeda et al.[69] manufactured epoxy resins especially useful in copper foil-clad laminates by reacting resoles of phenol and formaldehyde and polyhydric phenols derived from the resoles and $C_6H_3R_1R_2OH$ (R_1, R_2=H, C≤4 alkyl) with epihalohydrin compounds. Preparing a resole of phenol and formaldehyde, reacting the resole with phenol, heating with epichlorohydrin and aqueous sodium hydroxide gave an epoxy resin with epoxy equiv 188 g/equiv and softening point 53°C. The epoxy resin 62, bisphenol A-formaldehyde condensate 38, 2-ethyl-4-methylimidazole 0.2 part, and 1:1 MEK-ethylene glycol monomethyl ether gave a 60% varnish, which was used to prepare a copper foil-clad laminate.

Teodorczyk[70] prepared modified phenol-aldehyde resins by reacting 0.55-0.8:1 mixtures of aldehydes and difunctional phenolic compounds in the presence of alkaline catalysts, and reacting with modifiers selected from melamine, urea, and other suitable nonvolatile organic compounds. The inventive resins resisted precuring and were particularly useful in blowline blending procedures.

Parks and Anderson[71] prepared emulsifiable melamine-modified phenolic resole resins useful as glass fiber binders by preparing an alkaline resole by reacting formaldehyde and a phenol at formaldehyde to phenol molar ratio 1:1 to 6:1 at pH 8-10 in the presence of a basic catalyst, followed by reacting residual formaldehyde with melamine at pH 8-10 in the presence of a polyhydroxy compound(e.g., sucrose, sorbitol, triethanolamine) at unreacted formaldehyde *o*-melamine molar ratio 3:1 to 1:1.

Ueda and Kondo[72] manufactured resole resin molding materials by condensing phenol and formaldehyde at molar ratio F/P=1.2-2.5 (F=molecular number of formaldehyde, P= molecular number of phenol) in the presence of alkali, dehydrating to give liquid condensate, adding diglycidylaniline to the condensate under stirring, dispersing into filler, and granulating. The process reduced the content of free phenol monomer in the material. Thus, 2800 g phenol was polymerized with 3100g 47% formalin (F/P=1.63) in the presence of 20g zinc acetate at 100-120°C for 6 h and dehydrated under 40 Torr at 110°C for 3h to give liquid condensate showing viscosity(at 80°C) 40,000 cps, which was blended with 212g diglycidylaniline and added to filler composed of wood powder 2880, calcium carbonate 1780, cotton powder 680, and $Ca(OH)_2$ 310g to give a molding material containing ≤2% phenol.

Fukuzumi and Yonemoto[73] prepared resole compositions in the presence of tertiary amines as catalysts and ammonia with good impregnation into base materials, useful for laminates with high electrical insulation, by treating phenols and formaldehyde in the presence of ≤0.03 mol (vs. 1mol phenols) tertiary amines and then ≤0.09mol (vs. phenols) ammonia. Thus, 60 parts phenol and 40 parts tung oil were treated in the presence of 0.5 part p-tolune sulphonic acid then the composition was neutralized with triethanolamine, polymerized with 32 parts 37%-formaldehyde in the presence of 0.9 part triethylamine at 80°C for 60min, and treated with 1.8 parts 25% aqueous ammonia at 80°C for 30min to give a resole (I). Prepregs, obtained by impregnating craft papers with a varnish comprising 50% resole prepared from 100 parts phenol and 70 parts 37%-formaldehyde and 50% melamine-formaldehyde copolymer, were impregnated with a varnish of I then a stack of the thus processed prepregs was hot pressed with a copper-foil to give a laminate showing resistivity 8 ×108 Ω.

Maldas et al.[74] prepared wood-based resole resins from both water- and sodium hydroxide-catalyzed liquefied phenolated wood. The effects of various reaction parameters, e.g. the concentrations of phenol and formaldehyde, temperature, and time, on the extent of yield, free phenol content, molecular weight as well as the gluability of the resole resins have been evaluated. As far as the yield, free phenol content, and molecular weight are concerned, the optimum conditions of resole resin preparation were found to be a phenol-wood weight ratio of 4:6, a formaldehyde-phenol mol ratio of 1.5:1, a temperature of 82.5°C, and time 3h. However, these optimum conditions changed when the performance of the adhesives was considered in terms of the adhesive bond strengths for plywood joints. The yield, molecular weights, polydispersity, and gluability of resole resins prepared from water-catalyzed liquefied wood were lower compared with those prepared from sodium hydroxide-catalyzed ones. In most cases, the dry-bond strengths of the experimental plywood joints exceeded the min. Japan Agricultural Std. (JAS) values. On the other hand, except at a higher formaldehyde-phenol mol ratio (i.e., 2.0:1), the plywood joints of all samples delaminated during 'boil-dry-boil' cyclic treatments. However, both dry- and wet-bond strengths of the plywood joints could be improved to exceed std. values by using an additional crosslinking agent, e.g. poly(methylenepolyphenyl isocyanate) (polymeric MDI). The adhesive performance of the wood-base resole resins was explained on the basis of the adhesion between wood veneers and resole resin adhesives.

Urreiztieta et al.[75] prepared aqueous phenolic resin binder for manufacture of foundry sand molds and cores hardened in heated pattern boxes with the formaldehyde/phenol mol ratio of (1.1-2.2):1.0, and mixed with aqueous sodium hydroxide and/or sodium hydroxide for 45-65 weight% solids, and with an oxyanion (especially a borate) as the catalyst. The molds and cores in pattern boxes were gassed with carbon di-oxide for rapid hardening, especially at approximately 70°C. The process was suitable for manufacture of bulky molds with a short gassing time of nominally 5s, especially in casting of steel or gray cast iron with decreased veining defects. Foundry sand was then mixed with ≤10weight%

of aqueous phenolic resole resin binder, and the mix was shaped in pattern boxes and hardened with carbon di-oxide and optional heating at 20-100°C.?

Parks[76] developed a urea-extended phenolic resole resin, comprising of phenolic resole resin (prepared by reacting formaldehyde (F) and phenol (P) at an F:P mole ratio in the range of about 2:1 to 6:1 under aqueous alkaline reaction conditions) and reacting free formaldehyde in the phenolic resole resin with urea to form a urea-extended phenolic resole resin, the improvement comprised adding an alkanolamine to the phenolic resole resin, in an amount sufficient to improve the storage stability of the urea-extended phenolic resole resin, either prior to or contemporaneously with the urea reaction with the phenolic resole resin.

Black[77] prepared a guanidine salt-modified phenol-formaldehyde resole resin by reacting formaldehyde and phenol at a formaldehyde to phenol mole ratio above about 1.5:1 in the presence of an effective amount of an alkaline catalyst and in the presence of a catalytic amount of a guanidine salt. The resin was suitable for use in adhesives for high moisture content substrates such as wood.

Dando et al.[78] prepared the benzylic ether phenolic resole resins by heating phenol and an aldehyde in a sealed reaction vessel in the presence of a divalent metal catalyst without removing water generated by the reaction until an appropriate endpoint for the resin was reached. The benzylic ether phenolic resole resins produced by the process were preferably free or essentially free of unreacted formaldehyde and could be used in the resin component of phenolic-urethane foundry binders to make foundry cores and/or molds by the cold-box and no-bake processes. The cores and/or molds were used for making metal castings.

Matsuoka and Yagi[79] gave a production method of phenolic resole resins comprising resole formation using amine catalysts containing primary and tertiary amine groups. The resins were useful in laminates (e.g., with paper) which have good silver transferability resistance. Formaldehyde and phenol were reacted in the presence of 1-aminoethyl piperazine to give a resole.

Iwata and Isogai[80] manufactured resoles especially useful for impregnation of paper for lamination with melamine paper of decorative panels by reacting formaldehyde with phenol compound in the presence of an acid catalyst in an early stage, then reacting in the presence of a basic catalyst in the resole-forming stage where the formaldehyde:phenol molecular ratio was maintained at 0.3-1.5 and 1.1-1.5 in the early stage and the resole-forming stage, respectively, and the average molecular weight was set to end at 120-300 and 350-450 in the early stage and the resole-forming stage, respectively

Walisser and Johnson[81] prepared a curable, alkaline, melamine-modified phenol-formaldehyde resin from an initial phenol-formaldehyde resole resin containing 0.5-2.5% of free formaldehyde by scavenging formaldehyde with 1-12 parts of melamine for each 100 parts of the initial resin wherein the molar ratio of formaldehyde to melamine was 0.2-1.5 mol of formaldehyde for each mole of melamine to reduce the free formaldehyde to <70% of that in the initial resin. The modified resin was storage-stable, contained <0.7% of free formaldehyde, and maintained its stability under application conditions. An ammonium salt of a strong acid and additional water could be incorporated into the melamine-modified resin to provide a binder for binder-treated fiber glass.

Svensson[82] produced a substantially water-solution or water-dilutable sulfonated resole type phenolic resin by condensing ≥1 phenolic compound and formaldehyde, at phenolic compound-formaldehyde molar ratio 1:1.5 to 1:5, the presence of ≥1 basic catalyst. The condensation reaction was terminated when a free formaldehyde content of 1-10 weight% was obtained, and the condensation product was sulfonated with 1-10 weight% pyrosulfite at 30-60°C for ≥15min. Thus, 1112g 50% aqueous formaldehyde was added over 45min to a mixture of 666.5g phenol in 184g water and 37g aqueous 46% sodium hydroxide (1:2.6 phenol-formaldehyde) and the mixture reacted for 8h with continuous cooling to ≤60°C, giving a resole containing 5.1 weight% free formaldehyde. The resole was cooled to 40°C, 179g sodium pyrophosphite(sic) was added and allowed to react for 60 min, giving free formaldehyde 2.0 weight%.

Doronin et al.[83] manufactured low-toxic resole-type phenolic resins involving the reaction of bisphenol A and formaldehyde in the presence of sodium hydroxide and sodium tetraborate. The polymers prepared by this method had lower toxicity and better adhesion to wood. Thus, bisphenol A 100 weight parts, water 50, sodium tetraborate 3 and formaldehyde160 weight parts were mixed and kept at 50°C for 28min. The mixture was cooled to 30°C, sodium hydroxide(50 weight parts) is added, and the polymerization system was kept at 50°C for 60 min and at 94°C for 20min. The mixture was then cooled to 65°C, sodium hydroxide(30 weight parts) was added, and the polymerization system was kept at this temperature for 15min and at 80°C for 5 min.

Piotrowska et al.[84] manufactured a low-viscosity phenolic resole resin, useful for the manufacture of multilayer composites with good electroinsulating properties, especially filament wound tubes by polycondensation of phenol, nonylphenol and formaldehyde in the presence of ammonia at molecular ratio phenol/nonylphenol/formaldehyde/ammonia=1:(0.08-0.3):(1.2-2):(0.035-0.08) at reflux until the refractive index of the resin η 20D reached 1.520-1.580, preferably 1.561-1.567.

Higuchi et al.[85] manufactured resole resins by polymerising phenols substituted with C_{12-30} alkyls and formaldehyde under basic condition, wherein alcohols were used as the reaction solvents. The resins showed high conversion of the higher alkylphenols and good separation of the organic phase containing the resulting resoles from the aqueous phase in the polymerization process. Thus, 31.9g 2/1 mixture of o-/p-hexadecyl phenol(prepared from phenol and hexadecene-1) in 30.5g ethyl alcohol was polymerized with 37% aqueous formaldehyde in the presence of 4.2 g 48% aqueous sodium hydroxide at 60°C for 5h, then the mixture with 82.0% polymerization conversion was neutralized with 13.5% HCl to show good separation between the aqueous phase and the oil phase. The separated oil phase contained 31% dimer, 40% trimer, and 29% oligomers higher than tetramer.

Shang et al.[86] synthesized a resole phenol-formaldehyde resin containing large number of hydroxymethyl groups, a mold binder from phenol and aqueous formaldehyde using sodium hydroxide solution as catalyst. The structure of the resin was characterized by IR. The mass ratio of hydroxymethyl group in the resin was 32.8% and the inherent viscosity reached 2.68mL/g under the optimum conditions: n(formaldehyde):n(phenol):n (sodium hydroxide)=2.5:1:0.1, and reaction at 65°C for 3h.

Ma[87] prepared the phenolic resin by reacting a mixture of ≥2 alkylphenols selected from p-tert-butylphenol, p-methylphenol, p-tert-octylphenol and p-nonylphenol with formaldehyde in base to form a mixed phenol-formaldehyde phenolic resin,modifying with rosin and then esterification reacting with a polyols. Thus, p-tert-butylphenol 34 and p-tert-octylphenol 100 parts were reacted with 141 parts 37% formaldehyde in 60 parts 15% caustic soda, modified with 400 parts rosin and then reacted with 60 parts glycerol to give a modified phenolic resin with viscosity 6500 mpas, acid value 17 mg NaOH/g and n-heptane tolerance 7.2mL/2g.

Ziegler et al.[88] produced externally emulsified aqueous resole resin dispersions by reacting phenols and oxo compounds in the presence of alkaline catalysts, adding emulsifying agents and preparing dispersions. The alkaline catalysts were linear aliphatic, branched or cyclic tertiary C_4-C_{40}-monohydroxyamines, such as N,N-dimethylethanolamine, N,N-diethylisopro panolamine or 4-(dimethylamino)-1-butanol. Emulsifying agents were mixtures of protein emulsifiers and amides, such as urea, guanidine or melamine. The dispersions were used for production of binders for abrasives, especially supported adhesives. Thus, phenol-formaldehyde resin was produced by polymerising monomers in the presence of N,N-dimethylethano lamine, followed by preparing an aqueous dispersion by homogenizing with a mixture of casein, urea, dimethylethanolamine and water.

Li et al.[89] prepared a water solution phenol-formaldehyde resin from phenol and formaldehyde of molar ratio 1:3 in aqueous solution through a two-step alkaline catalytic reaction at 50°C-90°C procedurally heating up over 2h. The concentration of products was 45% and the residue formaldehyde in the resin was 1.2% (wt) in contrast with 16.5% (wt) for one step catalytic reaction product. The polymer gelled and viscosity got 2.9×104 mPa x s by 0.3% approximately 1.0% polyacrylamide solution with 0.3%-1.1% resole added as crosslinker at 50°C-55°C. The solid phenol-formaldehyde resin could be endured over 300°C after self condensation reaction at 100°C and be used as profile control and water shutoff agent for high temperature.

Kobayashi and Asami[90] manufactured resole-type phenolic resins using organophosphonic acids by treating phenols with aldehydes in the presence of organophosphonic acids and then treating the resulting novolak-type phenolic resins with aldehydes in the presence of alkali catalysts. Thus, phenol and formaldehyde were treated in the presence of Ferriox 115(1-hydroxyethylidene-1,1'-diphosphonic acid) and then treated with formaldehyde in the presence of sodium hydroxide to give a polymer with amount of unreacted phenol 0.5% and amount of unreacted formaldehyde 0.9% in yield 110%.

Ide et al.[91] developed a process for the manufacture of nitrogen-free solid resole phenolic resins which involved (i) reacting (A) phenols containing hydrophobic phenols with solubility to water at ambient temperature ??10 with (B) aldehydes in the presence of catalysts, (ii) crushing the obtained water-containing resolic phenolic resins, and (iii) drying the obtained granules under heat. The hydrophobic phenols gave hydrophobic resins, hence dewatering and drying could be done easily. Thus, bisphenol A (solubility. to water 0.036) 1.75, phenol 33.25, and formaldehyde 44 kg were copolymerized in the presence of triethylamine at 90°C, treated under reduced pressure to remove liquids, cooled at 100°C, crushed, and dried in a fluidized-bed drier to give a transparent resin granule with water content 1.0% and bulk d. 0.75.

Sasakura and Toyoda[92] produced a resin varnish for printing ink by condensing phenol and formaldehyde in an ink solvent to obtain an ink solvent solution of resole initial condensate, after which the resole initial condensate and a rosin ester containing 30-60 wt% non-aromatic conjugate resin acid and 20-60 wt% aromatic resin acid were reacted at 100-250°C. in a system containing ink solvent or in a system containing ink solvent and drying oil. A high-viscosity, high-molecular-weight ink resin was produced efficiently by reacting, with resole initial condensate in ink solvent, a rosin ester containing specified contents by percentage of conjugate acid and aromatic resin acid. The resin varnish obtained had very few decomposition components and nonuniformly gelled components, so it also was suitable for screen printing ink and letterpress printing ink, in addition to offset printing ink. Thus, a gel varnish was prepared by mixing 851 parts of p-octyl phenol-formaldehyde copolymer with 660 parts of tall rosin glycerin ester regulated to acid value 20 and 16 parts Chelope EP 12 (gelling agent) in 100 parts of AF 7(naphthenic oil).

Tsujimoto et al.[93] manufactured phenolic resin compositions from dry oils, phenols, triazine ring-containing compounds, and aldehydes, a 1st phenolic resin was prepared by reacting dry oil-modified phenols with aldehydes in the presence of acidic catalysts to give novolaks, followed with treating in the presence of basic catalysts to give resoles, and a 2nd phenolic resin with molecular weight lower than that of the 1st phenolic resins and prepared by reacting at least phenols with aldehydes in the presence of basic catalysts, the triazine ring-containing compounds being contained in the 1st and/or the 2nd phenolic resins. Thus, a methylolated melamine-phenol-formaldehyde resin solution(M-1) was diluted with methyl alcohol/water mixture to give a varnish for 1st impregnation(F-1). A varnish(P1-1) of a 1st phenolic resin contained M-1 and a resole(R-1) prepared by reacting tung oil-modified phenol with formaldehyde to give a novolak(N-1), followed with reacting with formaldehyde in the presence of triethylamine and aqueous ammonia. A varnish(P2-1) of a 2nd phenolic resin contained a phenol-formaldehyde copolymer resole(R-2) prepared in the presence of triethylamine and ammonia. A resin varnish for 2nd impregnation(S-1) comprised P1-1, P2-1, $(C_6H_5O)_3P$, and bisphenol A diglycidyl ether. A coated paper was impregnated with the varnish F-1, dried, impregnated with the varnish S-1, and dried to give a prepreg, 8 pieces of which was laminated, cladded with a copper foil, and press-molded to give a laminate board.

Coventry-Saylor[94] developed a process of phenolic resin having higher solid content containing steps of: (1) preparing an aqueous mixture containing phenol and formaldehyde, (2) adding a basic polymerization catalyst, (3) maintaining the aqueous mixture at a predetermined temperature during the polymerization to form the water-solution resole resin, (4) cooling and adjusting pH ≤ 3, and (5) adding curing catalyst, and phenolic resins were used as a binder for glass fibers.

Kage et al.[95] developed an acid-curable resole resin composition containing aldehyde-phenol resole resin with p-/o-bonding ratio ≥ 1.8, in the phenolic resin from phenol and 1 or 2 aldehydes phenol content is 25-50 weight% of the entire resole resin, and the phenolic resin had number average molecular weight 300-600, weight-average molecular weight 400-1100.

Samejima et al.[96] developed binders containing low-phenol-content resoles for refractories containing resoles manufactured from aldehydes, (0.3-0.6):1 mol aldehyde-phenol novolak copolymers, and optionally phenol. The residual content of Phenol in the resoles might be ≤1 weight%. The resoles might be manufactured from (0.5-4.0):1 mol aldehydes and the novolaks with average molecular weight 500-800 at pH 4-12 in the presence of catalysts.

Kobayashi et al.[97] manufactured solid resoles by reacting phenols with aldehydes in the presence of acid catalysts until novolaks with Mw ≤1500 by GPC and unreacted phenols content ≤5% were manufactured, reacting the novolaks with aldehydes in the presence of alkali catalysts, and dewatering the resulting resoles until the water content became ≤5%. Thus, phenol was polymerized with aqueous formaldehyde in the presence of Feliox 115 (1-hydroxyethylidene-1,1'-diphosphonic acid) to give a novolak with Mw 875 unreacted phenol content 1.2%, which was refluxed with aqueous formaldehyde in the presence of calcium hydroxide for 1 h and evaporated in vacuo to give 88% resole with m.p. 50°C, melt viscosity 1050 Pa-s at 110°C, and water content 1.7%.

Shimokage[98] manufactured fire- and heat-resistant phosphorus-containing phenolic resins for laminates by reacting phenols with aldehydes in the presence of acidic catalysts, neutralizing the resulting novolak phenolic resins, reacting the resins with aldehydes in the presence of basic catalysts, and reacting the resulting resole phenolic resins with phosphorous (P) compounds having H-P or halogen-P direct bonds at 100-150°C. The laminates were obtained by impregnating substrates with the P-containing phenolic resins, drying to give prepregs, and laminating the prepregs. Thus, phenol was reacted with formaldehyde in the presence of p-toluenesulfonic acid to give novolak phenolic resin, which was neutralized with sodium hydroxide and reacted with formaldehyde in the presence of triethylamine. The resulting resole phenolic resin was reacted with dimethylhydrophosphine oxide at 120°C to give phosphorous-containing phenolic resin, which was used to impregnate paper and formed to a copper-clad laminate showing UL-94 fire resistance V-0 and high solder heat resistance.

Wang et al.[99] studied phenol formaldehyde resins for the thermal-sensitive CTP plates were synthesized and their imaging performance. Firstly, 2402 resin was modified by the phenol and formaldehyde. The resulting binder resins were solution in dil. alkali aqueous and had good imaging performance. Secondly, o-cresol, p-cresol, p-tert-butyl phenol and their mixture reacted with formalin in the presence of catalysts. Then novolac and resole resins which ether groups in the main chain and hydroxy-methyl groups at the terminal of the polymer were obtained. The resins with ether groups could be used for acid-composed binder resin of positive thermal-sensitive CTP plates. The polymers with small account of hydroxy-methyl groups at the terminal might be crosslinked and cured when they heated, and then developed to result in negative graph with good performance.

Sato et al.[100] developed the composition especially useful for printed circuity boards comprise a drying oil-modified resole-type phenolic resin and a condensed phosphate ester, where the phosphate ester was incorporated at 20-60% based on the solids of the resin and 10-50% of which was incorporated during the manufacture of the resin. Reacting tung oil 350, phenol 900, and p-tolune sulphonic acid 0.6g at 90°C for 1h, adding 400g paraformaldehyde, 60g aqueous ammonium hydroxide, and 30% (on the resin solids) phosphate ester(CR 7411), heating 2 h at 75°C, mixing this resin with 30% CR741 and 10% VP08K (phenoic resin), and diluting with methyl alcohol gave a resole-type phenolic resin varnish. A kraft paper was impregnated with 10% melamine-modified phenolic resin, then with this varnish, and the resulting prepregs (8 pieces) hot pressed with a copper foil to give a laminate with UL 94 fire resistance V-0, no odor, and good soldering heat resistance.

Yang[101] prepared the water-solution resole by the reaction between phenol and formaldehyde with molar ratio 1:1.2-1.5 in the presence of catalysts at 80-85°C. The catalysts were made up of a kind of tertiary amine and a small amount of barium hydroxide. Free phenol content and free formaldehyde content in the water-solution resole were not more than 10% and 1.4% respectively. This water-solution resole was widely used in many applications such as plywood and insulation laminate.

Chen[102] made a high-carbon-yield (≥69%) resole by reacting formaldehyde and excess phenol to an endpoint (pre-cure) and then crosslinking with hexamethylenetetraamine HMTA. Similar high-carbon-yield resoles resulted with addition of DBE-2, furfuryl alcohol and furfural diluents. The crosslinked polymers were useful as refractory binders and had high temperature and oxidation resistance and viscosity 990-5200cP.

Sato and Nakamura[103] manufactured resole resins and their manufacture with no salt precipitation containing(A) condensing $R^0CHO(R^0=H, C_{1-8}$-hydrocarbon group) and (un)substituted phenols (substituent = alkyl, aryl, alkoxy, halo; number of substituent=0-3) in the presence of alkali catalysts and(B) neutralizing the reaction solutions with polycarboxylic acids $HOCO(CR^1R^2)^l(CR^5:CR^6)_m(CR^3R^4)_nCO_2H$ (l, n=0-10; m=0-5; l+2m+n=1-10; R^{1-6} = H, alkyl, alkenyl, alkoxy, halo, carboxy, OH). The resole resins were useful for plastic foams. Thus, phenol and formaldehyde were polymerized in the presence of sodium hydroxide, mixed with adipic acid, and dried to give a resole resin with good expandability.

Kage et al.[104] manufactured the resoles(M_n 100-1000, Mw 500-3000), useful for FRP, etc., by polymerization of aldehydes and phenols in the presence of divalent metal salts for polynucleus content ≤20% and further reaction in the presence of alkaline catalysts. Thus, phenol and formalin were polymerized in the presence of $Zn(OC_2H_5)_2$ to give a resole (polynucleus content 18%), which was further reacted in the presence of sodium hydroxide to give a resole with M_n 320 and M_w 660. A mixture of the resole and p-tolune sulphonic acid showed pot life 60 min and cured to give a specimen showing flexural strength 75 MPa and flexural modulus 2600 MPa.

Ingram et al.[105] prepared phenol-formaldehyde resole resin having low free formaldehyde and low formaldehyde emissions during B- and C-stage resin processing and curing using a relatively large quantity of catalyst, as compared with the quantity used for typical laminating resins, in combination with the addition of one or more formaldehyde scavengers during later portions of the A-stage of the resin cook. Such resin was particularly adapted for use in manufacture of paper-based laminate products.

Lubczak[106] gave a new results on the method of preparation of phenol-formaldehyde resins from phenol and multihydroxymethyl derivatives of some ketones were presented. The latter, known as the reactive solvents of melamine, were prepared by reacting acetone and methyl ethyl ketone(MEK) with excess of formaldehyde. A novel group of resole-type resins were obtained. The structure of the products was discussed and compared to that of classical resoles. Fragments of ketones were found incorporated into the structure of the resins.

Li et al.[107] prepared a water soluble phenol-formaldehyde resin by two step alkaline catalytic reaction from phenol and formaldehyde of molar ratio 1:3 in aqueous solution through a two-step alkaline catalytic reaction at 50°C-90°C procedurally heating up over 2h. After dewatering by decompressing, the concentration of products was 82% and the residue formaldehyde and the phenol in the resin were 1.1%(wt) and 0.05%(wt) respectively

Takahashi et al.[108] prepared resoles which contained structural units derived from more than one compounds chosen from $P(O)(A^1OH)(A^2OH)(A^3OH)$, $P(O)(A^4OH)(A^5OH)(OH)$, and $C_6H_5O\text{-}P+(A^7OH)(A^8OH)(A^9OH)(A^{10}OH)$ (A^1-A^8=C_{1-8} alkylene). Thus, phenol was polymerized with formaldehyde and tris(hydroxymethyl)phosphine oxide in the presence of sodium hydroxide to give a composition, which was cured by heat to give a product showing good hydrolysis resistance. Then, kraft paper was impregnated with melamine-formaldehyde-phenol copolymer, dried, impregnated with the composition, and dried to give a prepreg, 8 sheets of which were piled, sandwiched between copper foils, and hot-pressed to give a laminate.

Malhotra et al.[109] prepared low-emission water-solution phenol-formaldehyde resole resins as binders for mineral fiber insulating materials having water dilutability 20:1 at neutral pH after storage for three weeks at approximately 13°C and free phenol level ≤0.50%, useful for mineral fibers by reacting ≥1 hydroxy functional aromatic compound (e.g., phenol) with ≥1 reactive aldehyde (e.g., formaldehyde) at the presence of a high level of ≥1 basic polymerization catalyst (e.g., sodium hydroxide and/or sodium hydroxide) at

50-75°C.

Kage et al.[110] prepared resole phenolic resins by the reaction of aldehydes and phenols in the presence of alkali catalysts and neutralization of residual alkali compounds with acids with pKa ≤0 and acids with pKa ≥1 and (B) acids. Thus, reaction of phenol and formaldehyde in the presence of sodium hydroxide and neutralization with 8:2mol p-toluenesulfonic acid (I) and formic acid gave a resole, which was mixed with I and cured to give a test piece showing bending strength (JIS K 6911) 60 MPa and flexural modulus 2600 MPa. The compositions showed controlled pot life.

Gabrielson et al.[111] produced a phenol-formaldehyde resole resin which was combined with an ammonia-based formaldehyde scavenger to produce a product useful, for example, as a binder used in the production of glass fiber insulation products. The starting resin might have a free formaldehyde content 1.5-14 weight%, based on a total weight of the resin, and the resin and scavenger might be combined at a molar ratio in the range of 0.1 to 5. The resulting binder might have a free formaldehyde content of 1 weight % or less, based on a total weight of the reaction product. This binder might then be applied to a glass fiber base material in a conventional manner.

Tsujimoto et al.[112] manufactured the phenolic resins with Mw 1000-5000 containing ≥ 15% mols. with molecular weight 300-500 by primary reaction of drying oil-modified phenols with aldehydes in the presence of acid catalysts so as to form novolaks and second reaction to form resoles with addition of phenols, aldehydes, and basic catalysts to the reaction system and were impregnated into paper substrates and lamination-molded to give the laminated boards. Thus, 30 parts phenol was modified with 28 parts tung oil in methyl alcohol in the presence of p-toluenesulfonic acid, treated with 11 parts of 37% aqueous formaldehyde at 90°C for 60min, neutralized with triethanolamine, mixed with phenol 30, 37% aqueous formaldehyde 53, triethylamine 2, aqueous ammonia 1, and a methylolated melamine compound solution(m-1; prepared from melamine 130, phenol 20, 37% formaldehyde 300, sodium hydroxide 0.3, water 70, and Methyl alcohol 70 parts) 18 parts, heated to 90°C for 60 min, dehydrated, and mixed with 32 parts Methyl alcohol to give a tung oil-modified phenolic resin with Mw 1300 and 300-500-molecular-weight fraction 25%. Then 60 parts of the resin was mixed with 15 parts $(C_6H_5O)_3PO$ and 6 parts bisphenol A diglycidyl ether, applied on kraft paper preliminary coated with Methyl alcohol- and water-diluted m-1, and dried at 155°C for 100 s to give a prepreg, then 8 of the prepregs were laminated, covered with a copper foil via an adhesive, and hot-pressed to give a copper-clad laminate showing good heat and fire resistance and processability and insulation resistance $\geq 1\times 1010\Omega$.

Inoue et al.[113] manufactured resole-type phenolic resins with <1 weight% residual phenol content by reacting aldehydes with novolak resins of aldehydes/phenols =0.3-0.6 molecular Thus, novolak-type 0.75:1mol formaldehyde-phenol copolymer (I) with M_n 610 was reacted with formaldehyde in the presence of sodium hydroxide in methyl alcohol to give resole-type 1.20:1mol I with viscosity 200mPa-s and free phenol content 0.01%, with which filter paper was impregnated, dried, and cured. The amounts of evaporated phenols and formaldehyde were 20ppm and 52ppm, respectively.

Holopainen et al.[114] gave a two-level full factorial experimental design with three variables, formaldehyde-to-phenol (F/P) molar ratio, hydroxyl-to-phenol (OH/P) molar ratio, and condensation viscosity was implemented to determine the effect of the variables on the structure of phenol-formaldehyde resole resins for paper overlay impregnation. Ten resins were prepared with F/P molar ratios between 1.9 and 2.3, OH/P molar ratios between 0.09 and 0.13, and condensation viscosities between 60 and 180 mPa's. The effect of these three independent variables on the chemical structure was analyzed by ^{13}C-NMR spectroscopy, on the molecular weight distribution by gel permeation chromatography, and on the reactivity by differential scanning calorimetry.

Tsuihiji and Yamazaki[115] prepared phenolic resins $HOC_6H_3(X)[[CH_2C_6H_2(OR)(X)]_n CH_2C_6H_2(OH)(X)]_mH$ (R=methyl, ethyl; X=H, methyl; n=0-3; m=1-5; content of compound with n=0 is ≤10%), useful for curing agents for epoxy resins for semiconductor packaging. Thus, 108.0 g o-cresol was treated with 132.0g of an aqueous 50% formaldehyde solution in the presence of sodium hydroxide and further treated with 126.0g methyl sulphate to give a resole having methoxylated hydroxy groups, which was further treated with 282.0g phenol and 9.1g of 35% hydrochloric acid, neutralized with aqueous ammonia, and freed of free phenol to give a phenolic resin having softening point 77°C and ICI melt viscosity 0.8 P at 150°C. A composition of 184g/equiv epoxy resin (YX 4000), 160 g/ equiv of the phenolic resin, 3 phr triphenylphosphate, and 82% fused silica was transfer-molded to give a test piece showing spiral flow 200cm, Tg 135°C, moisture absorption 0.25% at 85°C and humidity 85% for 168 h, adhesion to copper 8.6kg, and breaking toughness 1.1 MPa-m$^{1/2}$.

Christiansen et al.[116] applied dynamic mechanical analysis(DMA) and DSC to samples of phenol-formaldehyde resole resins that had been previously exposed to dry precure conditions. The area under tan delta curves(tan delta is the dimensionless ratio of loss modulus to storage modulus) during DMA isothermal scans of such samples decreased as the degree of precure increased; this area was used as an empirical measure of the rate of mechanical cure for phenolic resins. Similarly, the DSC exotherm area decreased with greater sample precure; this area was used to measure the rate of chemical cure. Rates of mechanical and chemical cure differed for different resins and with temperature Under dry precure conditions at 115°C and 140°C, a high degree of mechanical cure was achieved at a low degree of chemical cure.

Follensbee et al.[117] used dynamic mechanical analysis(DMA) to measure the degree of cure achieved by aqueous resolic phenol-HCHO resins as a result of previous exposures to various temperature-humidity-time regimes. Procedures were developed that permitted obtaining of data that properly characterized and quantified the DMA behavior of these aqueous systems. Particularly important factors were substrate selection, samples clamping geometry, and sample humidification prior to analysis

Grenier-Loustalot et al.[118] studied the reaction mechanisms of formaldehyde condensation in perfectly controlled conditions (temperature, stoichiometry, catalyst and pH). The results obtained with a range of techniques, e.g. high-performance liquid chromatography, ^{13}C NMR and chemical assay, show that the reaction kinetics and the structures of the resole end-products depend on synthetic and operating conditions.

Kenny et al.[119] studied the polymerization of phenolic resole resin, used as a matrix for glass fiber-reinforced composite materials using DSC, and a kinetic model of the reaction was developed. Two distinguishable peaks were obtained in DSC and were assigned to two independent cure reactions with different activation energies. Kinetic constants, activation energies and reaction orders were determined for the two different kinetic equations. Both equations were integrated in a general model of the cure process through the inclusion of a weighting factor representing the fraction of heat developed in each reaction.

Umemura et al.[120] investigated the curing behavior of aqueous phenol-formaldehyde (PF) resole resin under steam-injection heating using several analysis methods. The curing reaction of 2-hydroxybenzyl alcohol, as a model compound, under steam-injection at 160°C was followed by rapid formation and then breakdown of the ether group. In the case of steam-injection at >160°C, the PF resin cured to some degree within a few minutes; after that, it did not reach a full cure. In resin heated by steam-injection, free water hindered the curing reaction, and byproducts were contained. The curing reaction under steam-injection heating at 120°C was delayed somewhat in contrast to conventional hot-platen heating.

Pushpalal et al.[121] discussed the chemical characteristics of a calcium aluminate-phenol resin composite with very high flexural strength. The flexural strength of the composite was found to be 120 to 220 MPa, which was greatly dependent on the fabrication method. The best system of these composites was made of calcium monoaluminate and the resole type of phenol resin. The evidence of possible cement-resin interaction has been found experimental in roll milling, during heat curing, and in the final product. They discussed the evidence of interaction of phenol moiety and calcium aluminate based on the observations in processing, experimental data of differential scanning calorimetry, electron probe microanalysis, conduction calorimetry, and X-ray diffraction analysis. Based on their findings, they proposed a crosslinking mechanism assumed to occur in processing and during curing.

Achary and Ramaswamy[122] prepared and characterized resole phenolic resins containing various p-cresol (PC) to phenol (P) mol ratios. These phenolic resins were blended with nitrile rubber (NBR) and the measurements of adhesive joint strength, stress-strain properties, DSC, TGA, DMA, TEM, and SEM were performed using a 50:50 NBR/phenolic resin blend. It was observed that the adhesive joint strength and the mechanical properties of the blend enhanced significantly upon incorporation of p-cresol into the phenolic resin, and the optimum p-cresol/phenol mol ratio was in the vicinity of 2:1. Observation of a more continuous phase and the increase in Tg of the rubber region in the blend indicated increased reactivity and compatibilization of NBR with phenolic resin as p-cresol was incorporated. The effect of silica filler on the properties of the nitrile rubber/phenolic resin blend was also studied without and with p-cresol modification and the results suggest that silica filler take not only the role of a reinforcing filler in the nitrile-phenolic-silica composite, but also a role as surface compatibilizer of the blend components.

Gao et al.[123] examined the curing behaviors and kinetic analysis of high-resin-content resoles prepared by the reaction of paraformaldehyde, phenol and metal compounds as catalyst by means of IR and DSC. In the curing process of resoles, hydroxymethyl groups react to form methylene and dimethylene ether linkages and release water or other low mol. content at the same time. The DSC thermograms with exothermicity of the condensation reaction and endothermicity of small molecules evaporation show wide and smooth peaks. Apparent activation energy of the resoles is 45.5 kJ/mol. It shows that the large resin content resoles are easily curable.

Papava et al.[124] studied the hardening process of resole oligomer in diatomite-containing phenol-formaldehyde polymer composition in isothermal conditions in vacuum and air at 120°-250°C. Mass-spectroscopic analysis showed that water and formaldehyde were extracted in the form of volatile products and diatomite remained constant. Mass reduction caused by water and formaldehyde extraction was taken as a criterion of quantitative evaluation of the process.

Kaledkowski and Hetper[125] prepared phenol-formaldehyde resole resins using tetraalkylammonium hydroxides as catalysts. The activity of these catalysts was compared with the activity of sodium hydroxide. Gas chromatography, thin layer chromatography, ^{13}C-NMR spectrometry, potentiometric titration and physicochemical methods were used to determine the composition of the resins and their properties. Tetraalkylammonium hydroxides were active catalysts and the resins obtained in their presence showed interesting properties.

Manfredi et al.[126] studied the relationship between the structure and the viscoelastic properties of resole resins. Six phenolic resins (resole) were synthesized with different molar ratios of formaldehyde to phenol. These resoles were cured by means of temperature and without catalyst. The characterization of the resole was done by means of IR spectroscopy and chemical methods. From the viscoelastic properties of fully cured resins, characteristic properties such as: storage modulus (E’), tan δ, width of the tan δ (ΔT) and damping peak (tan δ) were obtained. The compression modulus and the void content were also determined. A maximum in the methylene bridge and the result of the viscoelastic properties allow us to say that the resole with F/P between 1.3 and 1.4 has the highest crosslinking density.

Lenghaus et al.[127] found that the quinone methides to be involved in the curing of phenol formaldehyde resins, producing an intractable material which was resistant to conventional techniques of chemical analysis Novel models have therefore been used to investigate the curing of phenol formaldehyde resins, and have shown that ortho quinone methide has several unusual properties, including high site selectivity. Several aspects of resole curing could be explained in terms of this behavior.

Aierbe et al.[128] studied the influence of the initial formaldehyde/phenol molar ratio(F/P) on the formation kinetics of five resole type phenolic resin prepolymers. Initial formaldehyde/phenol mixts. were fixed to pH=8.0 by adding triethylamine as alkakine catalyst. The evolution of reactants and first formed addition products were followed by liquid chromatography (HPLC). ^{13}C NMR spectroscopy was applied to final prepolymers. The necessary amount of catalyst to adjust the initial pH decreased with F/P, influencing the rates of consumption and formation of the species. Final formaldehyde and phenol concentrations depend on the initial F/P ratio and on the added amount of triethylamine. The maximum concentrations of first formed addition products decreased with F/P whereas the maximum concentrations reached by di- and trisubstituted phenols was independent of this ratio. Higher molecular weight compounds were formed by joining phenolic rings by methylene bridges at para, para and ortho, para positions. No ortho-ortho bonds were detected.

Kim and Young[129] studied the resin structure, and the mechanism and kinetics of resole and novolak resin formation and cure. Resin syntheses were carried out in a laboratory glass reactor equipped with a stirrer, thermometer, and reflux condenser. Mixture of phenol and 37% formalin solution were heated up to temperature of 45°C and then the catalysts were added. FTIR spectrometer was employed for both resin characterization and kinetic study based on the fact that each chemical group in a sample absorbed IR radiation of some characteristics frequencies. Differential scanning calorimetry and thermogravimetric analysis were used to obtain thermal decomposition data for activation energy and conversion of the adhesives. The kinetic behavior based on spectra of the phenolic resin OH decreased due to internal reactions, which caused the phenolic resin to link together. The activation energy of thermal decomposition for novolac resins at the range of 0.05-0.35 was almost constant, while for resole, the activation energy decreased at initial conversion and then kept relatively constant

Lin and Chiu[130] prepared cocured materials based on resole/epoxy in wt. ratios of 100/0, 50/50 and 0/100 by using NaOH and 4,4'-diaminodiphenylmethane (DMA) as curing agents. These cocured samples were subjected to accelerated aging at 150°C in air for 45days. Continuous increase of carbonyl IR absorption at 1700-1740cm^{-1} indicated thermal oxidation. The sample with resole/epoxy =50/50 showed significantly retarded formation of carbonyls. Mechanical property tests of samples during the course of aging, including tensile stress-strain, modulus, and impact resistance confirmed a significant protection of epoxy by incorporating resole into the epoxy via cocuring.

Sugama et al.[131] studied the hydrothermal degrdation pathways of resole-type phenolic polymer coatings by XPS, SEM, TGA, EDX, and AC EIS. The 15-day-autoclave exposure tests for the coatings deposited on the carbon steel demonstrated that they suffered hydrothermal oxidation in a low pH (-1.6), geothermal brine at temperatures >150°C. The oxidative degradation pathway of phenolic polymer took place through three-step oxidation routes: first, the bridging methylene linkages in the network polymer structure were preferentially oxidized to form benzylhydroxy-type linkages in the oxidation-inductive stage; second, further oxidation led to the substitution of the benzylhydroxy linkages for the benzophenone-type linkages; and third, incorporating more oxygen into the oxidized polymer caused the breakage of C-C-C linkages in the benzophenone derivative, thereby forming salicylic acid as the ultimate oxidative degradation products of phenolic polymer.

Lenghaus et al.[132] examined two resole-type phenol-formaldehyde resins which were synthesized with a formaldehyde to phenol (F/P) molar ratio of 1.2 and 1.8 and their structure on curing by ^{13}C CP-MAS solid state NMR. The F/P=1.8 material was considerably more complex than the F/P=1.2 material. This has been interpreted as due to the formation and subsequent cleaving of ethers in the F/P=1.8 system. The structural changes in each resole after heating were observed by ^{13}C CP-MAS NMR up to 500°C, and their surface areas after carbonization at 1000°C were measured using N_2 and CO_2 gas adsorption. The F/P=1.2 material was found to possess narrower micropores than the F/P=1.8 material. These results were significant for those industries where the high-temperature behavior of phenol formaldehyde materials was important.

Gabilondo et al.[133] investigated phenol-formaldehyde resole resins as regards their cure behavior using both atmosphere and high-pressure conditions. Results obtained using Fourier transform IR spectroscopy and solid-state ^{13}C (cross-polarization/magic angle spinning) NMR showed different polymerization pathways of the resin into the usually used differential scanning calorimetry pressure-resistant crucibles and under atmosphere pressure. Under high-pressure conditions a competition between oxidation and polymerization reactions was detected, leading to less methylene bridge formation and more remaining free ortho-positions, with a consequent lower degree of polymerization (d.p.)

Bouajila et al.[134] studied the physicochemical and kinetic properties of resoles prepared with different catalysts[NaOH, LiOH, and Ba(OH)2] and variable formaldehyde/phenol ratios (2.5 or 3.5) were followed to determine their effects on the mechanisms and reaction products at a fixed pH and temperature. Kinetic monitoring and quantification of residual monomers were carried out by liquid chromatography coupled with mass spectrometry (LC/UV/MS), by ^{13}C NMR, and by chemical assay for formaldehyde. Oligomer formation (n ≥2) was determined by LC/UV/MS, size exclusion chromatography (SEC) and ^{13}C NMR. It was found that minor compounds form during syntheses and that the ratio R affects primarily the kinetics of formation of hydroxymethylated intermediates and oligomers, in contrast to the catalysts that modified reaction mechanisms. The understanding of the structure of the resoles was an important step for the determination of the final properties of the material.

Tan et al.**[135]** studied the chelation between borate ions and resole phenol-formaldehyde resin by measurement of pH of the solution and the analysis of IR spectra. The results showed that the reaction proceeded rapidly and completely. The reaction took place in phenolic hydroxyl groups and hydroxymethyl groups on the aromatic ring of the resin, and formed coordinate bond between boron atoms of borate ions and oxygen atoms on the hydroxyl groups. The reaction could also produce hydrogen ions and brought about the change in the pH of the resin solution.

Astarloa Aierbe et al.**[136]** studied the influence of the condensation temperature on phenolic resole resin prepolymer formation by liquid chromatography and ^{13}C NMR spectroscopy. Four resoles catalyzed with triethylamine and with initial pH 8.0 and formaldehyde-phenol ratio 1.8 were synthesized at 60°C, 80°C, and 95°C, and refluxing temperatures 98°C-102°C. On increasing the condensation temperature, reactant consumption rates and first formed addition products increased and condensation times decreased. Prepolymer synthesized at refluxing temperatures showed higher formaldehyde addition onto ortho positions with respect to the other resoles. Different types of phenolic ring connecting bonds were observed: para, para and ortho, para bridges as well as ether bonds were detected. No ortho, ortho bonds were observed for the condensation with the catalyst used. ^{13}C NMR measurements did not show qualitative differences between prepolymers. Residual phenol and formaldehyde concentrations and the amount of free unreacted ortho and para positions decreased with temperature.

Holopainen et al.**[137]** successfully predicted the formaldehyde/phenol (F/P) ratios of resole resins by the recording of IR spectra of both calibration and analyzed resins and by a multivariate analysis technique. In the creation of applicable models, the best correlating IR spectral areas were found between 1800 and 700 cm^{-1}. The positive effects of the increasing replicates and the omission of first-derivative preprocessing on model quality were proven by systematic testing. The characteristic statistical parameters were acceptable when the resin was similar to the calibration resins. Although the calibration samples had narrow F/P molar ratios (2.00-2.40), or a particular urea content or alkyl, the best calibration model could also successfully predict the F/P molar ratios of resins with greater F/P ratios, higher urea contents, and lower alkyl.

Lee et al.**[138]** investigated the thermal behavior, thermal degradation kinetics, and pyrolysis of resole and novolac phenolic resins with different curing conditions, as a function of the formaldehyde/phenol (F/P) molar ratio (1.3, 1.9, and 2.5 for the resole resins and 0.5, 0.7, and 0.9 for the novolac resins). The activation energy of the thermal reaction was studied with differential scanning calorimetry at five different heating rates (2°C, 5°C, 10°C, 20°C, and 40°C/min) between 50°C and 300°C. The activation energy of the thermal decomposition was investigated with thermogravimetric analysis at five different heating rates (2°C, 5°C, 10°C, 20°C, and 40°C/min) from 30°C to 800°C. The low molar ratio resins exhibited a higher activation energy than the high molar ratio resins in the curing process. This meant that less heat was needed to cure the high molar ratio resins. Therefore, the higher the molar ratio was, the lower the activation energy was of the reaction. As the thermal decomposition of the resole resins proceeded, the activation energy sharply decreased at first and then remained almost constant The activation energy of the thermal decomposition for novolac resins with F/P = 0.5 or F/P = 0.7 was almost identical in all regions, whereas that for novolac resins with F/P = 0.9 gradually decreased as the reaction proceeded.

He et al.**[139]** studied the curing behavior of two kinds of powdered resole phenolic resins by differential scanning calorimetry. Liquid-state ^{13}C-NMR spectroscopy was used to aid in understanding the curing behavior by detecting the structure of powdered resins. The reaction mechanism was interpreted with the dependency of activation energy on the degree of conversion. The results indicate that there are differences in the curing mechanism between core and face phenolic resins. The curing process of the core resin was faster than that of the face resin at the same reaction temperature. The water added to the curing system played an important role of plasticizer or diluent according to different curing stages and water content. In the initial curing stage, water mainly diluted the system and retarded the curing reactions. However, at the higher degrees of conversion, water played the role of plasticizer to decrease the effect of diffusion on the curing reactions to make the curing reactions more complete. Excess water added in the curing system played the role of diluent at almost all stages during the curing process.

Bouajila et al.[140] used to analyze nondestructive, solid state physicochemical techniques for the structure of phenolic resins, prepared with precise syntheses and thermal parameters. The results obtained with solid state ^{13}C NMR (CP/MAS) and FTIR were analyzed and related to the thermal characteristics of the networks (DSC and TGA/FTIR). The data were correlated with parameters and conditions of syntheses of resoles and of the initial prepolymers.

Zhou and Xu[141] synthessed resole-type phenol/formaldehyde prepolymer at lower molar ratio of formaldehyde/phenol (1.3:1) and investigated the pyrolysis behavior of the phenolic resin thermally cured by thermogravimetric-mass spectra (TG-MS). When the pyrolytic temperature was lower than 350°C, mainly the cleavage of intramol. ether linkage and the removal of end hydroxymethyl occurred, and some molecules such as H_2O, CO_2, and CH_3OH and their fragments were detected. When the pyrolytic temperature was between 350° and 750°C, the bond cleavage occurred at different positions of the resin main chain, and methylphenol, dimethylphenol, and trimethylphenol and their fragments were observed, implying that the improvement of thermal stability of phenolic main chain might be one of the key factors to avoid the defects in Resole-type phenolic resin-based C/C composites.

He and Riedl[142] studied the curing kinetics of resole phenol-formaldehyde (PF) resin and resin-wood interactions in the presence of wood substrates by differential scanning calorimetry (DSC) and Fourier transform infra-red (FTIR) spectroscopy. The activation energy of cure of PF resin generally increased when PF resin was mixed with wood, mainly due to the decrease of the pH values resulting from the presence of wood. However, wood decreased the curing enthalpy of PF resin through diffusion and the change in the phase of the curing system, which suggested that the curing reactions reached a lower final degree of conversion for the mixtures of PF resin with wood than for the PF resin alone. Moreover, DSC curves and the variation of activation energy with conversion indicated that wood accelerated the addition reactions and retarded condensation ones during the curing process of PF resin with wood. The study also revealed that almost no chemical reactions occurred between PF resin and wood, but the secondary force interactions of hydroxyl groups between PF resin and wood have been detected. These most significant secondary forces can catalyze the self-condensation reactions of PF resin, although their effect was not vital on the curing kinetics of PF resin.

Rego et al.[143] synthesized different resole phenol-formaldehyde prepolymer resins with different Formaldehyde/Phenol(F/P) ratios or different catalysts and characterized by ^{13}C NMR spectroscopy in solution. A fast quantitative measuring protocol was proposed based on the use of chromium(III)acetylacetonate as a relaxation agent. APT (attached proton test) and DEPT(distortionless enhancement by polarization transfer) spectra were acquired to enable proper resonance assignments, especially in the regions with severe signal overlap. Equations were presented in which the methylene bridges(MB), the methylol groups(MG) and the dimethylene ether bridges(DMEB) of resole resins were quantity taken into account. Important structural factors determined quantity for resole prepolymer resins are the F/P ratio after reaction, the d.p. (n), the number average molecular weight(Mn) and the content of free ortho and para positions.

Zhang et al.[144] prepared hydrogels(HG) by the sol-gel polymerization of phenolic resole, m-cresol resole and methylolated melamine mixtures with different recipes in basic aqueous solution at 85°C for 5 days. Water in the HG was displaced by acetone to obtain acetone gels (AG). Organic aerogels(OA) were obtained by drying of AG under supercritical carbon dioxide. Small angle X-ray scattering(SAXS) using synchrotron radiation as X-ray source was employed to investigate microstructure of HG, AG and OA. It is found that physical crosslinking was dominant in HG and supercritical drying of the physical dominant cross-linked gels caused the following microstructure changes: (1) random growth of large scatterers that “bury” the scattering peak; (2) shrinking of gels; (3) deswelling of gel network and (4) evolution of gel structure from tangled or rough interface to smooth or flat interface.

Puglia et al.[145] reported the effects of the addition of different epoxy resins on the thermal stability of phenolic resoles. Blends of phenolic resins with different compositions of epoxy resins, cured with amine hardener, were characterized by thermal gravimetric analysis and cone calorimetry to determine their thermal stability and fire resistance. The thermal degradation of phenolic resole characterized by a complex mechanism with at least two different processes which lead to the production of a stable and resistant char structure. On the other hand, the epoxy resins studied, either aliphatic or aromatic, degrade in a single step. The results demonstrated that the epoxy-amine content should be kept under 15wt. % to avoid a significant reduction of the thermal stability of the blend. However, blending with epoxy-amines was a suitable route to improve the mechanical properties of phenolic resins or to reduce the cure temp.

Shukla et al.[146] prepared blends of resole and epoxy were prepared by physical mixing, and cured with 30% polyamide based on blend resin and polyamide and studied their degradation kinetics by dynamic thermogravimetric analysis in nitrogen atmosphere at a heating rate of 10°C min^{-1}. The degradation of blends of epoxy and resole having 30wt% polyamide proceeded with 0.50th order. This result was found with the Coats-Redfern equation using best-fit analysis, and further confirmed by linear regression anal. The validity of data was checked by t-test analysis. From this value of reaction order, activation energy (E) and pre-exponential factor (Z) were calculated. The values of activation energy increased, whereas the values of pre-exponential factor decreased as the resole content in the blend decreased from 100 to 0 wt%.

Lin and Chiu[147] addressed the differences in curing behavior by blending and cocuring of resol and epoxy, using NaOH and 4,4'-diaminodiphenylmethane as curing agents. IR band shifts regarding the molecular interactions were investigated with FTIR. Exothermic peak shifts during cocuring reactions were studied with dynamic DSC. Viscosity increases were measured with a Brookfield LVT viscometer at 100°C. The dynamic mechanical properties of the cocured samples were investigated using rheometric dynamic spectroscopy (RDS). Experimental results revealed that the molecular interactions between resole and epoxy resulted in good compatibility as shown by the single damping peak in the RDS curve and the single glass transition for each cocured sample. Also apparent were accelerated curing rates, leading to shifts of the exothermic peaks to lower temperature and faster viscosity increases. Nevertheless, enhanced gel fractions and increased glass-transition temps. (Tg) of the samples were generally observed for this cocured system. The average molecular weight between crosslinked points calculated for the cocured materials also showed much less than the two components. These curing behaviors were quite different from those of the interpenetrating polymer network (IPN) materials, which usually indicated lowered gel fractions, decreased Tg, and higher average molecular weight between crosslinkings than for components.

Lin and Chiu[148] prepared cocured materials based on 100/0, 50/50 and 0/100 weight ratios of resole/epoxy prepared using NaOH and 4,4'-diaminodiphenyl methane as curing agents. Samples were spin-coated on Al plates and subjected to accelerated aging at 150°C in air for 49 days. The functional group changes during thermal oxidation were monitored with FTIR at various times. Spectra were obtained using the aromatic absorption at 1608 cm^{-1} as internal standard. A kinetic study was performed, and a first order degradation was demonstrated.

Srivastava and Mathur[149] prepared the blends of resole with epoxy resin having different wt. ratios (0/100, 25/75, 50/50, 75/25, and 100/0). These blends were cured by adding polyamide in a 60:40 ratio based on blend resins and polyamide. The degradation kinetics of these resins was studied by dynamic thermogravimetric analysis in nitrogen atmosphere at a heating rate of 15°C/min by using the Coats-Redfern equation. The degradation of each sample follows first-order(n=1) degradation kinetics. This is obtained on the basis of best fit analysis, and all the parameters are confirmed by regression analysis. From the reaction order value, activation energy and preexponential factor were calculated by the slope and intercept of the plot between X and Y, respectively.

Stachowiak[150] compared the performance of a new phenolic resole curing agent to that of phenolic resoles in a variety of epoxy/phenolic can coatings. The new material provided flexible coatings having good chemical resistance and excellent resistance to overbake. The reactivity of these epoxy/phenolic systems was evaluated by monitoring the viscosity during cure. Higher solids systems could be formulated by employing epoxy resins with a lower molecular weight than those normally used in can coatings.

Yamamoto et al.[151] developed a coating compositions for inner surfaces of cans with excellent curability and steel adhesion comprising bisphenol A-based epoxy resins, organic solvents, and phenolic resoles prepared by treating HCHO with phenols having ≥3 functional groups in the presence of alkali catalysts and treating the resulting methylol-containing phenolic resins[(wt.-av.mol.wt.(M_w) 500-800)] with difunctional phenols. Thus, bisphenol A 1, 37% aq. HCHO 2.5, and 25% aq. NH_3 0.2 mol were heated at 65°C for 3 h to give a phenolic resole (M_w 590, methylol concentration 0.48), which was treated with 1mol 4-$(CH_3)_3CC_6H_4OH$ (I) at 95°C for 30min, then extracted with iso-$C_4H_9COCH_3$/cyclohexanone/xylene to give 30%-solids phenolic resin solution The solution (40 parts solids) and 60 parts Epikote 1009 were mixed, applied on a tin plate, and baked at 200°C to give a coating which showed excellent resistance to S-blackening(sic) and good punching quality(no delamination of coating from tinplate) whereas coatings prepared without I showed poor punching quality.

Anderson[152] prepared blends of furan-formaldehyde resin-phenolic resole resin compositions crosslink under acidic conditions and are useful binders for foundry sand. Thus, treatment of furan with HCHO in a 4:1 molar ratio in the presence of oxalic acid at 100°C for 2 h gave a resin with viscosity approximately100 cps at room temp. A com. available resole (IMC Self-Set 130) 22.5, furan resin 7.5, and 75% benzenesulfonic acid 2.4 parts were mixed to give a solution which exothermically polymerized in 3min. to give a hard solid. When the composition contained a silane adhesion promoter it was suitable for use as a binder for foundry sand in the production of hardened foundry shapes.

Tumanov et al.[153] prepared blends of epoxy resin and resole-type aniline-formaldehyde-phenol oligomer with improved physicomechanical properties from layers of reinforcing fibrous filler and impregnating binder, which contained 100 parts bisphenol A epoxy resin and 30-100 parts resole-type aniline-formaldehyde-phenol oligomer (8-12% methylol groups) as hardener.

CONCLUSION

The preceding review shows that the epoxidized resole resins show excellent performances, such as rapid curing behaviour, high heat resistance, good adhesive properties, outstanding strength, solvent & chemical resistance and good thermal stability. The resins are used in paints which could able to withstand solvent attack because of their outstanding chemical resistance, physical properties, and may, therefore, be used in order to reduce maintenance and repairing cost to minimum in comparison to vinyls. These resins are also used as flooring to cover or topping on top of a sub floor. They are classified in number of ways for wearing surfaces. These floorings are most commonly used for domestic purposes because of low levels of sound insulation and lack of pleasing appearance. Many efforts have been made to improve the appearance of such flooring such as incorporation of color aggregates or spattering color on the floor surfaces and incorporating rubber crumbs as extenders to improve flexibility and also useful to reduce impact noise. The blend system based on epoxy resin and resole-type phenolic resins is less studied and further modification is needed for their thermal characteristics.

REFERENCES

[1] S.L.Gibson, J.S.Riffle;' Chemistry and Properties of Phenolic Resins and Networks', In Synthetic Methods in Step-growth Polymers, M.E.Rogers, T.E.Long (Eds.), John Wiley & Soms, Inc., 365 **(2003)**.

[2] A.Knop, L.A.Pilato; Phenolic Resins: Chemistry, Applications and Performance, Springer-Verlag,

Berlin, Heidelberg, **(1985)**.

[3] A.Knop, W.Scheib; Chemistry and Applications of Phenolic Resins, Springer-Verlag, New York, **(1979)**.

[4] M.K.Gupta, G.Sallee, D.W.Hoch; Am.Chem.Soc., Div.Polym.Chem.Polym.Prepr., **27**, 309 **(1986)**.

[5] R.W.Martin; 'The Chemistry of Phenolic Resins', John Wiley & Sons, Inc., **1,3**, **(1956)**.

[6] L.B.Manfredi, A.Vazquez; 'Chemical Reactions in Liquid and Solid Phase', G.E.Zaikov, A.Jimenez (Eds.); Nova Science Publishers, Inc., Hauppauge, New York, 69-18 **(2003)**.

[7] N.N.Prudnikova, G.A.Kutbedinova, M.P. Yakusheva, L.P.Vin, S.S.Dmitrienko; Primen, Fenoplastov Ionoobmen.Smol., Nauchno-Issled. Inst.Tekh.-Ekon.Issled. (NIITEKhIM), Moscow, USSR, 56-9 **(1976)**.

[8] L.Lederer; J.Prakt.Chemie., **50**, 223 **(1894)**.

[9] O.Manasse; Ber.Dtsch.Chem.Ges., **27**, 2409 **(1894)**.

[10] A.Weller; Prog.Reaction Kinetics, **1**, 187 **(1961)**.

[11] S.So, A.Rudin; J.Appl.Polym.Sci., **41**, 205 **(1998)**.

[12] H.C.Malhotra, V.K.Gupta; J.Appl.Polym.Sci., **22**, 343 **(1978)**.

[13] H.C.Malhotra, A.Kaur; J.Appl.Polym.Sci., **20**, 2461 **(1976)**.

[14] A.Zavitsas; Am.Chem.Soc.Div.Org.Coatings and Plastic Preprints, **26**, 93 **(1966)**.

[15] A.Zavitsas, R.D.Beauliew; Am.Chem.Soc.Div. Org.Coatings and Plastic Preprints, **27**, 100 **(1967)**.

[16] D.Park, B.Riedl; J.Appl.Polym.Sci., **77**, 1284 **(2000)**.

[17] Vollmert; Polymer Chemistry, Springer-Verlag, New York, **(1973)**.

[18] H.V.Wagner, R.Gompper; 'Quinone Methides', In S.Patani (Ed.) : The Chemistry of the Quinoid Compounds, Wiley, New York, **2**, Chap.**18** **(1964)**.

[19] P.F.Bruins; Epoxy Resin Technology, Interscience Publisher, New York, Chap. **1**, **(1968)**.

[20] A.May, Y.Tanaka; Epoxy Resin Chemistry and Technology, Marcel Dekker, New York, Chaps., **1-3**, **(1973)**.

[21] H.Lee, K.Neville; 'Hand Book of Epoxy Resins', McGraw-Hill, London, Chaps., **1-2**, **(1957)**.

[22] R.Houwink, G.Solomon; Adhesion and Adhesives, Elsevier, Amesterdam, Chap., **1**, **(1965)**.

[23] W.G.Potter; Epoxide Resins, Springer-Verlag, New York, Chaps., **1-2**, **(1970)**.

[24] Y.Ishii, S.Sakai, S.L.Regan; Ring Opening Polymerization, Marcel Dekker, New York, **2**, Chap., **4**, **(1969)**.

[25] S.A.Zahir, S.Bantle; 'Epoxy Resin Chemistry-IJ', R.S.Baur (Ed.); Am. Chem. Soc. Ser., **221**, 245 **(1983)**.

[26] L.Shechter, J.Wynstra; Industrial and Engineering Chemistry, **48**, 86 **(1956)**.

[27] L.Shechter, J.Wynstra, R.P.Kurkjy; Industrial and Engineering Chemistry, **49**, 1107 **(1957)**.

[28] K.Banthia, J.E.McGrath; Polymer Preprints, **20**, 629 **(1979)**.

[29] M.Sabiva, I.Spit; 'Epoxy Resin', C.E.S.Knecht (Ed.); Wiley Interscience, New York, Chap., **16** **(1977)**.

[30] W.D.Hawkins; Physics of Surface Films, Reinhold, New York, Chap. **5**, **(1952)**.

[31] B.Alvey; J.Appl.Polym.Sci., **13**, 1473 **(1967)**.

[32] S.Bantle, W.Burchard; J.Polymer, **27**, 728 **(1986)**.

[33] Renner, A.Heer, W.Seiz, A.Mergotte, W. Scheneider; Ang.Macromol.Chem., **54**, 91 **(1976)**.

[34] K.Holegawa, A.Fukuda, K.Vede; J.Polym.Sci. Part-C.Polym.Lett., **28**, 1 **(1990)**.

[35] K.E.J.Barett; J.Appl.Polym.Sci., **11**, 1617 **(1967)**.

[36] K.Ohachi, K.Hasegana, A.Fukuda, K.Vede; J.Appl.Polym.Sci., **44**, 419 **(1992)**.

[37] H.Danneberg, C.A.May; 'Treatise on Adhesion and Adhesives', R.L.Peterick (Ed.), Marcel Dekker, New York, **3**, Chap., **2** **(1973)**.

[38] M.T.Goosey; Plastics for Electronics, Elsevier Applied Science, London, Chap., **4** **(1985)**.

[39] A.May; ACS Symp.Ser., **285**, 557 **(1985)**.

[40] A.Bayer; Ber.Dtsch.Chem.Ges., **5**, 25 **(1872)**; Ber.Dtsch.Chem.Ges., **5**, 1095 **(1872)**.

[41] ter Mer; Ber.Dtsch.Chem.Ges., **7**, 1200 **(1874)**.

[42] A.Claus, E.Trainer; Ber.Dtsch.Chem.Ges., **19**, 3009 **(1886)**.

[43] L.Claisen; Justus Liebigs.Ann.Chem., **237**, 261 **(1887)**.

[44] A.Speier; Ger.Pat., **99**, 570 **(1897)**.

[45] A.Luft; Ger.Pat., **140**, 552 **(1902)**.

[46] L.H.Baekeland; U.S.Pat., **942**, 699 **(1907)**; U.S. Pat., **949**, 671 **(1907)**.

[47] A.Knop, W.Scheib; In 'Chemistry and Applications of Phenolic Resins', Springer, Berlin, 3 **(1975)**.

[48] K.Hultzch; In 'Chemie der phenolharze', Springer, Berlin, **(1950)**.

[49] N.J.L.Megson; In 'Phenolic Resin Chemistry', Buterworths, London, **(1958)**.

[50] K.Klatil, O.Filip, P.Jarolimek, J.Novotny, R.Jahnel, A.Oswald, P.Jehlar, F.Gajdos; Czech.,

Czech.Pat.No. CS 240157, 5 **(1986)**.
[51] P.A.Waitkus, B.Lepeska; U.S.Pat.No.US 4656239, 6 **(1987)**.
[52] R.Iyer, R.C.Shah; Eur.Pat.Appl.EP 211316, 8 **(1987)**.
[53] P.Shadbolt; Brit.UK Pat.Appl.GB 2177408, 6 **(1987)**.
[54] F.F.Abdel-Mohsen, F.M.Helaly; Acta Polymerica, **38(5)**, 291-3 **(1987)**.
[55] T.Kozutsumi; Japan Kokai Tokkyo Koho, JP 06322233, 5 **(1994)**.
[56] W.Hesse, K.Rauhut; Eur.Pat.Appl.EP 653450, 8 **(1995)**.
[57] M.A.E.Santana, M.G.D.Baumann, A.H.Conner; Holzforschung, **49(2)**, 146-52 **(1995)**.
[58] J.Majchrzak, B.Kaledkowski, M.Gryta, M.Szemien; Pol.Przemysl Chemiczny, **74(2)**, 59-61 **(1995)**.
[59] S.Ootani, M.Nakamura; Japan Kokai Tokkyo Koho, JP 07010945 **(1995)**.
[60] M.Ogiwara, H.Takada; Japan Kokai Tokkyo Sodium hydroxideo, JP 07173315 **(1995)**.
[61] J.Majchrzak, B.Kaledkowski, M.Gryta, B.Kriger, K.Kozubski, G.Czarnecka; Polish Pat.No.PL 163628 **(1995)**.
[62] T.Uragami, K.Yamaguchi, T.Yamaguchi; Japan Kokai Tokkyo Koho, JP 07048426 **(1995)**.
[63] M.Gryta, J.Majchrzak, B.Kaledkowski, B.Kriger, K.Kozubski; Polish Pat.No.PL 165546 **(1995)**.
[64] J.Majchrzak, M.Gryta, B.Kaledkowski, G. Czarnecka, E.Jasinski, C.Skupnik, J.Siedlecki, S. Wolski, M.Debski, K.Kozubski; Polish Pat.No.PL 165565, 4 Jan, 31 **(1995)**.
[65] S.Sun, X.Wang, Z.Yang, Y.Li; Huaxue Yu Nianhe, **3**, 141-143 **(1996)**.
[66] R.T.Sikorski, M.Amin; Polish Pat.No.PL 169183, 3, June 28 **(1996)**.
[67] Z.Wang, P.Chen, G.Cao, X.Yu, L.Hu; Gaofenzi Cailiao Kexue Yu Gongcheng, **12(5)**, 57-60 **(1996)**.
[68] Y.Ueda, A.Kondo; Japan Kokai Tokkyo Koho, JP 09208648, 3 Sept., 21 **(1998)**.
[69] K.Maeda, T.Watanabe, T.Fukuzawa; Japan Kokai Tokkyo Koho, JP 08134174, 8 **(1996)**.
[70] Z.Teodorczyk; U.S.Pat.No.US 5629083, 42 **(1996)**.
[71] C.P.Parks, K.F.Anderson; Can.Pat.Appl., CA 2143601, 18, Aug, 23 **(1996)**.
[72] Y.Ueda, A.Kondo; Japan Kokai Tokkyo Koho, JP 09208648, 3, Aug, 12 **(1997)**.
[73] H.Fukuzumi, K.Yonemoto; Japan Kokai Tokkyo Koho, JP 09067420, 4, March 11 **(1997)**.
[74] D.Maldas, N.Shiraishi, Y.Harada; Journal of Adhesion Science and Technology, **11(3)**, 305-316 **(1997)**.
[75] S.P.Urreiztieta, M.A.M.Castellanos; PCT Int.Appl., WO 9718913, 21, May 29 **(1997)**.
[76] C.P.Parks; U.S.Pat.No.US 5795934, 7, Aug, 18 **(1998)**.
[77] E.P.Black; U.S.Pat.No. US 5763559, 13, June, 09 **(1998)**.
[78] T.E.Dando, W.R.Dunnavant, R.B.Fechter, H.J. Langer; U.S.Pat.No.US 5756640, 8, May, 26 **(1998)**.
[79] H.Matsuoka, S.Yagi; Japan Kokai Tokkyo Koho, JP 10168146, 3, June 23 **(1998)**.
[80] T.Iwata, K.Isogai; Japan Kokai Tokkyo Koho, JP 11349652, 3, Dec 21 **(1999)**.
[81] W.R.Walisser, C.K.Johnson ; Eur.Pat.Appl., EP 913413, 22, May 06 **(1999)**.
[82] A.Svensson; PCT Int.Appl., WO 9915571, 13, April, 1 **(1999)**.
[83] Y.G.Doronin, V.P.Kondrat'ev, N.D.Aleksandrova, V.I.Kondrashchenko; Russia, RU 2154651, No Aug 20 **(2000)**.
[84] Z.Piotrowska, S.Wolski, E.Miasko, M.Piotrowska Baran, Z.Janowski, H.Magierska; Pol.Pat.No.PL 178067, 3, Feb, 29 **(2000)**.
[85] M.Higuchi, R.Okuda, Y.Koga; Japan Kokai Tokkyo Koho, JP 2000026563, 5, Jan, 25 **(2000)**.
[86] Y.Shang, X.Tan, Y.Li; Zhanjie, **22(5)**, 7-10 **(2001)**.
[87] G.Ma, G.Bai, C.Hou, L.Yuan, X.Ren; Faming Zhuanli Shenqing Gongkai Shuomingshu, CN 1341673, 11, March 27 **(2002)**.
[88] P.Ziegler, R.Schaefer, A.Has, F.Scholl, J.Wonner; Eur.Pat.Appl., EP 1264849, 7, Dec, 11 **(2002)**.
[89] G.Li, L.Wang, B.Dai, J.Xu; Hebei Gongye Daxue Xuebao, **31(4)**, 37-41 **(2002)**.
[90] Y.Kobayashi, M.Asami; Japan Kokai Tokkyo Koho, JP 2002206015, 5, July, 26 **(2002)**.
[91] I.Ide, T.Seki, M.Nishinoue; Japan Kokai Tokkyo Koho, JP 2002201245, 8, July, 19 **(2002)**.
[92] K.Sasakura, H.Toyoda; U.S.Pat.Appl.Publ., US 2003236331, 9, Dec, 25 **(2003)**.
[93] M.Tsujimoto, Y.Fukuhara, K.Miwa; Japan Kokai Tokkyo Koho, JP 2003306592, 9, Oct, 31 **(2003)**.
[94] K.H.Coventry-Saylor; U.S.Pat.Appl.Publ., US 2003224119, 6, Dec, 04 **(2003)**.
[95] T.Kage, T.Inoe, H.Azuma, C.Hirota, K.Ohira, K.Mori; Japan Kokai Tokkyo Koho, JP 2003292724, 6, Oct, 15 **(2003)**.

[96] K.Samejima, M.Akiba, M.Yokoyama; Japan Kokai Tokkyo Koho, JP 2003292556, 6, Oct,15 **(2003)**.

[97] Y.Kobayashi, T.Tochimoto, M.Asami; Japan Kokai Tokkyo Koho, 7, Oct, 15 **(2003)**.

[98] T.Shimokage; Japan Kokai Tokkyo Koho, JP 2003277457, 6, Oct, 02 **(2003)**.

[99] X.Wang, Y.Zou, S.Yu; Reguxing Shuzhi, **18(4)**, 1-3 **(2003)**.

[100] M.Sato, Y.Narabe, K.Sakai; Japan Kokai Tokkyo Koho, JP 2003213078, 5 **(2003)**.

[101] G.Yang; Hangtian Daxue Xuebao, **29(5)**, 459-462 **(2003)**.

[102] J.P.Chen; U.S.Pat.No.US 2003135012, 25 **(2003)**.

[103] T.Sato, T.Nakamura; Japan Kokai Koho, JP 2003176328, 4 **(2003)**.

[104] T.Kage, T.Inoue, H.Azuma, C.Hirota, K.Ohira, K. Mori; Japan Kokai Tokkyo Koho, JP 2003165817, 5 **(2003)**.

[105] W.H.Ingram, T.M.McVay, M.Letchas; U.S.Pat. Appl.Publ., US 2003096937, 5 **(2003)**.

[106] R.Lubczak; Macromole.Mat.and Engg., **288(1)**, 66-70 **(2003)**.

[107] G.Li, S.Zhang, L.Hao; Zhongguo Jiaonianji, **12(1)**, 18-21 **(2003)**.

[108] K.Takahashi, I.Makinose, N.Sano; Japan Kokai Tokkyo Koho, JP 2003040957, 12 **(2003)**.

[109] V.Malhotra, W.Walliser, S.G.Watson, P.C.Herault, D.Tessari, P.Espiard, S.Tetart, B.Malhieuxe; U.S.Pat.No.US 6646094, 32 **(2003)**.

[110] T.Kage, T.Inoue, H.Azuma, C.Hirota, K.Ohira; Japan Kokai Tokkyo Koho, JP., 2004091600, 7 **(2004)**.

[111] K.D.Gabrielson, K.Tutin, C.R.White, D.J.Bir; U.S. Pat.Appl.Publ., US, 2004039093, 13 **(2004)**.

[112] M.Tsujimoto, Y.Fukuhara, A.Miwa; Japan Kokai Tokkyo Koho, JP 2004059701, 20 **(2004)**.

[113] T.Inoue, H.Azuma, T.Kage, C.Hirota; Japan Kokai Tokkyo Koho, JP, 2004059841, 9 **(2004)**.

[114] T.Holopainen, L.Alvila, P.Savolainen, T.T. Pakkanen; J.Appl.Polym.Sci., **91(5)**, 2942-2948 **(2004)**.

[115] T.Tsuihiji, T.Yamazaki; Japan Kokai Tokkyo Koho, JP., 2004010700, 8 **(2004)**.

[116] A.W.Christiansen, R.A.Follensbee, R.L.Geimer, J.A.Koutsky, G.E.Myers; Holzforschung, **47(1)**, 76-82 **(1993)**.

[117] R.A.Follensbee, J.A.Koutsky, A.W.Christiansen, G.E.Myers, R.L.Geimer; J.Appl.Polym.Sci., **47(8)**, 1481-96 **(1993)**.

[118] M.F.Grenier-Loustalot, S.Larroque, P.Grenier, J.P.Leca, D.Bedel ; Polymer, **35(14)**, 3046-54 **(1994)**.

[119] J.M.Kenny, G.Pisaniello, F.Farina, S.Puzziello; Thermochimica Acta, 269/270, 201-11 **(1995)**.

[120] K.Umemura, S.Kawai, R.Nishioka, Y.Mizuno, H. Sasaki; Mokuzai Gakkaishi, **41(9)**, 828-36 **(1995)**.

[121] G.K.D.Pushpalal, T.Kawano, T.Kobayashi, M.Hasegawa; Advanced Cement Based Materials, **6(2)**, 45-52 **(1997)**.

[122] P.S.Achary, R.Ramaswamy; J.Appl.Polym.Sci., **69(6)**, 1187-1201 **(1998)**.

[123] Y.Gao, Y.Li, X.Kou, H.Zheng; Gaofenzi Cailiao Kexue Yu Gongcheng, **15(3)**, 45-47 **(1999)**.

[124] G.Papava, Z.Tabukashvili, N.Dokhturishvili, N. Gelashvili, M.Datuashvili, M.Gurgenishvili, M.Ramishvili; Bull.Geo.Acad.Sci., **164(2)**, 309-311 **(2001)**.

[125] B.Kaledkowski, J.Hetper; Polymer, **41(5)**, 1679-1684 **(1999-2000)**.

[126] L.B.Manfredi, O.De la Osa, Fernandez, N.Galego, A.Vazquez; Polymer, **40(13)**, 3867-3875 **(1999)**.

[127] K.Lenghaus, G.Qiao, D.H.Solomon; 'Book of Abstracts', 217th ACS National Meeting, Anaheim, Calif., POLY-295, American Chemical Society, Washington, D.C, 21-25 **(1999)**.

[128] G.A.Aierbe, J.M.Echeverria, M.D.Martin, A.M.Etxeberria, I.Mondragon ; Polymer, **41(18)**, 6797-6802 **(2000)**.

[129] H.J.Kim, Y.K.Lee; 'Proceedings of the Annual Meeting of the Adhesion Society', 24th, 190-192 **(2001)**.

[130] M.S.Lin, C.C.Chiu; Polymer Degradation and Stability, **71(2)**, 327-329 **(2001)**.

[131] T.Sugama, S.Kelley, K.Gawlik; Journal of Coatings Technology, **73(917)**, 65-71 **(2001)**.

[132] K.Lenghaus, G.G.Qiao, D.H.Solomon; Polymer, **42(8)**, 3355-3362 **(2001)**.

[133] N.Gabilondo, M.D.Martin, I.Mondragon, J.M.Echeverria; High Performance Polymers, **14(4)**, 415-423 **(2002)**.

[134] J.Bouajila, G.Raffin, H.Waton, C.Sanglar, J.O.Paisse, M.F.Grenier-Loustalot; Polymers & Polymer Composites, **10(5)**, 341-359 **(2002)**.

[135] X.Tan, Y.Shang, Y.Li, N.Huang; Lizi Jiaohuan Yu Xifu, **18(1)**, 69-75 **(2002)**.

[136] G.Astarloa Aierbe, J.M.Echeverria, C.C.Riccardi, I.Mondragon; Polymer, **43(8)**, 2239-2243 **(2002)**.

[137] H.Holopainen, L.Alvila, T.T.Pakkanen, J.Rainio; J.Appl.Polym.Sci., **89(13)**, 3582-3586 **(2003)**.

[138] Y.K.Lee, D.J.Kim, H.J.Kim, T.S.Hwang, M.

Rafailovich, J.Sokolov; J.Appl.Polym.Sci., **89(10)**, 2589-2596 **(2003)**.

[139] G.He, B.Riedl, A.Ait-Kadi; J.Appl.Polym.Sci., **89(5)**, 1371-1378 **(2003)**.

[140] J.Bouajila, G.Raffin, H.Waton, C.Sanglar, S.Alamercery, M.F.Grenier-Loustalot; Polymers & Polymer Composites, **11(4)**, 263-276 **(2003)**.

[141] F.Xu, W.Zhou; Yuhang Cailiao Gongyi, **33(1)**, 18-23 **(2003)**.

[142] G.He, B.Riedl; Wood Science and Technology, **38(1)**, 69-81 **(2004)**.

[143] R.Rego, P.J.Adriaensens, R.A.Carleer, J.M.Gelan; Polymer, **45(1)**, 33-38 **(2004)**.

[144] R.Zhang, Y.Xu, Q.Meng, L.Zhan, K.Li, D.Wu, L.Ling, J.Wang, H.Zhao, B.Dong; J.Supercrit. Fluids, **28(2-3)**, 263-276 **(2004)**.

[145] D.Puglia, L.B.Manfredi, A.Vazquez, J.M.Kenny; Polym.Deg.Stab., **73(3)**, 521-527 **(2001)**.

[146] S.K.Shukla, P.Kumar, D.Srivastava; Mat.Manuf. Proc., **16(2)**, 281-289 **(2001)**.

[147] M.S.Lin, C.C.Chiu; J.Appl.Polym.Sci., **80(7)**, 963-969 **(2001)**.

[148] M.S.Lin, C.C.Chiu; Polym.Deg.Stab., **69(2)**, 251-253 **(2000)**.

[149] D.Srivastava, G.N.Mathur; J.Macromole.Sci., Pure and Appl.Chem., **A34(1)**, 59-66 (**1997)**.

[150] S.Stachowiak; ‘Advances in Coatings Technology, Congress Papers’Cape Town, Paper **10**, 25-27 **(1996)**.

[151] A.Yamamoto, H.Kubota, A.Kikuchi, O.Naito; Japan Kokai Tokkyo Koho, JP., 61097371, 6 **(1986)**.

[152] H.C.Anderson; U.S.Pat.No.US 4083817, 5 **(1978)**.

[153] A.T.Tumanov, B.V.Perov, G.M.Gunyaev, I.P. Khoroshilova, T.R.Kapitonova, V.N.Tyukaev, E.M.Serebryanaya, G.I.Tolochko, T.I.Fomina; Russian Pat.No.SU 479791U.S.S.R.**(1975)**.