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ABSTRACTS FROM POSTER PRESENTATIONS

OILS AND RESINS FROM PLANTS IN VIETNAM

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This report focuses on oils and resins from some Vietnamese plants.

a) *Pinus Species:* Pine resin has been tapped from four resins yielding Pinus species in Vietnam: 1) *Pinus merkusii*, growing in the Quang Ninh and Nghe An provinces. 2) *Pinus khasya*, growing in the Lam Dong province. 3) *Pinus massoniana*, growing in Lang Son and Quang Niuh provinces. 4) *Pinus caribaca*, growing in the Vinh Phu and Yen Bai provinces. α- and β-Pinene were separated from the turpentine oil by fractional distillation. By high resolution GC and GC/MS, the components from these oils were separated and identified. Vietnam is capable to

TABLE 1

Year	Pine resins	Colophonium	Turpentine oil
1990	2500	1500	100
1995	4247	1171	150
2000	7825	7472	

produce turpentine oil for local demands and for export. Table 1 gives the estimated yearly capacity (in tons) of resins and turpentine oil from Vietnam.

b) *Cinnamomum camphora:* This is grown in the North of Vietnam and is relatively popular. From a study of the chemotaxonomy of this plant, we have found in Vietnam at least six chemotypes which were characterized as to content of camphor, 1,8-cineole, and sesquiterpenes (linalool, phellandrene) in the resin. One variety yields resin with a high content of camphor, which (like synthetic camphor) is used as a plasticizer.

c) *Aleurites montana (Lour.) Wils: Aleurites montana* grows in Ninh Binh, Hoa Binh, Vinh Phu, Turen Quang, Bac Thai, Cao Bang, Lang Son, Thanh Hoa, Nghe An, and other provinces. The oil of this plant is used for the synthesis of alkyd resins; the annual capacity is about 4000 tons.

d) *Canarium album (Lour). Raensch:* In Vietnam there exist three species of this plant. The resins of *Canarium album* contain 50–70% colophonium and 3–10% of essential oils with a high content of sabinene. Canarium album resins are used for coating houseware products and boats. The oil of the seeds of this plant has a high fat content.

e) *Styrax tonkinensis Pierre:* This plant is grown in Hoa Binh, Thanh Hoa, Nghe An, Ha Giang, and Tuyen Quang provinces. The resins contain coniferyl benzoate, benzoic acid, cinnamic acid, vanillin, and other components which are used in the perfume industry. The annual production is about 200 tons.

f) *Lacca Stick-Lac:* Grown in the North-West of Vietnam and in the Thanh Hoa and Nghe An provinces, these plants cover an area of about 4500 ha with a harvest capacity of about 300 tons/annum. The resins are used for the production of shellac.

g) *Castor Oil Plant:* This plant is grown in the North-East and South-central parts of Vietnam, and the growing area covers about 2000 ha. The resin capacity is about 250 tons/annum. Pyrolysis of this oil gives undecenoic acid for the production of polyamides and heptanal for the perfume industry.

h) *Rubber Tree:* The rubber tree grows very well in the South of Vietnam. The oil of the rubber tree can be obtained from the seed of this tree. A large amount of the oil is used for the production of alkyd resins. The hydrolysis reaction of this oil has been particularly studied.

REACTION OF THITSIOL WITH PHENYL GLYCIDYL ETHER

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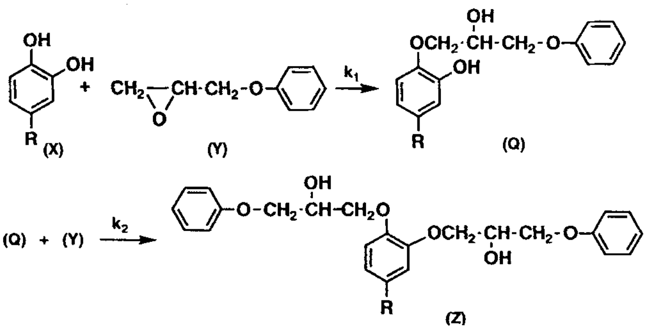
Thitsiol is the main component of lacquer latex extracted from the lacquer tree grown in the South of Vietnam as the Vietnamese and Kampuchea lacquer tree (*Melanorrhoea laccifera*). Thitsiol is isomeric with laccol, with a different position of the hydrocarbon side chain of the catechol ring. In laccol, the substituents are at the 1, 2, and 3 positions, but in thitsiol they are at the 1, 2, and 4 positions. Investigating the reactivity of the two phenolic groups in thitsiol is important not only for the characterization of each group but also for the determination of their behavior in forming polymer chains in the syntheses of thitsiol-based polymers. For this purpose the reaction between the phenolic groups in thitsiol and the epoxy group in phenyl glycidyl ether (PGE) has been carried out. Based on previous research with PGE [1], the probable mechanism of the reaction between thitsiol and PGE seems to be



or

$$X + Y \xrightarrow{k_1} Q$$

$$Q + Y \xrightarrow{k_2} Z \qquad (1)$$

The reaction rate equation has the following form:

$$-\frac{dY}{d\tau} = k_1[X][Y] + k_2[Q][Y] \tag{2}$$

$$-\frac{dY}{d\tau} = (a - x)(b - x)$$

where a = initial concentration of thitsiol [mol/L]
b = initial concentration of PGE [mol/L]
x = concentration of the product at τ [mol/L]

The reaction of PGE with thitsiol is found to be second order:

$$\ln \frac{a(b - x)}{b(a - x)} = (b - a)K\tau$$

$$\ln \frac{a(b - x)}{b(a - x)} = (b - a)K \lg e\tau$$

$$\mathrm{tg}\,\alpha = (b - a)K \lg e$$

then

$$K = \frac{\mathrm{tg}\,\alpha}{(b - a)\lg e}$$

According to Eq. (2), the shape of the kinetic curve depends on the relative rate constants of each reaction. The kinetic curve was determined to have two stages, as indicated above. To calculate the rate constants of each phenolic group, it must be observed that the reactivity of the first phenolic OH group is much higher than that of the second OH group, and that the second OH group participates significantly in the reaction only when the first OH group has been totally reacted with PGE. The rate constant k_2 can be determined from the second straight segment of the kinetic curve.

The reaction of PGE with thitsiol was studied at a 0.3–0.4 g-equiv./L concentration of thitsiol and an approximately 0.5 g-equiv./L concentration of PGE in chlorobenzene with tri-*n*-butylamine (TBA) as the catalyst. The temperature of the reaction was in the range of 120 to 130°C. The kinetic results and the calculated rate constants of the reaction (k_{exp}) are given in Table 1. According to the $k_{\mathrm{exp1}}/k_{\mathrm{exp2}}$ ratio, in the thitsiol molecule the reactivity of the first PhOH group is 3–4 times higher than that of the second OH group. This is in good agreement with the results obtained in a previous study of the reaction between laccol and PGE [1]. Therefore, the position of the hydrocarbon chain has little influence on the reactivity of the second PhOH group.

Experimental Part. PGE was obtained from phenol and epichlorhydrin by Linderman's method [2].

Thitsiol was extracted from the Vietnamese lacquer latex with toluene and purified by thin-layer chromatography. The epoxy group content was determined by titration with HCl in an excess of $HgNO_3$ [3]. The temperature was controlled automatically with 0.1°C precision.

TABLE 1. Rate Constants of the Reaction of Thitsiol with PGE in the Presence of Tri-*n*-butylamine (TBA) as the Catalyst in Chlorobenzene

Expt. no.	Initial concentration, g-equiv./L			Temp., °C	Experimental constants of reaction in two segments × 10^{-4}, g-equiv./L·s		
	Thitsiol 1	PGE	TBA		k_{exp1}	k_{exp2}	k_{exp1}/k_{exp2}
1	0.3	0.46	0.06	120	2.08	0.50	4.1
2	0.3	0.47	0.06	130	3.30	0.58	5.6
3	0.3	0.52	0.06	130	2.29	0.43	5.2
4	0.4	0.49	0.06	120	2.36	0.65	3.6
5	0.4	0.49	0.06	130	2.84	0.78	3.6

References. [1] Tran Vinh Dieu, Ph.D. Thesis, Moscow University, 1982. [2] Th. Linderman, *Ber. Chem., 24*, 2145 (1991). [3] Tran Vinh Dieu, Master Thesis, Moscow University, 1969.

CATHODIC PROTECTIVE ACTIVITY OF ZINC-RICH PAINTS BASED ON EPOXY-LACCOL BINDERS

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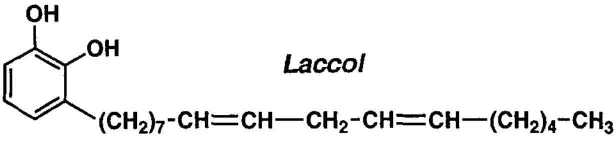
For years, epoxy-laccol resins have been studied and applied widely for the production of anticorrosive paints for the protection of containers for liquid foods, of structural steel, and of fishing ships [1]. Laccol is the main component of the natural lacquer of Vietnam (*Rhus succedanea*) and has the basic structural formula



Laccol

Paints based on laccol have good adhesion and high resistance against a corrosive environment. This paper presents the cathodic protective activity of zinc-rich paints based on epoxy-laccol (EL), epoxy-cardanol (EC), phenol-cardanol-formaldehyde (PCF), alkyd (AK) binders, and EP-057 (an epoxy-based primer containing zinc dust). The cathodic protection of carbon steel provided by zinc dust in zinc-rich paints has been investigated based on electrochemical techniques combined with the mechanical-physical properties of the paint films. The mechanical-physical properties of zinc-rich paints investigated are given in Table 1.

The electrode was a piece of carbon steel of dimensions 50 × 100 × 2 mm. The surfaces of the steel electrodes were cleaned and then painted with a zinc-rich coating with a 7.07 cm^2 trial area and 100 μm thickness. The electrode potentials of the painted electrodes and of an uncoated solid zinc electrode were recorded during 60-day exposure in an aerated 3% sodium chloride solution. The reference electrode was a saturated calomel electrode (SCE).

TABLE 1

No.	Binder	Zinc content, %	Impact strength, kg·cm	Flexibility, mm	Adhesion, %
1	Epoxy-laccol	92	50	3	100
2	Epoxy-cardanol	92	50	3	100
3	Phenol-cardanol formaldehyde	92	45	3	100
4	Alkyd	92	50	3	100
5	EP-057	92	45	3	100

Anodic polarization curves of the electrode of solid zinc metal and steel electrodes coated with zinc-rich primers were determined using a potentiostatic technique. An SCE was used as the reference electrode. The potential sweep rate was 20 mV/min. Before the anodic polarization curves were determined, the specimen electrode had been preexposed by immersion in aerated 3% sodium solution for periods of 3 and 60 days. The electrode potentials and the anodic polarization curves were measured by a Potentiostat Wenking LT-78 (Germany). The electrode with the zinc-rich paints and the solid zinc metal electrode were covered with a white corrosion product within a week after being exposed to a 3% sodium chloride solution.

X-ray diffraction analysis of the corrosion product showed that it was a mixture of several zinc compounds, including $Zn_4CO_3(OH)_6H_2O$ and $Zn_5(CO_3)_2(OH)_6$. From the electrode potential measurements it can be seen that the potential of the electrodes with a zinc-rich paint drifted toward a more positive value. In particular, after 25 days the alkyd-based zinc-rich paint came to the potential of corroding steel, indicating a complete loss of cathodic activity of the zinc particles in the paint. Compared with the solid zinc metal, the cathode active time of zinc-rich paints based on epoxy-laccol (EL), epoxy-cardanol (EC), and phenol-cardanol-formaldehyde (PCF) binders was substantially longer than that of the zinc-rich paint based on EP-057. The three paints showed cathodic protective activity for steel after 60 days of exposure.

After 3 days all of the zinc-rich paints showed cathodic protective activity on steel. After 60 days exposure only three paint films (EL, EC, and PCF) remained capable of cathodic protection on steel. After 60 days of exposure there was no appearance of iron rust under any of the investigated paint films. According to some authors [2–4], the duration of corrosion protection provided by zinc-rich paints under the immersed condition can be longer than their cathodic protection active time.

From the electrochemical investigations reported here, combined with the mechanical-physical properties of zinc-rich paints, the results can be summarized as follows: 1) After 60 days exposure in aerated 3% sodium chloride solution, three zinc-rich EL, EC, and PCF paints are still capable of cathodic protection of steel. The rank in cathodic protective activity of the paint films was found to be as follow: PCF > EL = EC > EP-057 > AK. 2) Corrosion protection given by zinc-rich paints lasts longer than their cathodic protective activity. The corrosion protection mentioned is probably combined with a corrosion-inhibitory effect on steel by the zinc corrosion products formed and by the high pH within the paint film. The cathode protection of steel provided by the zinc dust in zinc-rich paint based on epoxy-laccol binder was studied and discussed, based on potential-time, potentiostatic anodic polarization techniques and on mechanical-physical properties of zinc-rich paints.

References [1] Tran Vinh Dieu and Le Thi Pahi, *J. Chem.*, *16*(3), 11 (1978). [2] F. Theiler, *Corros. Sci.*, *14*, 405 (1974). [3] C. G. Munger, *Paint Technol.*, *33*(11) 42 (1969). [4] S. A. Lindqvist, *JCCA*, *67*, 10 (1984).

ISOLATION OF A 80-83 KDa GLYCOPROTEIN FROM THE AQUEOUS EXTRACT OF THE SEEDS OF GOSSYPIUM HERBACEUM, FAMILY MALVACEAE

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The basis of affinity chromatography is to adsorb covalently the molecules studied on an immobile solid matrix such as agarose bead. A mixture containing the desired macromolecule is then permitted to percolate through this matrix. The majority of molecules have no affinity for the bound molecule or ligand and flow directly through the matrix. The desired macromolecule, however, is retained. After the undesired components have been flushed from the column, a different wash solution is used to elute the bound macromolecule from the column. The desired macromolecule consequently appears in the effluent, largely purified from the original mixture.

The column packing bonding molecules used here were lectins. There were many investigations on different kinds of lectins. Concavalin A is a protein extracted from the beans of *Canavalia ensiformis*. Its molecular weight is 52,000 Da. Concovalin A was linked with Sepharose 4B, a Dextran B 1355 with an α-D-glucose chain which is highly branched and has a high molecular weight. An aqueous extract was obtained from the seeds of *Gossypium herbaceum* in a yield of 11%. The 50–100 KDa fraction obtained by ultrafiltration was subjected to cation-exchange chromatography on a Carbonylmethyl [CM] C 25 column, and a fraction P3 was obtained. Fraction P3 consists of proteins or glycoproteins. The investigation by affinity chromatography (with a ConA-Sepharose packing with a buffered eluent containing a 0.2 methyl α-D-glycopyranoside) and electrophoresis on this fraction was aimed to separate these two proteins and glycoproteins. A glycoprotein with a MW of 80–83 KDa was isolated. We have found that this glycoprotein is highly branched, and the terminal residues of the branches are D-arabinosyl or α-D-mannopyranosyl or α-D-glucopyranosyl units.

REACTION OF ROSIN (ABIETIC ACID) WITH GLYCIDOL

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The reaction of carboxylic acids with glycidol (2,3-epoxy-1-propanol) via the epoxy group has long been investigated using quaternary ammonium salts (obtained from the reaction of tetramethylammonium hydroxide with the respective carboxylic acid) as catalyst. This paper reports the reaction of abietic acid (AA), the essential constituent of rosin obtained from pine tree, with glycidol in toluene using quaternary ammonium salts as the catalysts. The reaction was carried out in stoichiometric proportions (equimolar) of the two reagents AA and glycidol. The variation of the conversion (indicated by titration of the residual AA with KOH/ethanol) with reaction time showed that $3t_{1/2} = t_{3/4}$ and that a plot of $X/[a(100 - X)]$ against the reaction time t was linear (where a = the initial concentration of the reagents). It appears that the overall order of this reaction is 2 in the reagents. from the linear correlation between log k and log c (where k = reaction rate constant, c = concentration of the catalyst), the reaction order with respect to catalyst is 1. According to J. C. Soutif, if the reaction is second order in the reagents and first order in the catalyst, the kinetic parameters can be analyzed using the following equation:

$$dx/dt = k_1(a - x)^2 - k_2c(a - x)2 \frac{X}{a(100 - X)t} = k_1 + k_2c = k$$

where x = [AA] at t
X = the conversion of AA = (x/a). 100%
a = [AA] = [glycidol] at $t = 0$,
c = concentration of catalyst,
k_1 and k_2 = the rate constants of the noncatalyzed and catalyzed reactions, respectively.

The values of rate constants k_1, k_2, and k were determined from plots of $X/[a(100 - X)]$ against t and of k against c. They are $k_1 = 0.11\ \mathrm{mol}^{-1}\cdot\mathrm{h}^{-1}$ and $k_2 = 250\ \mathrm{L}^2\cdot\mathrm{mol}^{-2}\cdot\mathrm{h}^{-1}$, in agreement with a first-order concentration dependence on each reagent and catalyst. From studies of the influence of the temperature (from 80 to 100°C) on the rate constant, the activation parameters AH^* and AS^* were also calculated; $AH^* = 59.57\ \mathrm{kJ}\cdot\mathrm{mol}^{-1}\cdot\mathrm{kcal}\cdot\mathrm{mol}^{-1}$, $AS^* = 146.1\ \mathrm{J}\cdot\mathrm{mol}^{-1}$. Based on the above results, it can be seen that the overall mechanism of this reaction involves

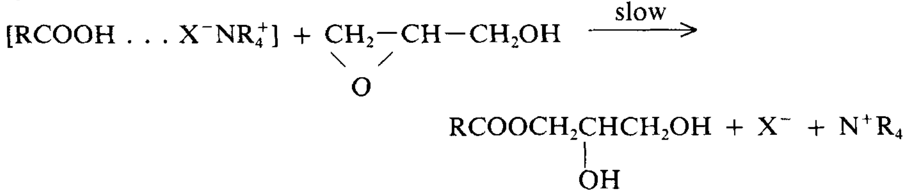
TABLE 1

No.	Catalyst	$10k(L \cdot mol^{-1} \cdot h^{-1})$
1	Noncatalyst	1
2	TEBA	14.14
3	Tetrabutylammonium bromide	14.34
4	Tetrabutylammonium chloride	5.05
5	Trietylbutylammonium bromide	9.10
6	Tetrabutylammonium abietate	1.26
7	Tetramethylammonium abietate	1.20

an intermediate. The reaction of the carboxylic group with the oxiran ring proceeds via the formation of a hydrogen-bonded salt between AA and the ammonium salt:

$$\mathrm{RCOOH + R_4N^+X} \xrightarrow{\text{rapid}} [\mathrm{RCOOH}\ \ldots\ \mathrm{X^-NR_4^+}]$$

The hydrogen bond in the above complex results in a charge distribution change with the formation of a partial negative charge on the carboxylic oxygen, which leads to increased nucleophilicity. The latter complex attacks the electrophilic glycidol to yield a diol ester:



$$[\mathrm{RCOOH}\ \ldots\ \mathrm{X^-NR_4^+}] + \underset{\diagdown\ \mathrm{O}\ \diagup}{\mathrm{CH_2{-}CH}}\mathrm{{-}CH_2OH} \xrightarrow{\text{slow}}$$

$$\mathrm{RCOOCH_2}\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2OH + X^- + N^+R_4}$$

The strength of the hydrogen bonds in these complexes depends on the nature of the alkyl groups R and the anions X^-. Thus the smaller (harder) cations R_4N^+ are the more effective as they are more tightly bound to X^-. The larger (softer) anions X^- are then more efficient since they are less associated with RCOOH in [RCOOH . . . $X^-NR_4^+$] complexes. The influence of the nature of the quaternary ammonium salt on the rate constants is shown in Table 1.

The reaction was carried out under the following conditions:

$[AA] = [glycidol] = a = 0.40476\ mol^{-1} \cdot L^{-1}$

$[catalyst] = c = 0.0054\ mol \cdot L^{-1}$ (solvent: toluene at 90°C)

Tetraalkyl ammonium salts of AA are less effective than the corresponding tetraalkylammonium bromides and chlorides, and salts with a bromide counterion are superior to those with a chloride counterion. In conclusion, the kinetics of the reaction of AA with glycidol and the role of ammonium salts as catalysts have been studied. From these results a mechanism of this reaction has also been suggested.

UNSATURATED POLYESTER RESIN MODIFIED WITH EPOXY ESTER OF CASTOR OIL

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Having the advantages of low cost and appropriate physicomechanical properties, unsaturated polyester resins (UPE) are one of the most popular resins used in composite materials. However, UPE have some disadvantages, such as poor flexibility and lack of inherent thixotropy. In order to overcome these disadvantages and to improve the mechanical properties and the environmental resistances, we have modified UPE with epoxy esters (EE) of castor oil. EE is the product of the reaction of the fatty acid of castor oil and a liquid epoxy resin (MW = 500), catalyzed by 1-methylimidazole at 150°C. This reaction is complete when the acid value goes down to 10 mg KOH/g. EE contains some OH-groups and can be used partly instead of glycol in the preparation of UPE. The UPE modified with EE was synthesized in a two-stage reaction with a mol ratio of the reactants of phthalic anhydride/maleic anhydride/glycol = 1/1/2.2 and the percentage of EE in the EE/glycol mixture varying from 0 to 23%. Table 1 shows the physical properties of the modified UPE, especially the great increase in the viscosity in comparison with the nonmodified resin.

Based on the physicomechanical properties of the modified UPE resins (Table 2), it is concluded that the resin with the best physicomechanical properties was produced when the percentage of EE in the EE/glycol mixture was 10%.

The physicomechanical strengths were determined in accordance with ISO 179-1982, 604-1973, 3268-1978, 178-1975. We have produced a composite material on the basis of 10% EE modified UPE reinforced with a mat glass fiber (the resin/fiber ratio was 1/1). The results are shown in Table 3.

TABLE 1. Some Physical Properties of UPE Modified with EE

% EE in EE/glycol mixture (w/w)	Compatibility with styrene, % (w/w)	Viscosity, in Pa·s
0	28	–
7	33	–
10	35	750
13	36	1410
18	37	1780
23	40	–

TABLE 2. Effects of the Content of EE on the Physicomechanical Properties of UPE

	% EE					
Property	0	7	10	13	18	23
Tensile strength, MPa	46.51	44.87	54.64	49.6	48.05	39.11
Tensile modulus, MPa	1258	1002	1213	1053	1028	899
Flexural strength, MPa	69.50	94.18	104.3	97.85	87.32	72.32
Compressive strength, MPa	187	132	134	130	122	99
Impact strength, kJ/m^2	0.182	0.252	0.250	0.242	0.308	

TABLE 3. Physicomechanical Properties of Composite Materials Containing Unmodified UPE and UPE Modified with 10% EE and Reinforced with Glass Fiber (the resin/fiber ratio = 1/1) (asterisks indicate the properties of the material after it was tested in a sun exposure box for 52 hours; the water spraying time was 12 min/h)

Kind of UPE	Flexural strength, MPa	Tensile strength, MPa	Compressive strength, MPa	Impact strength, kJ/m^2
Unmodified	106	156	367	104
	99*	142*		
10% EE modified	182	192	392	230
	171*	150*	355*	

ALGINATE FROM ALGAE AND THE USE OF ALKALINE ALGINATE AS IMPRESSION MATERIALS

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Alginic acid and alginate salts are materials widely used in industry, agriculture, medicine and pharmacy, the food processing industry, and construction. The use of alginate in medicine and pharmacy has been increasing. Different materials are used in maxillofacial dentistry to make molds with a view to creating samples reflecting the relation between teeth and other parts, the form of jaws, and the fibrous structure of mucous membranes. In poor countries such as Vietnam, with low technology levels and a shortage of materials, agar and gypsum are used for the preparation of molds, although these materials have not been used in developed countries for over 30 years.

These substances provide discomfort for the patients and are difficult to handle since it is hard to prepare precise molds from them. At the present time, Vietnam is producing binary alginate for the preparation of molds. This is not very convenient because the mold is prepared with a package of powder and also with glue, which are not easy to handle. However, this method has some advantages. Being aware of the importance of the material for the preparation of molds, we here discuss this technique of the preparation of molds.

1. Extraction of Alginate from Sargassum. The volume and viscosity of alginate from two species of sargassum in the Sea of Nha Trang in Central Vietnam were identified: *S. crassofolium* j. Ag. and *S. meclurel* Setchell. Some factors affecting the effectiveness and viscosity of the alginate impression material, such as the use and ratios of water and formaldehyde, were studied. An extraction method which has the highest effectiveness and gave materials with the highest viscosity was discovered. Results of the aforementioned research can be applied in the manufacture of alginate from available sargassum; the method was widely applied.

2. Alginate Impression Materials. (a) Two-component alginate impression materials. Based on the number of reports, we chose the following formulas to extract two-component alginate impression materials. Component 1: Sodium alginate-water. Component 2: Na_3PO_4-$Na_2B_4O_7$-talc powder.

In our experiments, a portion of the alginic acid solution was mixed with some gypsum. Our results showed that the materials can be used to make a mold but they are not soft and elastic enough to make details of the mold. Their setting time is also too short (40–50 seconds). This does not fit the time required by the standards of the American Dental Association (ADA), 2–5 minutes. It was necessary to find out the relationship between the different substances and their ratio, the temperature of the environment, and the reaction rate so as to set up formulas suitable for the real conditions and to ensure the quality of mold-making materials:

$$Na_n alg + {}^n/_2 CaSO_4 \leftrightarrows {}^n/_2 Na_2SO_4 + Ca_{n/2} alg$$

The setting time of a mold depends on the rate of reaction of alginate and gypsum. The reaction rate also depends on the particle size of the substances that take part in the reaction, the temperature of the environment, and the presence of other substances in the mixture such as $Na_2B_4O_7$ and Na_3PO_4. Our experiments showed that the ratio of water to alginate plays the most important role in determining the mold quality (50%). The ratio of alginate to water should be 15 g alginate in 300 mL water. This ratio was used in the following experiments. This mixture played the role of a good disperser; it also made the mold harden more quickly.

Results. Parameters showing the relationship of the substances taking part in the reaction and a formula suitable for different weather conditions in Vietnam were identified. Materials used were readily available, enabling low production cost. Disadvantages: Binary alginate impression materials were not convenient for either protection or use. The powder was not soft enough; consequently, the mold quality was not as good as that of imported materials.

(b) 2.2 One-component materials. The use of binary substance mixtures for the preparation of denture molds is not convenient because these mixtures have a low working life and cannot meet the requirements of the market. There is a pressing demand for one-component systems. A number of both chemical and physical problems in the process of changing binary to one-component systems need to be followed. It is also necessary to identify through research the characteristics of each alginate impression material and its influence on the material and its quantity. As mold material exists in the form of power, instructions from the manufacturers must be followed properly whenever it is used. The powder must be soft and easily dispersed and protected.

Results. Molds have been prepared but have not reached the desired criteria of softness, elasticity, and solidity. The mold setting time of one-component alginate-based systems is rather long (5–6 minutes). Nevertheless, both one- and two-component mold materials have been used in hospitals in Hanoi.

NEW IMMOBILIZED CELLS BIOCATALYSTS FOR A PROCESS FOR PRODUCING ETHANOL

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In recent years the immobilization of microorganisms has been investigated widely for use in large scale fermentation processes as well as in diagnostics, public health, and medical therapy [1]. One of the main tasks has been to search for suitable techniques and carriers for immobilization. With the objective of applying immobilized cells as biocatalysts for the ethanol fermentation process, we have produced two new kinds of biocatalyst beads by entrapping appropriate cells in ionotropic gels [2]. 1) A simple ionotropic gel (SI Gel) was formed by the ionotropic gelation of carboxy methyl cellulose (CMC) with a low molecular weight counterion. 2) The formation of a polyelectrolyte complex gel (PEC Gel) was the result of PEC formation between CMC and chitosan.

Some important properties of these biocatalyst beads have been tested. These beads were found suitable for the ethanol fermentation process and, to some extent, better than commonly used carriers for the process. The favored of our two biocatalysts was prepared as follows: 2% (w/v) viscous CMC and chitosan solutions were prepared from powders of CMC (commercial reagent M_n = 100,000) and chitosan from the Laboratory of Biopolymers, Institute of Chemistry, National Center for Natural Science and Technology (M_n = 300,000). The solutions were heated in an autoclave at 121°C for 20 minutes to obtain sterile solutions. *Saccharomyces carlsbergensis*, a respiration deficient strain of yeast, was the organism used in this work.

The fermentation process was carried out using the Hennberg medium with variant concentrations of the main substrate (glucose) in a discontinuous tank reactor. Spherical beads of the biocatalysts were formed by dropping suspensions of cell mass in CMC solutions (up to 12 g wet cells/100 mL solution) into diluted solutions of $Al_2(SO_4)_3$ for crosslinking. In order to make the PEC, the beads, after 5 minutes in the $Al_2(SO_4)_3$ solution, were soaked in the chitosan solution. The beads were hardened by completing the gelation in the counterion solutions and then by partial freeze drying. The immobilization processes occurred rather simply, inexpensively, and mildly. The polymer and crosslinking solution are nontoxic to the cells and the

TABLE 1. Characteristics of the Biocatalyst Beads

	SI Gel beads	PEC Gel beads	Free cells
Diameter (mm):			
Before drying	2.5	3.5	–
After drying	1.5	3.0	–
Cell loading (g wet cells/g catalyst)	0.952		0.396
Activity (g EtOH/h-g wet catalyst)	0.763		0.465
Effectiveness factor (g EtOH/h-g wet cells)	0.431		0.631

microorganisms in general. As a consequence, the cell viability was retained as demonstrated in our fermentation experiences after the immobilization of the enzymes. Our gels have good mechanical stability, which was shown by an agitating test. The data in Table 1 reflect the structural characters of the biocatalyst beads.

Although the SI Gel has a higher activity, as a result of the substantially higher cell loading, than the PEC Gel, the internal effectiveness factor due to pore diffusion (u) of the latter is higher. This can be explained by the higher permeability to water and substrates of the PEC films [3]. The shrinking capability of the SI Gel of CMC is also interesting. SEM photomicrographs of the two kinds of bead also show a typical structure of gel entrapping microbial cells with microporous bead surfaces and larger cavities within the matrix [3]. The stability and swelling capability of the beads in buffer solutions, especially in phosphate buffer, is a feature useful for biochemical purposes (Table 2). Both of the beads have good chemical stability, but the PEC Gel has a limited swelling or shrinking capability in electrolyte solutions.

From the kinetic data of the processes that were catalyzed by the two kinds of bead, a Lineweaver-Burk diagram could be plotted. It verifies the higher permeability to substrates of the PEC Gel. This biocatalyst has lower value of K_m; consequently, it has a higher reaction rate. The PEC Gel beads can be more effective than the SI Gel beads.

TABLE 2. Swelling Behavior of the SI Gel Beads and PEC Gel Beads (in 50 mL, 48 hours)

		Remarks	
Solution	pH	SI Gel beads	PEC Gel beads
0.1 M phosphate buffer	6	Unchanged	Unchanged
	7	Unchanged	Unchanged
	8	Dissolved	Unchanged
0.1 M citrate buffer	3	Swollen	Unchanged
	4	Swollen	Unchanged
	5	Swollen	Unchanged

References. [1] *Biochemical Engineering and Biotechnology Handbook*, Academic Press, 1993, pp. 770–774. [2] J. Klein and F. Wagner, "Methods for the Immobilization of Microbial Cells," *Bioengineering, 4*, 34 (1983). [3] K. D. Vorlop and J. Klein, "New Developments in the Field of Cell Immobilization. Formation of Biocatalysts by Ionotropic Gelation," *Enzyme Technol.* (1983).

REGENERATION OF CHITIN FOAM WITH LOW CRYSTALLINITY BY NEW SOLVENT SYSTEM

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Chitin, one of the biodegradable, nontoxic, and naturally abundant mucopolysaccharides, is known to be sparingly soluble in general organic solvents except in harmful reagents, mainly due to its high crystallinity. A mild and nontoxic solvent system has been desired to regenerate chitin as a biomedical material because of the advantages of chitin. The most desired properties are biodegradability, low toxicity, and acceleration of epidermal cell recovery.

Formic acid has been applied as a solvent of chitin for the regeneration of chitin into fibers and films in spite of its aggressive nature [1]. The molecular weight of chitin also tended to decrease due to the strong acidity of formic acid during the preparation of fiber and film. A saturated solution of calcium chloride dihydrate in methanol, a well-known good solvent for polyamides, was applied to dissolve chitin due to the analogous chemical structure of the chitin side chain to that of the polyamide main chain, since formic acid has also been well known as a good solvent for nylon 6 and nylon 6.6 [2].

The saturated calcium chloride dihydrate in methanol system was found to be the best solvent among other solvent systems that we tried to dissolve chitin, which included several calcium salts and magnesium salts in various alcohols. The solubility of chitin in saturated calcium chloride solution in methanol was found to depend significantly both on the molecular weight and on the crystallinity of chitin. The molecular weight of chitin was determined by viscometric measurements of chitin dope directly using the viscosity equation which was defined by us for reacetylated chitosan of various molecular weights. A chitin thin gel was prepared by casting chitin dope on a glass plate and then removing the calcium ions by treating the film with a 1/1 mixture of ethylene glycol and 20% aqueous sodium citrate solution. A porous chitin foam was also prepared by the lyophilization of a chitin thin gel. Several dyes with various types of functional groups were applied to measure the holding ability of chitin foam through ionic or hydrophobic interaction.

Chitin Dope. Chitin powder was prepared from Queen Crab shells according to the method of Hackman [3] and dissolved in saturated calcium chloride solutions in methanol by refluxing the mixture for 1 hour (1–5 g of chitin powder into 100 mL of solvent). The slightly turbid and viscous chitin solution was filtered through filter paper to prepare a transparent chitin solution (chitin dope). Reacetylated chitosans of various molecular weights were applied to prepare a clear chitin solution by refluxing for 10–20 minutes.

Method 1. Chitin dope was cast on a glass plate, and the plate was placed in a 1/1 mixture of ethylene glycol and 20% (w/v) sodium citrate aqueous solution to remove calcium ion by gentle agitation. The resulting chitin gel was extensively rinsed with deionized water until the effluent water was neutral. The gel was lyophilized to prepare a porous chitin foam.

Method 2. Chitin dope was diluted with large amounts of water or methanol (any kind of alcohol can be used) to precipitate chitin. The precipitated chitin was then rinsed extensively with deionized water to remove the calcium ions and methanol. The resulting swollen chitin was treated with the 1/1 mixture of ethylene glycol and 20% (w/v) sodium citrate aqueous solution. Chitin was dried in air after extensive rinsing with deionized water and acetone.

Lysozymic Hydrolysis. The lysozymic susceptibility of porous chitin foam and chitin powder was investigated by the method reported previously [2].

SEM Views. Scanning electron microscopic observations of porous chitin foams was performed at the surface and on cut sections using a Hitachi Scanning Electron Microscope S-2400.

X-Ray Diffraction Pattern. X-ray diffraction patterns of chitin powder and porous chitin foam were obtained by the use of Rigaku X-ray diffractometer RAD-HSR.

Chitin dope was prepared successfully by applying a new solvent system. The best solvent for chitin seems to be calcium chloride dihydrate saturated methanol as shown in Table 1. The dissolution mechanism is believed to be chelate formation between the calcium ion and the acetamide group at the C-2 position of the *N*-

TABLE 1. Solubilities of Chitin in Mixtures of Various Calcium and Magnesium Salts and Alcohols (0.5 g chitin was stirred in 50 mL of each solution at room temperature)

Solution	Solubility[a]
Saturated anhydrous $CaCl_2$–MeOH	+
Saturated $CaCl_2$–$2H_2O$–MeOH	+ + +
Saturated $CaCl_2$–$2H_2O$–EtOH	+
Saturated $MgCl_2$–$6H_2O$–MeOH	–
100% (w/v) $Ca(NO_3)_2$–$4H_2O$–MeOH	–
100% (w/v) $Mg(NO_3)_2$–$6H_2O$–MeOH	–
200% (w/v) $Ca(SCN)_2$–$4H_2O$–MeOH	+

[a] + + + transparent solution; + partially soluble; – insoluble.

acetylglucosamine residue. Gradual calcium chelation seems to be the cause of the destruction of the rigid crystalline structure of chitlin. The better solubility of reacetylated chitosans as compared to that of natural chitin over a wide molecular weight range seems to confirm the above assumption because reacetylated chitosan does not reform into a rigid crystalline structure.

The preparation of thin gels of chitin was carried out under mild conditions using very simple procedures. Therefore, the molecular weight of chitin was expected to be maintained for a considerable amount of time at room temperature. Porous chitin foam of low crystallinity was also prepared easily by lyophilization and showed higher lysozymic susceptibility than the original chitin powder. The porous surface was observed by SEM microscopy; the pore size was shown to depend mainly on the freeze-drying process.

References. [1] S. Tokura, N. Nishi, S-I. Nishimura, and O. Somorin, *Sen-i Gakkaishi*, 39, 507 (1983). [2] S. Tokura, A. Shirai, H. Kaneko, K. Itoyama, L. Ren, and H. Sekiguchi, *Carbohydr. Polym.*, Submitted. [3] R. H. Hackman, *Aust. J. Biol. Sci.*, *7*, 168 (1958).

CHEMICAL MODIFICATION OF CHITOSAN VIA ITS DECRYSTALLIZATION

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Chitin and chitosan are believed to be substantially intractable polymers. In order to chemically modify these materials, one has to treat them under severe conditions, e.g., at low temperatures for a long time (−20°C, 12 hours) to weaken their hydrogen linkages, and in highly polar organic solvents (DMSO, *N*-methylpyrrolidone). The operations must be repeated successively several times to obtain a degree of substitution (DS) greater than 1. The crystalline nature and structure of chitin and chitosan may be the most important reason for these materials to go into solution. Could the "decrystallization" of chitosan give us the opportunity to facilitate its chemical modification? The crystal structures of these two types of materials were investigated by means of scanning electron microscopy and by x-ray diffraction. It was observed that the crystallinity of the initial chitosan, which has a degree of acetylation (DA) = 56%, is 73%. Its surface is hard and compact. That can explain why crystallized chitosan does not easily take part in many chemical reactions. After "decrystallizing," its crystallinity is about 10%. Chitosan treated in such a way is soft and porous, but after recrystallization it becomes harder, smoother, and more crystalline than the initial chitosan, and has a crystallinity of 85%. Our experiments have shown the advantages of using decrystallized chitosan for chemical modification. The below-mentioned process can help justify the convenience of "decrystallized" chitosan in making many kinds of water-soluble derivatives: *O*,*N*-carboxymethylchitosan, *N*-carboxymethylchitosan, *N*,*N*-dicarboxymethylchitosan, *N*-quaternized chitosan, and nearly totally deacetylated chitosan.

The products have been synthesized and characterized by NMR spectroscopy (^{1}H-, ^{13}C-DEPT, ^{1}H-^{1}H, ^{1}H-^{13}C-NMR spectroscopy). Their chemical structures have been confirmed. All the modification processes are easily carried out in water in only one operation and with high yields (nearly 100%) without gel formation (products are totally water-soluble).

BIOPOLYMER PRODUCTION USED IN DRILLING FLUIDS SUITABLE FOR THE CONDITIONS OF VIETNAM

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The biopolymers described in this paper are microbial polysaccharides obtained by fermentation from sugar. They are widely used as viscosifiers for water-based drilling fluids and as agents suitable for use of workover fluids. Recently, biopolymers based on microbial polysaccharides have been used for secondary oil recovery techniques. Biopolymers are used as a primary viscosifier in a wide variety of polymer fluids and can be considered as the best polymers for this purpose. They provide fluids with excellent rheological properties and also with thixotropic properties. Ours is the only polymer that will suspend barite satisfactorily at low or zero shear rates and provide effective viscosity and suspension at low concentration, thereby eliminating the need for high bentonite usage to maintain fluid viscosity.

Due to its superior suspension characteristics, a wide range of fluid densities is possible with this biopolymer by the addition of soluble salts or other conventional weight-increasing agents. Since 1979 in Vietnam, foreign companies have used a drilling fluid containing biopolymers for oil exploration and production in offshore Vietnam. Current requirements for high-temperature stabilizing biopolymers are several hundred tons per year and will increase in the coming years, especially for the secondary oil recovery techniques. Research for the production of biopolymers for oil exploitation processes for conditions in Vietnam has therefore been started.

This undertaking is a multisection scientific project including technological research, biochemical application, chemical engineering apparatus, and the theory of drilling fluids. The following problems have been solved. 1) Microorganism species have been isolated from Vietnamese plants, and a suitable fermentation process for products of the sugar cane industry have been determined. 2) The main technological processes have been evaluated, and equipment for pilot-scale production in Hanoi and industrial production in Quang Ngai province has been designed. The focus was on the two key stages, fermentation and drying, which decided the efficiencies of the production line and its feasibility for Vietnamese conditions.

The approach was as follows. (a) Building kinetic models for the biological process in order to determine the optimal fermentation conditions while calculating the fermentation equipment upgrade for Levels I, II and III (equivalent to fermenters with volumes of 100 L, 900 L, and 4.5 m^3, respectively. (b) Improving the drying mechanism suitable for Vietnamese conditions and leading to a well-sticking paste drying by a surface evaporating process, not counting the effect of capillary diffusion from the interior of the material block. (c) Methods for increasing biopolymer thermal stability, pH stability, and salt tolerance have been established. A technological line of biopolymer production used in oil drilling fluid with a capacity of 100 tons per year has been established in the Quang Ngai province. The product was tested by the laboratories of the Vietsovpetro, The Vietnam Petroleum Institute, and the Anchor Drilling Fluids—Vietnam Joint Venture Company. The product was shown to have the same quality as imported products of the SC-Polymer group. (d) Our research also suggested some formulations for preparing drilling fluid with the biopolymers produced in Quang Ngai province which permit: (i) a drilling fluid with a high viscosity and low density which helps increase the penetration rates and provides longer bit life through improved hydraulic efficiency; (ii) a foaming solution prepared for drilling through the granitic basement reservoirs of the Bach Ho oilfield; (iii) a foaming solution prepared for well treatment (using XP I and XP II chemicals made by the DMC Company) in order to increase the production capacity of wells. The biopolymer is able to produce the high viscosities needed for well treatment solutions and also provides increased cuttings transport and improved hole cleaning.

References. Vietnam Patent HI-0119 (August 29, 1994). *Vietnam. J. Chem.*, *31*(4), 37-38 (1993). *Oil Gas J.*, No. 1, 33-38 (1994). *Vietnam. J. Sci. Technol.*, *32*(5), 1-10 (1994).

POLYSACCHARIDES USED IN DRILLING FLUIDS

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The use of polysaccharides in drilling muds first began in 1937. Since that time the polysaccharides used for this purpose have become more sophisticated and often specifically designed for a particular drilling situation, even to the extent where clays were entirely replaced by polysaccharides in such cases as drilling water-sensitive shales.

The range and versatility of polysaccharides have continuously been extended, and it is the ability to tailor-make a polysaccharide with particular properties to suit a specific purpose that will ensure that polysaccharides will solve drilling problems in the future. The purpose of this article is to describe the structures of some polysaccharides used in drilling muds and to relate the structure to the function, the role and application, so that the use of polysaccharides in drilling muds is understood. Polysaccharides are the most widely used group of polymers in drilling fluids. Included are cellulose derivatives, modified starches, bacterial xanthan gums, and other polysaccharides. They are constructed through oxygen atoms connecting carbon atoms of glucose units to form a gludosidic linkage. An extensive range of polysaccharides can be manufactured by modifying natural products. They all contain the same monomeric units but differ one from another in molecular weight, type of linkage, and chemical modification. The different structures can be related to the different functions of molecules.

Some typical polysaccharides used in drilling fluids are described as follows. (a) Carboxymethyl cellulose (CMC) is prepared by the reaction of cellulose with sodium chloroacetate in the presence of sodium hydroxide. By addition of antioxidants (phenol, hydroquinone, and others) during the NaOH treatment, CMC with a degree of substitution (DS) as high as 0.8 to 1.2 has been prepared. High molecular weight CMC can be used as a viscosifier and also possesses some other interesting properties. (b) Xanthan gum: *Xanthomonas campestris* can be grown by aerobic fermentation on a carbohydrate source such as green bean sprouts and gives xanthan gum. The latter is a heteropolysaccharide having a branched structure and containing polar carboxyl and ester groups. Xanthan gum solutions have excellent suspension properties that cannot be matched by other polymers at equivalent concentrations. (c) Starch ethers are prepared by suspending starch in an organic solvent and adding a water solution of the derivatizing reagent. (It is important that the organic solvent used be immiscible with the aqueous derivatizing reagent phase; i.e., the solvent does not dissolve the reagent or the polysaccharide derivative as it is formed).

Experimental Part. 585 parts of toluene, 58.5 parts of sorbitan monooleate, 227 parts of cornstarch with a moisture content of 10%, and 27 parts of monochloroacetic acid were slowly added to the reactor. The suspension was treated with 75 mL of 18 N NaOH over an hour while the temperature rose to 38–40°C. The mixture was heated for 3 hours at 65°C to 70°C. Water was removed at 16 kPa (120 mmHg) and 324 parts of carboxymethyl starch (CMS) were obtained.

It is found that polysaccharides such as CMC, CMS, and xanthan gum can usually be added to drilling muds to reduce the water loss and to control the thixotropy precisely. Addition of these polysaccharides also brings desirable changes in the flow properties of drilling muds. These factors are very important because of their effect on drilling rate, hole cleaning, and gas entrainment.

References. N. H. Huiliuc et al., *Krakhmaloproductu M.* (1985). J. C. John, Industrial Starch Technology, New York, 1970. Xanthan Gum and Method of Producing It by Fermentation, European Patent Application 0032293A3.

CHEMICAL NATURE OF SODA LIGNINS OF SOME VIETNAMESE BAMBOOS AND UTILIZATION OF BAMBOO BLACK LIQUOR FOR SYNTHETIC ADHESIVES

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Of the nearly 100 species of bamboo found in Vietnam, only about 10 are presently being used by the pulp and paper industries. The cell wall of bamboos consists mainly of two chemical constituents, the carbohydrate fraction and the amorphous lignin fraction. So far very little work has been done to study the content and the nature of lignin of Vietnamese bamboos and especially the utilization of bamboo black liquor from the lignin fraction. In order to understand the content and the nature of lignin of common Vietnamese bamboos and to possibly utilize the bamboo black liquor, extensive work has been carried out in the Forest Science Institute of Vietnam on the isolation and characterization of soda lignins adhesives. They were prepared from 10 Vietnamese bamboos: *Neuhouzeanua dullooa*, *Arundinaria sp.*, *Dendrocalamus sp.*, *Dendrocalamus sericeus*, *Lingnania sp.*, *Bambusa tulda*, *Dendrocalamus membranaceus*, *Sinocalamus sp.*, *Dendrocalamus hamiltonii*, and *Oxypanthera albocilita*.

Three stalks each of the 10 species of bamboo mentioned above were taken up for this investigation. While selecting the stalks, care was taken to see that they were mature, i.e., over 3 years old. Five kilograms of the chips from each species were treated at 160°C for 4 hours using the so-called soda process. Crude soda lignin obtained from the black liquor was purified using anhydrous 1,4-dioxane. The lignin contents of the bamboos were determined according to TAPPI standard. Carbon, hydrogen, and methoxyl contents were determined by standard methods. According to our analytical data, the lignin content of the 10 above-mentioned bamboos are as follows: *Neohouzeanua dullooa* 25.3%, *Arundinaria sp.* 25%, *Dendrocalamus sp.* 21.5%, *Dendrocalamus sericeus* 26.4%, *Lingnania sp.* 25.1%, *Bambusa tulda*, 24.2%, *Dendrocalamus membranaceus* 22.4%, *Sinocalamus sp.* 22%, *Dendrocalamus hamiltonii* 24.2%, and *Oxypanthera albocilita* 23.3%. It seems from the above results that the lignin content of the different species varies within narrow limits of 24 ± 2%. It is observed that carbon and hydrogen contents of these lignins are 50 ± 2% and 3 ± 0.5%, respectively, and the methoxyl content is 10 ± 2%. The exception is *Bambusa tulda* whose methoxyl content is exceptionally high (16%).

Our studies revealed that in bamboos of Vietnamese origin the number of C_9 units varies from 13 to 21 with an average of 16. The average pine kraft lignin molecule is composed of more than 20 units, and the average molecule of hardwood lignin contain more than 15 units. This shows that the structure of bamboo lignin skeleton is more akin to that of hardwoods than that of conifers. The IR spectra of all the lignins are similar, which infers that bamboo lignin is composed of polymers that have mainly propyl guaiacyl, propyl syringyl, as well as *p*-hydroxybenzal units.

Utilization of Bamboo Black Liquor for Synthetic Adhesives. For many years, phenol-formaldehyde resins have been the preferred adhesives for bonding weather-resistant wood and bamboo products such as plywood, chip board, bamboo pressed mat, etc. Phenolic resin prices, generally paralleling phenol in price, have increased by a factor of 2 over the past 5 years. Meanwhile, a number of natural products have become available which have in their molecular structure units resembling phenol and are capable of undergoing reactions similar to that of phenol. Lignin-derived products have these characteristics, and consequently lignin is a promising alternative source as the raw material for adhesives. Lignin constitutes approximately one-quarter of the weight of bamboo and represents a plentiful naturally occurring polymer, second in abundance only to cellulose.

To produce 1 ton of pulp from bamboo, 0.5 ton of lignin must be removed. Lignin is present in black liquor, and almost all black liquor produced is presently discharged into the rivers of Vietnam. This situation is a serious contributor to pollution of the environment and is a loss of a valuable natural polymer.

For economic reasons, black liquor has been studied extensively for the synthesis of adhesives, but the recovery of lignin from black liquor has been grossly overlooked. Assembled panels using adhesives from black liquor were tested according to the Vietnamese standard TCVN. The panels were not affected after 24 hours in cold water or after 4 hours in boiling water. The tension shear strength of plywood was 22.3 N/cm^2. The price of this lignin-based adhesive is about one-third of the price of the phenol adhesive. At the present time in Vietnam, black liquor adhesive has completely replaced phenol adhesives for the production of bamboo pressed mats.

POLYSACCHARIDES FERRIC IRON COMPLEX FOR TREATING IRON DEFICIENCY ANEMIA

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For the prevention and treatment of iron deficiency in piglets and pregnant sows, we studied and prepared iron dextran complexes some years ago. Because of its high cost and side effects, we could not introduce our product to the market. That is why we tried to look for other raw materials that also form complexes with iron but give cheaper and safer products. We found that modification of a low-molecular weight polysaccharide obtained from rice in Vietnam also gives good complexes with ferric iron and satisfies our purpose.

I. Preparation of the Complexes. 1. Method of preparing the polysaccharide. Rice flour was pretreated and hydrolyzed with dilute hydrochloric acid at room temperature. After neutralization the polysaccharide was precipitated with alcohol or acetone and washed. The product could be used directly for complexation, or the complexation could be performed in the modified form. *2. Modified polysaccharide.* In order to produce a physiologically acceptable product with low toxicity which has a relatively high iron content, the aldehyde groups on the terminal glucose units had to be cyanated to form cyanohydrin groups, followed by hydrolysis to the corresponding acid. *3. Complexation.* Iron complexes may be formed by the reaction of the above-mentioned polysaccharide or the polysaccharide hoptonic acid (PHA) with ferric hydroxide. Hydroxy polycarboxylic acids (HPA) such as citric acid and tartaric acid (also glycerol) may be added as an additional ligand.

The ratio of the components is the main factor which determines the stability of the complex and thus the safety of the product. The weight ratio between $FeCl_3$/PHA/HPA/glycerol may be 9-15/8-10/1.2-2/1-1.5. At ratios outside this range, the toxicity was found to increase. If, on the other hand, the iron content in the complex is very low, it is not very useful when the complex is used as an additive for cattle breeding.

The complexing was carried out at temperatures from 60 to 120°C. The pH value was adjusted to 7.5 to 8 by the addition of a base. After the complexation reaction, the mixture was heated to about 120°C to complete the reaction. The complex was precipitated by pouring the aqueous solution into alcohol or acetone. The complex was redissolved in distilled water and precipitated. The procedure was repeated several times to obtain a low content of free iron (less than 0.065%). The purified complex is dark red-brown and contains 39.4% of iron by weight. It is possible to prepare an injectable aqueous solution having an iron content of 10%, or even 20% if necessary. The solutions are viscous and are suitable for injections.

TABLE 1

	No injection		2 × 100 mg Fe i.m.	
Time, days	Erythr. number [Mio/mm^3]	Hemoglobin [g/100 mL]	Erythr. number [Mio/mm^3]	Hemoglobin [g/100 mL]
2	4.6 ± 0.3	9.3 ± 0.4	4.7 ± 0.3	9.2 ± 0.4
7	4.4 ± 0.2	9.1 ± 0.4	4.9 ± 0.2	9.8 ± 0.2
14	4.3 ± 0.5	8.8 ± 0.3	5.0 ± 0.3	10.0 ± 0.5
21	4.1 ± 0.5	8.3 ± 0.3	5.5 ± 0.2	11.3 ± 0.2

They have an LD_{50} = 2000 mg of iron per kilogram of body weight when injected intramuscularly into mice. The product solution has a pH from 6.5 to 6.7 and an electrical conductivity of 0.47×10^{-3} Ω/cm at 25°C. It is stable toward sterilization, heating, and long time storage. It was found that the product is readily absorbed because of its relatively low viscosity. It also has a high iron content and has low toxicity for animals. In the infrared spectrum of the complex, the major peaks are at 3100–3400 cm^{-1} (ψOH); 1385 cm^{-1} (OH); 1150 cm^{-1} (ΨC—O—C); 1000–1400 cm^{-1} (y prim. and secondary OH); 700 cm^{-1} (OH).

II. Applications in Cattle Breeding. Twenty litters of pigs (160 pigs) were used in the experiments. Records of the hemoglobin levels and weight gains until weaning (60 days) were made weekly. The use of the iron polysaccharide complex not only prevents the fall of the hemoglobin level but also increases it in comparison with the other iron compounds (Table 1).

The increase in weight was from 1.6 to 1.8 kg in 60 days in comparison with the control. The new product was also found not to accumulate in the body. This is the first example of the production of an injectable iron compound for cattle breeding in Vietnam.

Our thanks are due to the National Institute of Veterinary Medicine for the biological tests and the results of application in cattle breeding.

References. Na. Flram, French Patent 1,422,870 (1966). Alsop. Ranulph Michel et al., German Patent 1,768,362 (1971). Truong Dinh Thac, Pham Ngoc Ha, and Nguyen Mau Phuong, in *2nd Vietnam National Congress on Chemistry*, 1993, p. 353.

DEGRADATION OF COTTON CELLULOSE BY ELECTROGENERATED OXYGEN

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Cotton fabrics are often bleached using hydrogen peroxide applied under alkaline conditions. During this process, "catalytic damage" was observed and involved the degradation of cotton cellulose. Typically this effect manifested itself in nonlevel dyeing of, and hole formation in, the fabric. Bleaching and hole formation, similar to those observed in practice, have been qualitatively demonstrated in the laboratory using a Pt electrode at which oxygen species similar to those associated with peroxide bleaching are generated [1, 2]. In these studies a cotton fabric was secured to an anode in an electrolytic cell and a constant current was applied for a selected period. During this galvanostatic experiment, apart from oxygen gas, reactive species such as $OH\cdot$, $O_2\cdot$, and $HO_2\cdot$ were produced at the Pt anode [3]. Cotton-cellulose polymer underwent oxidation in this highly reactive environment, producing damaged cotton fibers which contain carbonyl and carboxylic groups. Holes may form under severe treatment conditions.

Using staining methodology, Meyer et al. [1] demonstrated qualitatively that the degree of damage obtained depended on the conditions of the bleaching process such as temperature and current applied during the electrolysis at the Pt anode. A model to explain the catalytic damage phenomenon in cotton fabric was proposed by Meyer et al. [1]. In it, a small trapped metal particle, usually containing iron or copper, is assumed to have an oxidized surface that facilitates metal ion hydrolysis. The metal ions in the aqueous solution then catalyze the decomposition of hydrogen peroxide near the metallic particle.

The effect of the significantly high amounts of oxidizing products produced by this mechanism was a much more aggressive attack on the cotton-cellulose fabric which is in close proximity to the metal particle. It is this process that is regarded as the underlying cause of the damage effect. In addition, metal ion hydrolysis, which occurs in a very small volume of solution near the metal particle, lowers the pH of this solution quite significantly, thereby contributing acid hydrolysis as another pathway for the degradation of cellulose.

In the case of the electrolytic studies, the oxidizing species are electrogenerated at the Pt electrode. Similarly highly reactive intermediates such as $OH\cdot$ and $O_2\cdot$, present during the decomposition of hydrogen peroxide at the surface of the metallic particle, were also formed at the Pt electrode's surface. However, the mechanism involved in generating these oxidizing species in the two systems was probably somewhat different. It is still unclear which reactive species was largely responsible for the fabric modification. In general, dioxygen, various oxygen radicals, and protons have all been cited in the damage mechanism, but a recent kinetic study has suggested that perhydroxyl ion HOO^- is the important reactant in the hydrogen peroxide bleaching mechanism [4].

Although the effect of a metal particle and metal ion hydrolysis is not apparent with the Pt electrode, the catalytic effect of copper and iron has been demonstrated in studies involving iron and copper electrodes in place of platinum [1, 5]. The pH drop attributed to the hydrolysis of the metal ion at the metal particle interface in the Meyer model was simulated by the depletion of the OH ion at the surface of a Pt electrode. We also recorded a pH drop at the electrode interface in experiments with Fe and Cu electrodes; presumably this was, in part, a result of metal ion hydrolysis similar to that invoked for the Meyer model. Thus the region between the fabric and the electrode mimics the environment between the fabric and the metallic particle. Furthermore, the degree of damage to the fabric at the electrode was controlled by the temperature and the electrode current.

It was this aspect that was particularly attractive in this approach for the study of the mechanism of catalytic damage, and for further development of fabric treatment procedures at the electrode surface. We are currently involved in studies of cellulosic and woolen fabrics treated by electrogenerated species at the electrode interface with the aim of assessing the possibility of designing systems that could be used for similar treatments in practice.

References. [1] U. Meyer, S. Kokot, R. Weber, and J. Zurcher-Vogt, *Textilveredlung, 22*, 185 (1987). [2] L. D. Marahusin, S. Kokot, and D. P. Schweinsberg, *Corros. Sci., 33*, 1281 (1992). [3] V. I. Birss, A. Damjanovic, and P. G. Hudson, *J. Electrochem. Soc., 133*, 1621 (1983). [4] K. H. Thompson, W. P. Griffith, and M. Spiro, *J. Chem. Soc., Chem. Commun.*, No. 21, 1600 (1992). [5] L. Marahusin, S. Kokot, and D. P. Schweinsberg, *Corros. Sci., 34*, 1007 (1993).

CELLULOSE ACETATE MEMBRANE USED IN REVERSE OSMOSIS

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Polymers based on cellulose derivatives, especially cellulose acetate (CA), are used broadly to produce membranes used in ultrafiltration and reverse osmosis. The process of CA membrane production includes many stages, and there are many factors affecting the filtration ability of the resulting membranes. This report shows that by choosing the proper conditions for the preparation of the membranes, CA membranes with optimal filtration capabilities could be produced. CA membranes, which have an asymmetric structure, were prepared by the method of phase reversal. The effectiveness in reverse osmosis of CA membranes was compared and evaluated based on the results of filtration of a 5% sugar solution with the experimental filtration model designed by us.

The first factor surveyed was the concentration of CA in the membrane-producing solution because it was the most important variable which affected the structure and the filtration capability of the membrane. The results showed that an increase of the CA concentration in the CA dope used for the production of the membrane made the separation index *R* to increase considerably while the flux *J* decreased. When the concentration of CA was increased above 22%, the separation index did not increase further whereas the flux decreased continually (Table 1). These results can be explained on the basis of the dependence of the structure of the skin layer and the subskin layer (supporting layer) of the asymmetric membrane on the concentration of the polymer in the membrane-producing solution.

After the initial forming of the CA membrane by controlled precipitation in water, an important factor was the condensing temperature. This temperature was changed from 5 to 40°C, and it was found that the most suitable precipitation

TABLE 1. Effects of CA Concentration on the Membrane Filtration Ability

Concentration AC1, %	Driving pressure, MPa	Flux *J*, $mL/cm^2 \cdot s$	Separation index *R*, %
18.90	2.4	4.74	39
20.40	2.4	2.10	73
21.85	2.9	2.04	74
23.25	4.3	1.93	74

temperature is 5°C. Otherwise, the precipitation time was also influenced, and the flux and the separation index were affected. The results showed that the most suitable condensing time was 15 minutes at a temperature of 5°C and the attainable separation index was 98%. To increase the effectiveness of the membrane filtration, heat treatment in water for a period of 15 minutes was desirable. It was concluded that when the temperature increased from 30 to 95°C in this stage, the separation index increased by a factor of 2 and the flux decreased by a factor of 1.5. Still, the heat treatment was indispensable.

SYNTHESIS OF LIQUID NATURAL RUBBER

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The high molecular weight of natural rubber (NR) causes difficulties in its processing. Therefore, many investigations on the most effective way to depolymerize natural rubber have been carried out. Some of the early investigations used alkaline permanganate solutions with benzene solutions of NR [1], later investigations used H_2O_2 [2] and H_2O_2 in the presence of CH_3COOH [3]. Certain metals, such as Cu, Mn, and Co [4], were also used as extremely active catalysts for the oxidation of rubber. Recently, rubber was depolymerized in toluene solutions by H_2O_2 and *p*-toluene sulfonic acid [5], or at pressures of 1.3–3.0 MPa and 150°C [6], by H_2O_2/UV [7] and by phenylhydrazine/atmospheric oxygen [8].

In our work the depolymerization of NR was carried out directly from rubber latex using H_2O_2 at high temperature without any other agent. As described in the above-mentioned works, H_2O_2 attacks the α-position of the double bond of the polyisoprene chain and causes oxidative depolymerization, leading to the formation of liquid natural rubber with —OH terminal groups on both ends.

Materials. 40% rubber latex from the Thong Nhat farm, Thanh Hoa. 50% aqueous H_2O_2.

Depolymerization. 300 mL NR (latex stabilized by lauryl sulfate and neutralized to pH 7) was placed in a 1000-mL glass bottle equipped with a stirrer. The bottle was installed in a thermostat which had been adjusted to the desired temperature. H_2O_2 was added dropwise into the emulsion in such a way that the foam formed during the reaction did not overflow. Each sample was purified by dissolving it in toluene and precipitating it in methanol several times.

IR spectra were recorded on an IR-75 spectrophotometer. The molecular weight of the samples was determined by GPC. The following factors have been studied. (a) Influence of the ratio H_2O_2/NR on the molecular weight of depolymerized NR. (b) Influence of temperature on the changing MW as a function of the reaction time. (c) MW distribution of the depolymerized NR. The MW of the liquid NR decreased with an increasing ratio of H_2O_2/NR. The rate of depolymerization increased with increasing temperature. (d) Liquid NR MW is distributed over a wide range. (e) In comparison with the IR spectra of the original NR, the IR spectra of liquid NR have a new absorption band with a peak at 3400 cm^{-1} which belongs to the —OH groups that were newly formed during the reaction.

References. [1] C. Harries, *Ber., 37*, 2708 (1904). [2] M. C. Boswell et al., *Ca. Chem. Metal, 6*, 237 (1922). [3] J. M. Robertson and J. A. Mair, *J. Soc. Chem. Ind., 46*, 41T (1927). [4] W. H. Stevens et al., *Trans. I.R.I., 5*, 374 (1930). [5] R. Pautrat and J. Marteau. Belgium Patent 824.654; *Chem. Abstr., 84*, 45773e (1976). [6] S. K. Gupta et al., *J. Appl. Polym. Sci., 30*, 1095 (1985). [7] P. L. Dung, Dang Van Luyen, et al., *J. Chem. NCSR, 30*(1), 11 (1992). [8] P. H. Ly, Ph.D. Thesis, Institute of Chemistry, NCNST, 1991.

LIQUID RUBBER FROM NATURAL RUBBER LATEX

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Liquid natural rubber (LNR) can be prepared from both masticated crepe in solution [1] and from raw natural rubber (NR) in the latex [2]. The system phenylhydrazine-ferrous chloride is used in these processes as an effective catalyst. surfactants play an important role in the stabilization of NR latex, storage time, and oxidative process. Systems containing phenylhydrazine and other transition metals are effective in the oxidative degradation of NR in latex form. These problems are investigated in this work.

Materials and Reagents. Raw latex (stabilized with NH_4OH to pH 10 and higher. 1) Surfactants: Na dodecylsulfonate (DBSA), Na laurylsulfate as anionic surfactants. Sanimal H as a mixture of nonionic and anionic surfactants. Zelon C, nonionic mixture. Verol-S 15. Teika-W, nonionic surfactants. 2) Catalysts: Phenylhydrazine. Metals sulfates. 3) Analytical reagents.

Procedures. The NR latex is passed through 325-mesh sieves. Surfactant: 3% of dry rubber. Metal salt: 3–6 mmol and phenylhydrazine 10–18 mmol per rubber mol. Oxygen is bubbled through the suspension at a rate of 2 L/min per 1 mol of rubber, with moderate stirring. Samples of raw and degraded samples of latexes were coagulated, washed, and treated with ethanol. The effect of surfactants and catalyst systems was evaluated by the variation of M_w values and spectrometric methods.

Results. 1) Anionic surfactants were suitable for stabilizing NR latex in an alkaline medium. Nonionic surfactants could be used for changing the latex medium to acidic values, but in this case the shelf life of these latexes was shortened. DBSA and Teika-W exhibited the greatest effect on stabilization of the latex for the process of NR oxidative degradation. 2) Systems consisting of Fe(II) and Co(II) together with phenylhydrazine are the best catalysts for this reaction. $M_w < 6 \times 10^3$ after 1 hour; $<3 \times 10^3$ after 3 hours. The activity of Mn(II)-containing systems as catalysts was only moderate, and other catalyst systems were even lower in activity. 3) Temperatures in the range of 30 to 40°C were suitable for this reaction. 4) The IR and UV spectral data of the low molecular weight degradation products showed that there was only a small amount of phenylhydrazine residues in the LNR in the chemically bonded state, which also corresponded with the results of Refs. 1 and 2.

References. [1] N. Kawabata et al., *Bull. Chem. Soc. Jpn.*, No. 51, 22 (1978). [2] Hathuc Huy et al., *J. Chem., V.N.I.S., T28*(2), 22 (1990).

LIQUID NATURAL RUBBERS WITH REACTIVE END GROUPS AND BLOCK COPOLYMERS

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The production of liquid natural rubbers (LNRs) with reactive end groups is of great importance, particularly for the synthesis of new macromolecular structures. Hydroxyl-terminated liquid natural rubber (HTNR), with M_n of 5,000–15,000 and a functionality $f = 2$, was prepared by photochemical degradation of natural rubber (NR) (10% toluene solution) using H_2O_2/MeOH and H_2O_2/THF in sunlight [1]. Carboxyl-terminated LNR (CTNR) and amino-terminated LNR (ATNR) have been synthesized by reacting HTNR with an excess of adipoyl chloride and subsequently hydrolyzing the residual terminal acid chloride functions to produce CTNR or by reacting the terminal acid chloride functions with an excess amount of 1,6-diaminohexane to produce ATNR.

The synthesis of α,ω-di(methacryloyl)-poly-*cis*-1,4-isoprene involved the reaction of HTNR with an excess of methacryloyl chloride in the presence of triethylamine (Et_3N) as the acid acceptor. ^{1}H-NMR, ^{13}C-NMR, IR, GPC, and chemical analyses of the above-mentioned new telechelic prepolymers based on LNR indicated quantitative introduction of two reactive groups, i.e., OH, $CH_2{=}C(CH_3)$ —CO—, COOH, or NH_2, per *cis*-1,4-polyisoprene molecule. The new telechelic prepolymers can be used for the synthesis of a number of new materials, e.g., rubber-toughened epoxy resin, crosslinked carboxylic elastomers, polymer networks, interpenetrating polymer networks, macroinitiators, block copolymers, and others.

It is well known that block copolymers can be formed if suitable reactive end groups of two polymers can react together or react with a linking molecule. Many basic types of block copolymers can be synthesized by this technique, including AB, ABA, and sequential ABAB block copolymers [2]. Based on HTNR, two types of block copolymers have been synthesized: (a) (i) Polystyrene (PSt)–natural rubber di- and triblock copolymers were prepared as follows. The carboxyl-terminated PSt (CTPSt) was synthesized by the free-radical polymerization of St initiated by a functional azo-initiator by a unimolecular termination mechanism. Conversion of the carboxyl end groups to acid chloride groups gave acid chlorodeterminated PSt (ATPSt [3]). (ii) Di- and triblock copolymers having the basic structure of PSt-NR and PSt-NR-PSt, respectively, were prepared by dissolving stoichiometric quantities of the homopolymers, i.e., HTNR and ATPSt (up to 10% by weight) in dry benzene or THF in the presence of a small amount of triethylamine (Et_3N).

$$\mathrm{PS{-}COCl + HO{\sim}NR{\sim}OH \xrightarrow{Et_3N} PS{-}CO{-}O{-}NR{-}OH}$$

$$\mathrm{2PS{-}COCl + HO{\sim}NR{\sim}OH \xrightarrow{Et_3N} PS{-}COO{-}NR{-}OCOPS}$$

(b) Poly(methyl methacrylate)-NR di- and triblock copolymers were synthesized by the following method. (i) Hydroxyl-terminated PMMA (HO-PMMA) of varying molecular weights was prepared by free-radical polymerization of MMA initiated by AIBN in the presence of mercaptoethanol. The HO-PMMA obtained was then converted into the corresponding isocyanate-terminated PMMA (NCO-PMMA) by reaction with an excess of Hylene W (bis-4,4′-isocyanatocyclohexyl) methane [4]. (ii) Di- and triblock PMMA-NR copolymers were prepared by the reaction of HTNR with NCO-PMMA at 65 °C in the presence of a few drops of dibutyltin dilaurate as the catalyst.

$$\mathrm{PMMA{-}NCO + HO{\sim}NR{\sim}OH \xrightarrow{Catalyst,\ 65\,^{\circ}C}}$$
$$\mathrm{PMMA{-}NR{-}OH}$$

$$\mathrm{2PMMA{-}NCO + HO{\sim}NR{\sim}OH \xrightarrow{Catalyst,\ 65\,^{\circ}C}}$$
$$\mathrm{PMMA{-}NR{-}PMMA}$$

All new, regular AB-type diblock and ABA-type triblock copolymers mentioned above were characterized by GPC, vapor pressure osmometry, viscometry, and IR and NMR spectroscopies. Quantitative estimation of the block segments has been carried out by measuring the areas under the peaks assigned to the various protons in the NMR spectra of the polymers. The solubility and solution viscosity behaviors of the polymers have also been studied.

References. [1] T. Ravindran, M. R. G. Nayar, and D. Francis, *J. Appl. Polym. Sci., 35,* 1227–1239 (1988). [2] G. A. Stahl, in *Polymer Alloys II: Blends, Blocks, Grafts and IPNs* (D. Klempner and K. C. Frisch, Eds.), Plenum Press, New York, 1980. [3] K. Ishizu, *J. Polym. Sci., Part A: Polym. Chem., 28,* 1887–1894 (1990). [4] J. H. Grezlak and G. L. Wilkes, *J. Appl. Polym. Sci., 19,* 769–786 (1975).

NATURAL RUBBER-POLYETHYLENE BLENDS

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The mutual influences of mix technology and blend compositions on the phase structure and on the properties of natural rubber-polyethylene (NR-PE) blends have been studied. The mixing process in internal mixers by high shear tension and high pressure gave uniformly dispersed blends after 4 minutes of mixing time with particle size in the μm range as observed by TEM. A change of tension set of various blend compositions followed by peroxide curing gave highly plastic blends. The production of NR-PE blends by electrically heated roll-mixers required a longer mixing time of 20 minutes because of the lower shear tension and lower mixing pressure provided by this technique.

NR-PE blends were also subjected to sulfur curing. Composition strongly influences the tension set of sulfur-cured high rubber blends. It was observed that rubber particles with a size of 10 μm were dispersed in the PE matrix. It was also concluded that the PE provided some protection against radiation and improved the weather resistance of NR-PE blends.

APPLICATION OF POLY(VINYL ALCOHOL)/NATURAL RUBBER BLEND FOR PHOTOSENSITIVE MATERIALS

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Poly(vinyl alcohol) (PVA) is widely used in photogravure and photolithography. However, it does not always meet the specific technical requirements of these applications. In order to improve its stability, we prepared and studied PVA-NR blends by using IPN (interpenetrating polymer network) techniques.

Materials. Rubber: NR was depolymerized in the latex form to obtain liquid natural rubber (LNR) with OH-terminal groups with a MW of about 10^4. PVA: MW ~ 78,000, 98% hydrolyzed. Photosensitizer: Ammonium dichromate. Traditional vulcanizing agents, accelerators, and stabilizers were also used.

Blending. PVA was dissolved in water (10% solution). Depolymerized NR latex with a LNR concentration of 30% was added to the PVA solution according to the following (weight/weight) ratios: NR/PVA = 1/9, 2/8, 3/7, 4/6, 5/5, 6/4, 7/3, 8/2, 9/1. Ammonium dichromate (ADC), vulcanizor (Vul), accelerator (Acc), and stabilizer (St) were added to the mixture in the ratio: ADC-PVA = 1/10 (w/w), Acc/NR = 1 phr, Vul/NR = 2 phr, St/NR = 0.5 phr. A defoaming agent was added to the system. The mixture was thoroughly stirred and left several days in the dark to promote phase separation.

Film Casting. Each mixture was coated on a glass disk and dried in the dark. Samples were exposed to UV light from a high pressure Hg lamp and then vulcanized at 140°C for 2 hours. To determine whether they possessed the properties of a photosensitive material (or photoresist), the samples were first exposed through an image-film, then developed in water, and then vulcanized.

Results. The solubility of the mixtures before the exposure and vulcanization process decreases with an increasing amount of NR in the mixtures. With NR $>$ 50%, the resolution of the blend is very poor, so it cannot be considered as a photoresist. The physical modulus of the photoresists increases with an increasing amount of NR.

Systems with NR/PVA = 3/4, 4/6, and 5/5 were selected for further investigations and tests.

References. E. Eloid and T. Scharowsky, *Kolloid Z., 72*, 69 (1935). K. Horie and H. Ando, *J. Soc. Photogr. Sci. Technol. Jpn., 47*(5) (1984). A. H. Smith, *Print Technol., 11*, 19 (1967). H. Keskkula, *Polymer Modification of Rubbers and Polymers, J. Appl. Polym. Sci., Appl. Polym. Symp., 7* (1968). K. Tsumitsu and Y. Murakano, in *Polyvinyl Alcohol, Properties and Applications* (C. A. Finch, Ed.), 1992, Chap. 12. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum Press, New York, 1976. Y. Nishio and T. Haratani, "Miscibility and Orientation of PVA/PVP Blends," *J. Polym. Sci., Polym. Phys. Ed., 28*, 355 (1990).

BLENDS FROM CASHEW NUT SHELL LIQUID-FORMALDEHYDE RESIN WITH NATURAL AND SYNTHETIC RUBBER

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Phenol formaldehyde resins (CNSLF) from cashew nut shell liquids (CNSL) and formaldehyde were considered as active reinforcing fillers for many kinds of rubber, natural and synthetic. CNSLF was synthesized by condensing CNSL and formaldehyde at a molar ratio of 1/1 in xylene for 50 minutes. The water was eliminated at 110–115 °C azeotropically. The product was then mixed with natural or synthetic rubber.

Blend with Synthetic Rubber. A blend of 40% nitrile rubber with CNSLF was mixed on a roll-mill with the following ingredients (phr): NBR 100, stearic acid 1.5, zinc oxide 1, sulfur 1.5, accelerator MBT 1.5, and the CNSLF amount varied as in Table 1. Hexamethylenetetramine (HMTA) was used as curing agent for the phenolic resin.

Blend with Natural Rubber. The best result was obtained at a HMTA/CNSLF ratio of 3/47. The DTA and DTG analysis of these samples showed that the weight loss of the sample having CNSLF is smaller than that of the sample without CNSLF. The CNSLF resin showed enhanced compatibility with NR, better than that of the phenol resin. The greater the amount of CNSLF used, the higher the Mooney viscosity obtained, which means that the compatibility was increased. The best results were observed at 18% CNSLF. On the basis of DTA and DTG analyses, we concluded that the weight loss of the samples with CNSLF is smaller than that of those without CNSLF, and their swelling capacity in toluene at 25 °C was also increased. It was concluded that an interpenetrating network had been formed in these blends.

TABLE 1

CNSLF	44	45	46	47	48	49	50
HMTA	6	5	4	3	2	1	0
Elastic modulus (MPa)	21.5	23	40.5	66.8	60.5	40.2	15.4
Harness, Shore A at 25 °C	67	80	82	85	83	75	62

SYNTHESIS, PROPERTIES, AND APPLICATION OF EPOXYDIZED NATURAL RUBBER

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Latexes of natural rubber (NR) cultivated in North Vietnam (Nghe An and Thanh Hoa provinces) were used in this research. These latexes were characterized before use. Dry latexes have dry rubber contents from 31.5 to 38.4%, total solid contents from 33 to 41%, and contents of acetone extractables from 2.1 to 2.3%. The latexes were stabilized by nonionic surfactants and acidified by AcOH, HCl, or HCOOH to a suitable pH range before epoxidation. The conditions for synthesizing and preserving peroxyacetic acid were investigated in detail. The peracid was stable at room temperature for only a few days, but when kept at low temperature it was stable for months. Its rate of decomposition was approximately 0.7% per month.

The kinetics of epoxidation of NR by peracid was investigated at temperatures ranging from 4 to 35°C. The reaction is very sensitive to pH, temperature, and time of reaction, as well as to some impurities present in the system. By using peracetic acid at moderate temperature, one can obtain epoxidized natural rubber with epoxide contents from 5 to 75 mol%. The epoxidation process was followed by chemical titration and spectral analysis (IR, ^{1}H-NMR). To avoid side reactions (such as ring-opening of the already formed epoxide), the epoxidation should be carried out at moderate pH and at a suitable dry rubber content for a successful reaction. Excessive local heating should be avoided.

In-situ epoxidation using H_2O_2 and HCOOH was also studied at pH 2-5 in the temperature range from 15 to 60°C. The stability of the reaction mixture depended on the nature and concentration of the surfactant and the extent of epoxidation. Depending on the temperature, the duration of this reaction was from a few hours to a few days. The epoxide content obtained by the in-situ method was the same as that obtained by the first method. The products were analyzed by IR, ^{1}H-NMR, DSC, and chemical analysis. A series of IR and ^{1}H-NMR spectra of epoxidized natural rubber (ENR) samples was prepared.

The introduction of epoxide groups into NR resulted in an increase in the glass temperature (T_g) of the NR. The relationship between the T_g and epoxide contents was found to be linear and could be used as a standard for the determination of the epoxide content. The ENR was vulcanized successfully by using, besides the usual additives, activators, stabilizers, antiscorching, and covulcanizing agents. Under optimal conditions, ENR vulcanizates possess mechanical strengths comparable to those of traditionally vulcanized NR samples of comparable MW. The ENR products were used successfully for preparing adhesives for speciality purposes (rubber to metal bondings, adhesives for steel conveyor belts). The technical characteristics of our steel belt adhesives are as follows:

1. Density	0.875-0.895 g/cm^3
2. Viscosity after VZ-4 cup	120–160 s
3. Shear strength	35.5 MPa
4. Peel strength (180° peel test)	55–65 N/cm
5. Vulcanizing conditions:	
temperature	149°C
duration	30 min
pressure	0.7-1.0 mPa

PHOTOCROSSLINKABLE EPOXIDIZED AND ACRYLATED NATURAL RUBBER

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Epoxidized natural rubber (ENR) and acrylated natural rubber (ANR) having various molecular weights (MW) and polymer chain structures, and different degrees of epoxidation and acrylation were prepared. The kinetics of the reactions and photocrosslinking of the obtained products were studied. The mechanical properties and solubility characteristics of the UV-cured ENR and ANR films were also investigated. The formation of dual or interpenetrating polymer networks of NR-based systems containing both epoxy and acrylate groups has been considered.

ENR was synthesized from peracetic acid and masticated NR (M_n = 80,000), liquid natural rubber (M_n = 10,000), and partially cyclized rubbers containing 60 or 30% residual double bonds and having M_n = 5700 and 5100, respectively. At a reaction temperature of 5 °C, with an equimolecular initial concentration of isoprene double bonds and peracetic acid in chloroform = 0.208 mol/L, almost all isoprene double bonds were converted into epoxy groups after 4 hours. Structure and molecular weight studies showed that practically no side reactions had occurred. There was no difference in the rate of epoxidation of masticated NR and cyclized rubbers, and the kinetics were shown to obey the second-order law.

ANR was prepared by acrylation of ENR at 35 °C in toluene, using a fivefold excess of acrylic acid. Acrylated epoxidized natural rubbers (AENR) with different degrees of acrylation and epoxidation were obtained by stopping the reaction at different reaction times. The complete acrylation of ENR (M_n = 80,000, degree of epoxidation ~50%) and complete epoxidation of liquid NR (ELNR M_n = 10,000, degree of epoxidation ~30%) were achieved within 16 hours. The changes of these rubbers to those with acrylate functional groups was demonstrated by IR spectroscopy.

The ring-opening reaction of the epoxy group in these processes was found to follow simple first-order kinetics. The photoinitiated crosslinking polymerization of ENR as well as of ANR was shown to occur very fast; it reached a conversion of over 80% in a few seconds upon exposure to a 80 W/cm medium pressure mercury lamp in the presence of air and influenced by other factors. During UV exposure, the reaction rate and final conversion of the epoxy group by the customary cationic photopolymerization mechanism of ENR in the presence of photosensitive salts (TAS) were found to increase with the degree of rubber epoxidation. In the radical photopolymerization of ANR containing an aryl ketone photoinitiator, the reaction rate was found to increase linearly with the degree of acrylation of NR, reaching values up to 3 $\mathrm{mol \cdot kg^{-1} \cdot s^{-1}}$, and a kinetic chain length of 10^3 mol/radicals. At the final conversion the amount of acrylate groups remaining in the cured polymers was the same regardless of the degree of acrylation of the ANR.

One of the distinct features of cationic photopolymerization of ENR is that the polymer chains continue to grow in the dark after a very short exposure (0.1 second), thus allowing the curing line to be operated at high speed (100 m/min). The isoprene double bond, which is inactive in virgin natural rubber, was recognized to undergo polymerization upon UV exposure when epoxy or acrylate groups were present. The photopolymerizations of epoxy and acrylate groups simultaneously proceeded during UV curing of AENR bearing both epoxy and acrylate groups in the chain and containing both cationic and radical photoinitiators. The polymerization processes were found to proceed in solid films of AENR, with epoxy and acrylate group ratios of 1:1 and 1: 0.6, upon exposure to UV radiation.

After a fast start, the radical polymerization of acrylated NR slowed down and reached a maximum conversion of about 65% in 3 seconds upon UV exposure while the polymerization of the epoxy proceeded at a sustained pace until near completion. A dual polymer network, strongly crosslinked, can thus be formed within seconds. It combines the properties of the two moieties, i.e., the toughness of an acrylate polymer and the elastomeric character of the ether crosslinked rubber. In contrast, the addition of a diacrylate monomer (50 to 67% of the formulation) to ENR and liquid ENR was found to accelerate surprisingly both the cationic and radical curing processes due to the plasticizing effect of the reactive diluent.

In 0.5-1 second upon UV exposure in the presence of cationic and radical photoinitiators, almost all of the acrylate groups—and over 80% of the epoxy groups—were converted. The induced polymerization of acrylate groups and the cationically initiated polymerization of epoxy groups occurred simultaneously but also independently of each other.

The photopolymerization of the ENR and ANR based systems led to the formation of crosslinked polymer networks and remarkable changes in the properties of the UV-cured films. After some seconds upon UV exposure, ENR and ANR films became totally insoluble and very hard, but still flexible. Their Persoz hardness could reach values as high as 250 and 350, respectively, depending on the molecular weight and the degree of epoxidation or acrylation of the rubber used. These results were achieved in fractions of seconds in UV-irradiated ENR films containing 30-50% acrylate monomers in the formulation. A 100% gel fraction of the UV-irradiated liquid ENR (degree of epoxidation of 85%) film was achieved when material containing 5.8 epoxy equivalents/kg (epoxy equivalent weight 172) was cured. The gel fraction was about 50% when acrylated liquid natural rubber with a degree of acrylation of 30% was exposed to UV irradiation. The formation of tetrahydrofuran structures on the rubber chain during UV exposure of ENR was observed and confirmed by IS spectroscopy and showed that, apart from the formation of intermolecular crosslinked networks, there were intermolecular reactions by which part of the epoxy groups were consumed.

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HOMOGENEOUS COMBINATIONS OF OXIDIZED NATURAL RUBBER AND PHENOL-FORMALDEHYDE RESIN

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Alkyl- and arylphenol-formaldehyde resins have been used as vulcanizers for natural rubber (NR). These products exist in hetero- or microheterogeneous states [1, 2]. Several blends of NR or other rubbers with phenol-formaldehyde resins (PF) have been investigated [3]. Recently, a phase modification of NR and PF novolac resin blend by phenylhydrazone-terminated liquid NR (PLNR) was described. The homogeneity of the new blend is higher than that of corresponding nonmodified blends [4]. The preparation of a homogeneous blend or NR and PF resin which can meet the requirements of a high-grade film former is mentioned in this paper.

NR (smoked sheet) was degraded by passing oxygen through a solution of 10% NR in *n*-decane. This product, an oxidized NR (ONR), has a $M_v = 2.0\text{–}2.5 \times 10^{-4}$ and an oxygen content of 8–9%. The homogeneous blend (HB) was prepared by mixing ONR and butylphenol-formaldehyde resin (BPER) in xylene solvent at 120–180°C until the mixture became transparent and reached the desired viscosity. This compounding process was investigated in detail by chemical determinations and by IR and NMR methods. The experimental data show that in the process of compounding, the acid value of the HB decreased 15–5 units. The hydroxyl and carbonyl groups, a small amount of double bonds, and the methylene groups of ONR also took part in the reaction with active centers of BPFR (such as hdyroxy groups and active hydrogens of aromatic rings) to form a homogeneous product. HB is soluble in common solvents.

Coatings formed from the above-mentioned HB were examined according to national standards. HB having an F/P = 1.4–1.6 and a ratio of ONR/BPER of 0.8–1.2 gave products of the best quality. They were found to have suitable adhesiveness to various substrates, moderate water and chemical resistance, good thermal and mechanical properties, and high voltage insulating resistance.

References. [1] R. I. Dorokina et al., *Kauch. Rezina*, No. 3, 28 (1978). [2] J. Borowith and R. Kosfield, *Angew. Makromol. Chem.*, No. 100, 23 (1981). [3] Valin and Regin, *Rev. Gen. Caoutch. Plast.*, *58*(615), 78 (1981). [4] P. H. Ly et al., *Proceedings of the Vietnam National Congress of Chemistry, December 1993*, p. 70.

WATER-SOLUBLE NEGATIVE PHOTORESISTS

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Water-soluble negative photoresists based on poly(vinyl alcohol) (PVA), gelatine, polyacrylates as carriers, and ammonium dichromate (ADC), using diazonium salts as photosensitizers, have been studied by many authors who have found many applications. In this publication we deal with the study of water-soluble photoresists in which the carriers are based on polymer mixtures of PVA, poly(vinyl butyral) (PVB), and novolac resins. The photosensitizers are ADC and *p*-diazodiphenylamine salts. The work includes the study of the compatibility of the polymer mixtures, their physical and chemical properties, the influence of the components on the photosensitivity of the photoresists, and their applications.

Materials. PVA: MW = 78,000, 98% hydrolyzed (Poval, Japan). PVB: an acetalized product of the above PVA with *n*-butyraldehyde, *n*-butanol-modified Novolac resin, MW ~ 800. The components of the system have no common solvent. Therefore the PVA-PVB/Novolac resin polyblends were made in an oil-water emulsion. The total concentration of the polymers in the emulsion was about 10%. The concentration of the photosensitizer (ADC Diazo) was in the range of 10 to 20% based on the PVA in the emulsion.

Film Casting. The photoresist dope was coated on a glass plate with a size of 10 × 10 cm on a centrifugal spreader with a rotational speed of about 120 rpm. The film was then dried by exposing it to a moderately warm air stream in the dark. For the exposure to radiation, a high pressure Hg lamp was used. The pattern was developed by dipping the exposed film into pure water. The mixtures listed in Table 1 were tested.

Our photoresists showed a considerable photosensitivity with a resolution as high as that of the standard system (PVA sensitizer). With increasing proportions of PVB in the mixtures, the water solubility of the polyblends decreased. Mechanical and physical properties of the photoresist films after hardening by UV light showed a better

TABLE 1

Components	Parts by weight								
PVA	50	50	50	60	60	60	70	75	80
PVB	30	25	20	20	15	10	0	0	0
Novolac resin	20	25	30	20	25	30	30	25	20

improvement than that of the comparable standard system, and the photoresists are applicable for screen and offset printing technology.

Bibliography. K. Tsunemitsu and Y. Murakani, in *Poly(Vinyl Alcohol), Properties and Applications* (C. A. Finch, ed.), 1972. B. Duncalf and A. S. Dunn, *J. Appl. Polym. Sci., 8*, 1763 (1964). J. C. Jayne and E. L. King, *J. Am. Chem. Soc., 86*, 3989 (1964). D. W. Kemp and E. L. King, *J. Am. Chem. Soc., 89*, 3433 (1967). K. Horie, H. Ando, K. Morishita, and I. Mita, *Soc. Photogr. Sci. Technol. Jpn.*, 47(5), (1984). P. F. Bruin, *Polymer Blends and Composites, J. Appl. Polym. Sci., Appl. Polym. Symp., 15*, (1970).

REPAIRING OLD CONCRETE BRIDGES WITH POLYMER-CONCRETE COMPOUNDS AND EPOXY RESIN

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There are about 700 old concrete bridges in Vietnam that have been damaged seriously after long service. Typical forms of deterioration are: cracks that have appeared at the midspans and at beam ends, exfoliation of concrete, exposures of steel reinforcement, draining of water leaks, damage of the bridge waterproof layer, and concrete degradation. These structures must be replaced by new structures as soon as the national economy allows, but this type of work requires a long construction time and a substantial budget. The Railway Research and Design Institute has used polymer-concrete compounds and bonding steel plate technologies for reinforcing four bridges containing 12.6 m beams.

Repair Method of Beams. Removing damaged concrete parts at the bottom of the beams, sanding the reinforcements, injecting the epoxy compound into the cracks, restoring the original size of the sections and shaping them by use of polymer-concrete, bonding a new steel plate at the beam bottom, and coating a new paint layer.

Repair Method for Waterproof Layer. Removing all the old ballast volume, cleaning the beam top surface, coating a new 2-3 mm waterproof layer of composite material, and placing it against the ballast volume and rails.

After 1 year of service, all four bridges are in good shape. The repairs allow a train speed exceeding the safe speed prior to repair, which was about 60-70 km/h. The method of repairing old concrete bridges using polymer-concrete compounds and bonding steel plates is completely acceptable for traffic safety under the present economic situation.

DURABILITY, CHARACTERISTIC FEATURES, AND SKELETON-PROTECTING CAPACITY OF POLYMER-CEMENT CONCRETE

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Studies using polymers to modify concrete and cement mortars has been carried out since the 1920s and 1930s and has now reached substantial accomplishment [1–3]. Our studies began in 1986 on the use of water-soluble polymers to modify concrete and mortar, to raise the physicomechanical durability, particularly the durability of permeation resistance, and the adhesive capacity of healing the blocks of old concrete [4, 5]. This paper presents some results describing the durability characteristics and the protecting capacity of water-soluble polymer–cement concrete for bridge reinforcement in a corrosive environment. Material combinations were prepared according to Vietnamese Standard TCVN 3015-1992. They consist of Portland cement PC-30; sand; stone; and synthetic polymers labeled HKT-15B, HKT-15BM, and MFS-92A; and 163 EX, Sikalatex from a Swedish firm.

Characteristic Feature of Mixed Concretes. Soft retractibilities of mixed concrete, which is 7% by weight of a HKT-15B solution (calculated according to cement), and a reference concrete sample.

Characteristic Feature of Extractibility and Permeation Resistance of Concrete Combinations. Compressive and flexural strengths, permeation resistance, and adhesive capacity toward old concrete surfaces of concrete and mortar combinations are presented in Table 1. High characteristic permeation resistance of polymer–cement concrete is important for durability and for the protection of the armored concrete base [1, 6].

Skeleton-Protecting Capacity of Polymer–Cement Concrete. The skeleton-protecting capacity of cement mortar with a sand:cement ratio of 1.2 with polymers HKT-15B and MFS-92A in comparison with control mortar was estimated by electrochemical methods and by weight. We determined the variation of potential and current of steel CT-3 protected by mortar layers of thickness 2,0 cm through a dry/wet experimental cycle in NaCl 3% solution.

Conclusion. The mortar and concrete material combination can be modified by water-soluble polymers. The following characteristic features of these materials were observed. (a) Mixed concrete has increased flexibility and decreased retractility. (b) Polymer–cement concrete has enhanced physicochemical and mechanical durability, in particular the permeation resistance and skeleton protection in a corrosive environment.

TABLE 1. Compressive and Flexural Strength When Bending and Permeation Resistence of Concrete and Mortar Combinations (concrete using 325 kg cement PC-30/1m^3)

Sample	Additive used		Water tightness at	Compressive strength, daN/cm^2		Flexural strength, daN/cm^2	
	Kind of additive	% Rate		After 28 days	After 180 days	After 28 days	After 180 days
Concrete mix	HKT-15BM	0	6	206	232	41	43
	HKT-15BM	1.2	15	238	325	41	49
	HKT-15BM	1.5	29	221	262	42	44
	MFS-92A	2.0	39	245	273	43	49
	Sikament	1.0	43	295	313	58	62
	163-EX	1.0	16	271	327	57	63
Mortar layer plastered to strengthen. Thickness: 2.5 cm upon the arch measuring the antipermeable durability	HKT-15B	7.0	25	–	–	–	–
	Sikalatex	18.0	26	–	–	–	–
Mortar vertically gluing old concrete sample with new concrete to measure the antipermeability capacity	0	0	3	–	–	–	–
	HKT-15B	7.0	27	–	–	–	–

References. [1] S. Chandra and P. Flodin, *Cem. Concr. Res.*, *17*, 75–90 (1987). [2] Y. Ohama and K. Demura, *Cem. Concr. Res.*, *21*, 309–315 (1991). [3] J. E. Isenburg, *J. Am. Ceram. Soc.*, *57*(6), 242 (1974). [4] Tran Nhu Tho and Nguyen Van Cau, *Tap chi Xay dung*, No. 3, 18 (1991). [5] Tran Nhu Tho and Nguyen Dan Do Tuyen, *Tap cac cong trinh, KHKT Vien KHKT Xay dung* (*1984–1993*), pp. 261–268, *NXB Xay dung 1993*. [6] O. D. D. Egiory, *Nord. Concr. 2-4*, 147–151 (1982).

GAS PERMEABILITY OF ASYMMETRIC IMIDE–SILOXANE BLOCK COPOLYMER MEMBRANES

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Polyimide films with characteristics of heat stability, solvent resistance, and excellent mechanical properties are especially used for electronic devices which require heat stability, low dielectric constant, and thin film formability. Polyimides have the possibility of developing various kinds of structures composed of different dianhydride and diamine moieties giving rise to specific functionalities like gas separation and permeation. Polyimides can be utilized as gas separative and permeable membranes with high temperature stability. Furthermore, one would expect advanced membrane performance of polyimides containing certain specific molecular structures.

In the present paper, imide–siloxane block copolymer membranes are prepared by a freeze-drying method, and the permeability and permselectivity of these membranes are examined. An imide–siloxane block copolymer (siloxane content 15 wt%, 8.3 block length of siloxane unit) was dissolved at 20 wt% in a 1,4-dioxane solution which was freeze-dried for 12 hours on a Teflon petri dish whose bottom side was cooled with liquid nitrogen. The membrane was finally dried at 200°C at 130 Pa for 3 hours to remove the residual solvent.

Scanning electron micrographs of these freeze-dried membranes indicated that the membranes had an asymmetric morphology which was composed of dense and porous layers on the surface and dish side, respectively. The pressure dependence of the CO_2 permeability coefficient of freeze-dried and “as-cast” membranes is explained in terms of a partial immobilization of the model, characteristic of a glassy polymeric membrane. The former membrane had about a 10 times higher permeability coefficient than the latter, indicating the presence of a porous layer in the asymmetric membrane.

As for other gases like O_2 and N_2, similar permeabilities were also observed. The selectivity of both membranes was essentially the same but the freeze-dried membranes exhibited a remarkably higher permeability. Such a behavior of similar selectivity and higher permeability would be needed for development of high performance separation membranes.

POLYPROPYLENE/CELLULOSIC FIBERS COMPOSITES: CHEMICAL TREATMENTS OF THE CELLULOSE ASSUMING COMPATIBILIZATION BETWEEN THE TWO MATERIALS

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Composites based on a polypropylene matrix are widely used, particularly in the automobile industry. The matrix is often reinforced with glass fibers, but these fibers have a high density, lead to abrasion of the processing machines, and produce a large amount of ashes on combustion.

Cellulosic fibers do not present such disadavantages. In particular, this material of vegetable origin is renewable and the whole composite is completely combustible at the end of its life cycle. Regarding composite reinforcement, these fibers exhibit—as single filaments—a modulus as high as those of aramidos, and they can easily withstand the processing temperature of polypropylene (~200°C).

For many years, numerous agricultural by-products have been incorporated in thermoplastic matrices, but the problem remains of poor adhesion due to the lack of compatibilization between the hydrophilic cellulosic fiber and the hydrophobic matrix. This can be corrected by chemical treatment of the cellulosic fibers using hydroxyl groups to graft hydrophobic alkyl chains.

The objective of this work concerns comparison of the two following ways for chemical treatment.

(a) Treatment of the Fibers Apart from the Matrix. Polypropylene grafted with maleic anhydride (PPgMA) is preactivated by heating at 180°C for 5 minutes in order to transform all carboxyl functions into anhydride ones. The sisal fibers are treated with PPgMA (5% of the weight of fibers) in toluene. After removal of the treating solution, the fibers show a weight gain of 0.76% due to chemically linked and physically adsorbed molecules of PPgMA. These fibers, treated or not, are then incorporated into the matrix by using a double-screw extruder which produces granulates. The loading rates of the fibers into the matrix are 20 and 40% by weight.

(b) Mixing of the Components in One-Step Process. The sisal fibers, the polypropylene matrix, and the PPgMA are introduced into the extruder at the predetermined rates: 20 and 40% for the fibers; 0, 3, and 5% for PPgMA. Only a small

amount of the added PPgMA reacts with the fibers; the remaining part is adsorbed on the fibers and/or dispersed in the matrix.

In both cases the fibers are used as received, or after washing (sodium hydroxide 4.5 N aqueous solution), or after washing and PPgMA treatment. Two types of PPgMA with different molecular characteristics were tested.

1) For reactive extrusion: M_n and M_w: 13,660 and 133,700 $g \cdot mol^{-1}$. Maleic anhydride content: 1.6% by weight.
2) For the pretreatment of the fibers in toluene: M_n and M_w: 5,700 and 31,000 $g \cdot mol^{-1}$. Maleic anhydride content: 4 to 5% by weight.

Composite specimens were prepared by injection molding from the extruded granulates obtained by the two stated methods. The influence of the method used for fiber treatment will be evaluated based on the mechanical properties of the composites: ultimate elongation, tensile strain, and impact strength.

POLYIMIDE-SILICA HYBRID MATERIALS

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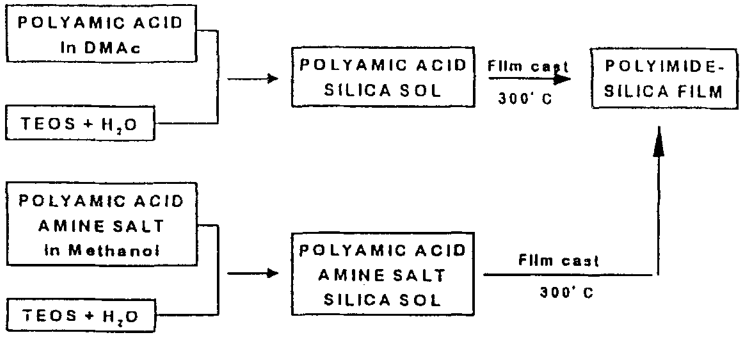
Sol-gel reactions, which are fascinating method to prepare fine ceramics, have attracted increased attention by polymer scientists. The in-situ sol-gel reaction in polymer solutions is one of the methods used to produce new types of organic-inorganic hybrid materials [1]. The key point of a sol-gel process is that the starting materials are metal alkoxides, which are low molecular weight organic compounds, soluble in polymer solutions. The process consists of the hydrolysis of metal alkoxides, followed by polycondensation of the hydrolyzed intermediates.

We have recently prepared polyimide-silica (PI-SiO_2) hybrid materials [2]. The preparative method is shown in Scheme 1. Tetraethoxysilane (TEOS) and water were added to a solution of polyamic acid (PAA). After the mixture was stirred for several hours, the homogeneous solution was cast into film. The dried film was peeled off and heated to 300°C to convert the matrix from polyamic acid to the polyimide. In a previous paper the polymer solution system was PAA in DMAc, where the hybrid films obtained showed a macrophase separation but were flexible [2]. In this work a new system of the polyamic acid triethylamine salt (PAA-NEt_3) in methanol was applied to prepare Pl-SiO_2 hybrid materials [3]. Because the sol-gel product from TEOS is more soluble in methanol than that made in DMAc, different morphologies of the resulting hybrid films were observed.

In this paper, we discuss the preparation and morphology of the polyimide-silica hybrid films. The preparation of the hybrid films from the PAA solution in DMAc was described in a previous paper [2]. Alternatively, the Pl-SiO_2 hybrid films were



SCHEME 1.

prepared from the PAA-NEt_3 salt in methanol. It was remarkable that all the films prepared by the latter methanol method were transparent and uniform [3] whereas the hybrid films prepared by using the free PAA and TEOS in DMAc (DMAc method) were transparent only in the case of films of less than 10 wt% silica content [2]. The methanol method hybrid films having silica content up to 50 wt% were obtained in the self-standing form, while those of over 50 wt% silica content were too brittle to keep self-standing. In the SEM photographs of the fracture surfaces of the PI-SiO_2 hybrid films prepared by the DMAc method, the particle size, which was 3–7 μm, increased with increasing silica content.

As mentioned in a previous article [2], the expected quantity of silica can be obtained by the complete thermal decomposition of the polyimide when the hybrid films are heated at 800°C in air. It is interesting to note that in the case of the methanol method to form the sol–gel structure, a self-standing white film of silica can be obtained from the hybrid film. An SEM photograph of the cured silica film shows fine uniform globules of 0.2 μm diameter, whose size is independent of the silica content in the hybrid films. Furthermore, the silica particles in this system are connected with each other. The connected-globule structure implies a two-phase morphology of the interconnected spherical domains dispersed regularly in the polyimide matrix. However, with this evidence alone it is difficult to rule out the possibility that the formation of the globule structure is caused by curing at 800°C to decompose the polyimide matrix.

Next, the matrix polyimide in the hybrid films were removed by hydrazinolysis with hydrazine hydrate. The same interconnected globular structure was observed with the same size of silica globules. This fact suggests that the morphology of the hybrid films is retained even after thermal oxidation at 800°C. Such an interconnected globular structure was reported in the epoxy resin and poly(ether sulfone) system, where the formation of the morphology was explained as a reaction-induced phase separation [4]. Since the silica exists in an expanded state in the methanol solution of PAA-NEt_3, the sol–gel reaction induced phase separation with spinoidal decomposition to form a co-continuous structure.

It was concluded that phase separation between the polyamic acid and silica occurred with spinoidal decomposition in the PAA-NEt_3 system. To examine the phase separation behavior in the case of the PAA in DMAc, the formation of a thin film from the reaction mixture was observed by an optical microscope while the DMAc evaporated. A typical spinoidal phase separation pattern was then observed. Thus, both systems, which produced different morphologies, had a similar phase separation process.

If the phase separation of the PAA system also proceeded via reaction-induced phase separation, the mechanism could be explained as follows. When the sol–gel reaction of TEOS with the PAA solution was carried out in DMAc, the silica phase began to separate in the earlier stage because of the poor solubility of silica in the solution. As a result of this reaction-induced phase separation, fine globules of the silica were produced. Since the unreacted TEOS still existed in the mixture, the silica phase grew into larger particles.

References. [1] A. Morikawa, Y. Iyoku, M. Kakimoto, and Y. Imai, *J. Mater. Chem., 2,* 269 (1992). [2] A. Morikawa, Y. Iyoku, M. Kakimoto, and Y. Imai, *Polym. J., 6,* 107 (1992). [3] A. Morikawa, H. Yamaguchi, M. Kakimoto, and Y. Imai, *Chem. Mater., 6,* 913 (1994). [4] Y. Yamanaka and T. Inoue, *Polymer, 30,* 662 (1989).

HIGHLY ELECTRIC-CONDUCTING POLYMER BLENDS

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Heterocyclic polymers such as polythiophene and polypyrrole (PPy) have received a great deal of attention due to their high electrical conductivity and good environmental stability. However, they possess poor mechanical properties and poor processability. In recent years, several attempts to overcome these drawbacks have been made, in particular methods of blending with conventional polymers. However, mechanical blending in the melt state is undesirable because the conductivity of the polymers decreases due to thermal effects during processing. Furthermore, a high concentration of conducting polymer is required to create a conduction path.

We have developed a novel method to prepare films of conducting polymer blends. The most attractive features of this method are that polymerization of pyrrole is carried out after film fabrication and the construction of conducting networks can be controlled by the polymerization conditions.

A solution of ferric chloride (oxidant) and poly(vinyl acetate) (PVAc) was first prepared by dissolving them in methanol. The oxidation potential of the solution was controlled within the optimum range by changing the amount of ferric chloride. Then pyrrole (Tokyo Kasei Kogyo Co.) was added to the mixed solution with stirring. (Pyrrole had been purified by distillation prior to its use.) A conducting polymer composite film was prepared by casting the mixture on a substrate. After sufficient drying it was rinsed with methanol to remove the remaining ferric chloride and ferrous chloride formed during the polymerization of pyrrole. The electrical conductivity of the film was measured under vacuum by the four-probe method.

When the mixture was cast into a film on a substrate, its color gradually changed from lightly yellow to dark green. This indicates that the polymerization of pyrrole progressed because the evaporation of the solvent caused an increase in oxidation potential of the cast solution.

The morphology of the PPy–PVAc composite film was very different from that of the PPy–PVAc composite when it was prepared from the preformed polymers in solution; PPy aggregates were connected with each other in the film, which resulted in a PPy network throughout the composite, while PPy aggregates separated from each other in the composite prepared from the preformed polymers. It is thought that in the former case a spinoidal decomposition occurred during the phase separation process because of the sudden changes in the concentration of pyrrole and ferric chloride and also because of the high viscosity of PVAc. These sudden changes were caused by evaporation of the solvent. The high conductivity of the film probably resulted from the PPy network structure.

The conductivity of the solution-cast films depended on the initial oxidation potential of the solution as well as on the holding time of the solution before casting. If the initial oxidation potential of the solution was either too low or too high, no highly conducting films could be obtained. It was thought that pyrrole monomer also evaporated together with solvent when the oxidation potential was too low, while phase separation had already progressed to a considerable extent before casting when the oxidation potential was too high.

The optimum range of the initial oxidation potential of the solution is believed to be 48–560 MV (compared to SCE). The holding time of solution before casting may be associated with the degree of polymerization of pyrrole and the extent of phase separation. It is worth noting that an electrical conductivity as high as 10 $S\cdot cm^{-1}$ could be obtained in composites in which the pyrrole was polymerized during film casting, even when only 5 wt% of pyrrole monomer was incorporated, while the incorporation of even 40 wt% of pyrrole monomer into the polymerization mixture led to conductivities of only 0.01 $S\cdot cm^{-1}$ in the polymer blends prepared using our solution polymerization technique. The network structure of PPy was maintained even when the ratio of pyrrole monomer to PVAc polymer was decreased. Therefore, a network structure of PPy could be obtained even if only 5 wt% of pyrrole was incorporated, and this brought about the highest conductivity.

POLYMER BLENDS BY REACTION-INDUCED SPINOIDAL DECOMPOSITION

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The spinoidal decomposition induced by a chemical reaction is demonstrated in an epoxy/polyethersulfone (PES) system with a LCST (lower critical solution temperature) type phase diagram. The binary mixture of the components was homogeneous at cure temperature (< LCST). As the curing reaction proceeded, the system was placed into a two-phase regime caused by molecular weight increase, and the phase separation took place via a spinoidal decomposition [1]. The reaction-induced spinoidal decomposition yielded a variety of two-phase structures: interconnected globules or an isolated domain structure with a uniform domain size and a bimodal domain structure, depending on the relative rates of chemical reaction and phase separation. The cured epoxy/PES is a tough thermoset which was applied as the matrix resin of carbon fiber reinforced plastic (CFRP).

A new high-impact poly(methyl methacrylate) (PMMA), having a PMMA particles/ethylene–vinyl acetate copolymer (EVA) matrix structure, was obtained by radical polymerization of a 80/20 methyl methacrylate (MMA)/EVA mixture.

A processing window for injection molding of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) was explored by blending PPE with triallyl isocyanurate (TAIC). Compared with conventional thermoplastics such as PP and PC, the PPE/TAIC mixture is less viscous even at lower temperatures. The PPE/TAIC blend, cured with peroxide, has a bicontinuous two-phase structure with a periodic distance of ca. 0.2 μm. It shows excellent flexural strength, high heat resistance, and excellent dielectric properties.

Another example may be the very high strength rubber (tensile strength 60 MPa) obtained by peroxide cure of a hydrogenated acrylonitrile-butadiene rubber (NBR)/zinc dimethacrylate mixture. The structure formation in the reaction-induced spinoidal decomposition was interpreted by computer simulation as the growth of the concentration fluctuation under a successive increase in the thermodynamic quench depth [2].

References. [1] K. Yamanaka and T. Inoue, *Polymer, 30*, 662 (1989). [2] T. Ohnaga, W. Chen, and T. Inoue, *Polymer, 35*, 3774 (1994).

JUTE FIBER UTILIZATION IN THE PRODUCTION OF COMPOSITE MATERIALS

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Great attention has been paid to natural fibers that may be used in the production of composite materials in order to reduce their price. This paper presents some results on the possibility of using the jute fiber readily available in Vietnam to produce composite materials with a matrix of unsaturated polyester (UPE). To increase the compatibility between the jute fiber and UPE, we surveyed the treating mechanism of the raw jute fiber with a 0.5% NaOH solution under different conditions of temperature and reaction time. After treatment at 120°C for 20 minutes the results showed that the water uptake of the fiber decreased to 6.5%, the tensile strength increased to 265 MPa, and the physical-mechanical properties became more appropriate as compared to treating the fibers at low temperature. The physicomechanical properties of the composite materials made from jute fiber and glass fiber are shown in Table 1.

Table 1 shows that increases in fiber content in the composite material considerably improved the physicomechanical properties. However, we were unable to increase the percentage of jute fiber in the composite material any further because of the limited compatibility of jute fiber with UPE resin. We combined jute fiber and glass fiber to produce another composite material. The results (Table 2) show that the physicomechanical properties of the two kinds of fibers on the composite materials are in between those of the glass fiber composite and those of the jute-fiber-filled composites.

TABLE 1. Effects of the Type of Fiber and Content of Jute Fiber on Physicomechanical Properties of Composite Material on the Base of UPE

Kind of fiber	% Fiber in composite	Tensile strength, MPa	Compression strength, MPa	Flexural strength, MPa
Jute mat fiber	6.3	3.96	51.0	34.8
	11.8	12.64	61.0	48.5
	15.4	18.15	71.8	61.5
	19.5	18.04	69.6	54.8
Jute roving woven	16.2	10.66	36.5	69.0
	21.8	12.50	31.4	82.0
	25.2	14.57	28.4	98.4
	32.4	13.62	26.4	94.4
Glass mat fiber	32.4	10.83	144.5	191.1
	44.5	137.05	167.2	273.3
Glass roving woven	44.8	158.16	61.3	201.3
	60.6	204.48	44.0	244.8

TABLE 2. Effects of the Ratio of Jute Fiber/Glass Fiber on Physicomechanical Properties of Composite Material

% Fiber in composite		Tensile strength, MPa	Compression strength, MPa	Flexural strength, MPa
Jute	Glass			
15	5.6	21.6	82.6	75.5
15	7.8	34.8	89.3	81.3
15	10.3	45.2	94.8	112.3
15	12.7	57.4	101.5	123.6