Phenolic–Nitrile Rubber Copolymers

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The use of phenolic resins or their intermediates for vulcanizing rubbers is known.[1] Also, the use of various rubbers, including butadiene–acrylonitrile rubbers, as plasticizers in mixture or as copolymers with various resins is too well known to need documentation. Where phenolic resins, have been used, however, the result has apparently usually been a mechanical mixture.[2] Such treatment may indeed plasticize and make flexible the resin; however, the mixtures do suffer from some disadvantages in that they "bleed."

While such mixtures are often used advantageously for molding materials, they are not well suited for use in making laminates. During lamination, the resin must be used in solution for coating of the paper, glass cloth, or other base stock. Nitrile rubbers (such as Hycar) may be of high enough molecular weight to minimize bleeding. In that case, however, they are generally soluble only in solvents (such as methyl ethyl ketone and toluene) which are incompatible with phenolic resins or otherwise undesirable in the coating procedure. Emulsions or suspensions might be used, but these suffer from segregation and selective absorption during coating, so that the composition of the resin solution used for treating changes with time.

These difficulties can be largely or entirely eliminated by true reaction of the phenolic resin with the intended plasticizer. It is known that phenolic resins will react with drying oils.[3] Even with oleic acid, which contains only a single carbon-carbon double bond, a chroman ring is formed by reaction under appropriate conditions with o-methylol phenols.[4] Butadiene–acrylonitrile rubbers retain sufficiently many carbon-carbon double bonds with probably sufficient reactivity that they react in a similar manner with phenolic resins or their precursors. In bringing about such a reaction, certain conditions should be met for optimum results.

Reaction with a carbon-carbon double bond will take place only where a phenolic resin retains methylol (hydroxymethyl) groups or dibenzyl ether groups *ortho* to a phenolic hydroxyl group.[3,4] These o-methylol groups are indeed formed in large numbers in the course of the normal alkaline reactions for making phenolic resins, but they also rapidly react further to form a polymer.[5,6] For this reason, it is necessary to optimize conditions for the formation of methylol groups or their reaction equivalents and to bring about reaction with the nitrile rubber at an early stage of condensation when many such reactive groups are still present. It is known, further, that the reaction with the nitrile rubber should be carried out at a nearly neutral pH, since both acid and basic media promote other reactions.[4,7] At present, no catalysts promoting the chroman reaction, which is formally of the Diels-Alder diene type,[4] are known.

As to the rubber component, it should be preferable to use a rather low molecular weight rubber from several points of view. Such a rubber may be itself liquid, making it more accessible to reaction with use of a cosolvent. And the molecular weight increase to be expected from the reaction with phenolic resin will not result in such large and relatively insoluble molecules, if a low molecular weight rubber is used initially.

A decrease in the number of crosslinks from what is normal for phenolic resins may be desirable in a plasticized resin of this type. Nevertheless, the molar ratio of formaldehyde to phenol must be increased in order that there may be a sufficient number of methylol groups to react both with the rubber and with the phenolic rings present.

The resulting copolymer should be permanently plasticized, from several points of view. For one, the phenolic resin main chains are separated by a flexible chain "diluent" to which they are permanently fixed by reaction. This should also greatly decrease the degree of hydrogen bonding in such a resin, which may be responsible for a

portion of the mechanical response of ordinary phenolic resins at room temperature.[8] Further, the chroman reaction itself eliminates phenolic hydroxyl groups responsible for such hydrogen bonding as well as for some part of the electrical properties.

EXPERIMENTAL

The degree of plasticization of the resins was judged on the basis of punchability of 0.060–0.075-in. thick laminates made from the resin to be tested, treated on cotton linters paper. Punching tests were carried out at room temperature according to A.S.T.M. D617-44 and ratings were given in points according to this specification. Unplasticized phenol resins treated and tested as above will show punch ratings from 50 to 85 on the above scale.

Reasonably complete reaction of the rubber with phenolic resin was indicated by the solubility of the end product in 95% ethanol in which nitrile rubbers are not themselves soluble. This was checked by testing resistance to extraction by boiling trichloroethylene, in which nitrile rubbers of the sort used are completely soluble. Also, with the low molecular weight rubbers used, incomplete reaction showed up in bleeding and surface tackiness of the laminates. Adequately coreacted resins yielded laminates with surfaces that were and remained perfectly dry and hard. Such laminates were considerably more flexible than corresponding straight phenolic resin laminates.

All phenolic resin solutions were made in such a way as to yield low molecular weight phenolic resins with maximum practical methylol group content for the formaldehyde/phenol ratio involved.

Reactions with Nitrile Rubber Latex

Since phenolic resins are made in aqueous solution, it seemed advantageous to react them with rubber latices, which are miscible with the aqueous phase. The rubber can indeed be reacted to combine with a phenolic resin in this way. For example: 660 g. (6.0 moles) of 85% phenol, 540 ml. (7.2 moles) of 37% formalin, and 7.2 g. NaOH were reacted at 60° for two hours, neutralized to pH 6.5 with HCl, after which was added 65.6 g. → Hycar 1551 Latex (51.4% soln.). The batch was heated and H_2O distilled off under vacuum at 80-100°C., then taken up to 125-130°C. with vacuum and held there for 10-15 min. The resulting resin was soluble in ethanol or acetone. The NaCl of neu-

tralization was filtered from the solution. Laminates made from this resin had a punch rating of 86 points.

This type of copolymer suffers somewhat from the effects of emulsifying agents and other impurities introduced by the latex. Since liquid nitrile rubbers are much purer and yield comparable products with phenolic resins, this line of investigation was not pursued further.

Reactions with Liquid Nitrile Rubbers

Liquid nitrile rubbers were reacted with phenolic resins by two methods. In the first reaction, which was similar to the latex-phenolic reaction, a phenolic methylol solution was prepared prior to the addition of the Hycar 1312 liquid nitrile rubber. For example: 770 g. (7 moles) of 85% phenol, 578 ml. (7.7 moles) of 37% formalin, and 8.4 g. NaOH were heated to 60°C. for 2 hr. and then neutralized to pH 6.5 with HCl; then 56 g. of Hycar 1312 was added. The reactants were heated and water was distilled off under vacuum at 80-100°C., and then the solution was taken to 115°C. without vacuum. Ethanol or acetone was added and the NaCl of neutralization was filtered from the resin solution.

Since it was difficult to remove the NaCl neutralization product, other phenolic resins made with an ammonium hydroxide catalyst were also reacted with nitrile rubber. For example: 770 g. (7.0 moles) of 85% phenol, 578 ml. (7.7 moles) of 37% formalin, 7 g. % (0.28 mole) of NH_4OH (30% HN_3 soln.), and 56 g. of Hycar 1312 were heated and the water distilled off under vacuum at 80-100°C.; then the batch was taken to 120°C. without vacuum. Alcohol was added as the solvent. No neutralization was needed, for the amine reacted into the resin or escaped as a gas.

Preparation of Laminates for Punchability Tests

Laminates were prepared with the use of cotton linter paper. A typical preparation is shown as an example.

Resin viscosity: adjusted to 22 sec. no. 1 Demmler cup.

Impregnation ratio (impregnated paper/dry paper): 2.5-3.0.

Precure: temperature held at approximately 135°C. for several minutes to give adequate resin flow in press.

Lamination: eight impregnated sheets were laminated at 155°C. for 30 min. under 1000 psi.

Per cent greenness (weight of resin flow/weight of impregnated paper) × 100: regulated between 8 and 12.

Punchability Tests

As previously explained, the plasticization of the resins was judged from the punchability of their paper base laminates. Photographs which appeared in the A.S.T.M. D 617-44 standard served as guides to the proper evaluation of each punching. Sample thickness affected the rating little within the limits shown.

Numbers from 0 to 100 were assigned to the edges, the surface, and the holes, respectively. The final rating of the punched sample was the average of these three values. A rating of 95–100 was considered to be excellent. Below this value, certain flaws began to show up such as cracking on the surface and chipping or dragging at the edges or hole cuts.

In order to observe the plasticization properties in terms of punch ratings, laminates were tested that had been prepared from unmodified phenolic resoles. Laminates 8, 11, and 13 in Table I were fabricated from such unmodified resins. Number 8 showed a punch rating of 91, owing apparently to the plasticization by unreacted phenol (extractable). This of course was an external form of plasticization which would eventually bleed from the laminate, leaving it brittle. Phenol is not recommended as a plasticizer in any case, because of its corrosive properties and extractability with solvents.

Laminates 11 and 13 show that increasing the formaldehyde content of unmodified phenolic resins diminished the plasticity and thus lowered the punch rating.

Laminate 23 showed a punch rating of 80 which was believed to be the effect of excess nitrile rubber in the resin. Here, the [F]/[P] (formaldehyde/phenol) ratio tolerance for rubber was exceeded, which showed in bleeding of the rubber.

The low punch ratings found in laminates 19 and 33 are believed to be the result of too little nitrile rubber in the resin for the [F]/[P] ratio used.

Laminates 21 and 30 gave excellent punch ratings of 95. Here, the [F]/[P] ratio was matched quite well to wt.-% Hycer for optimum results.

The catalysts used in the phenolic resin to be used for reaction with nitrile rubber proved to have no effect on the degree of plasticization of the copolymers. Resins were prepared with NaOH and NH₄OH as catalysts, utilizing 8.5% nitrile rubbers; laminates prepared from these proved to have identical punch ratings.

Heat and Solvent Testing

Laminates prepared from 8.5% nitrile rubber-modified phenolic resin were tested for heat resistance by floating a $1^1/_2 \times 1^1/_2$-in. specimen on solder at 255°C. for 45 sec. Although this test was specified for use on electrical circuit punch plate, it showed qualitatively whether any low molecular weight material such as unreacted nitrile rubber was present, for if it was, blistering invariably resulted. No ill effects were noted with the above samples.

The same type of sample was suspended in hot trichloroethylene vapor for one hour with no "leaching out." Since the nitrile rubber used to modify the resin was very soluble in trichloroethylene, it follows that the rubber had reacted with the phenolic resin.

Although laminates prepared with 30% nitrile rubber-modified resins could be punched successfully, in the hot solder test they blistered slightly, and they became spotty after being exposed to hot trichloroethylene vapors. Thus, 30% probably represents the upper limit for the proportion of nitrile rubber of this molecular weight that can be reacted into the resin.

It is apparent from the above and from Table I that there is for any given [F]/[P] used in making the phenolic resin a maximum amount of nitrile rubber that can be coreacted. The maximum amounts are approximately the highest ones shown in Table I. At the same time, a phenolic resin with a higher [F]/[P] requires a larger amount of coreacted nitrile rubber for adequate plasticization.

TABLE I
Punch Rating Tests of Plasticization

Resin no.	Formaldehyde-phenol, moles	Content of Hycar 1312, % (based on weight of phenol)	Thickness, mils	Average punch rating, %
8	0.8	None	67	91
11	1.0	None	64	83
13	1.5	None	67	85
19	1.5	10	60	86
21	1.5	30	67	95
23	1.1	20	81	80
30	1.1	8.5	64	95
33	1.1	5	72	86

CONCLUSION

Plasticization of phenolic resins can be effected by reacting various amounts of acrylonitrile-butadiene rubber with the resin. The rubber is probably incorporated into the resin by a chroman reaction.

The amount of nitrile rubber necessary for effective plasticization is directly dependent upon [F]/[P] for the resin. When this ratio is 1:1, the most effective rubber content is 8.5% based on the phenol weight; if this ratio is 1.5, the necessary and tolerable rubber content is nearly 30%.

Of the two optimum resins prepared, the one with the lower concentration of nitrile rubber gave a better plasticized laminate. The 8.5% nitrile rubber-modified phenolic laminate withstood the hot trichloroethylene vapors for 1 hr. and the 255°C. solder bath for 45 sec. without change. The laminate prepared from the 30% nitrile rubber-modified resins, although giving excellent punch ratings, blistered slightly on exposure to the 255°C. solder and became spotty after the trichloroethylene exposure. These effects indicate a slight excess of rubber over the amount that can be effectively coreacted.

References

1. Van der Meer, S., *Rec. trav. Chim.*, **63**, 147, 157 (1944); R. G. Neuberg et al., *Rubber Age*, **62**, 533 (1948).

2. Fisk, C. F., and A. W. Meyer, U. S. Pat. 2,659,706, to U. S. Rubber Co. (Nov. 17, 1953); F. S. Groten and R. J. Reid, U. S. Pat. 2,459,739, to Firestone Tire & Rubber Co. (Jan. 18, 1949); A. F. Shepard and J. F. Boiney, *Modern Plastics*, **24**, 153 (1946).

3. Hultzsch, K., *J. prakt. Chem.*, **158**, 275 (1941); J. I. Cunneen, E. H. Farmer, and H. P. Koch, *J. Chem. Soc.*, **1943**, 472.

4. Sprengling, G. R., *J. Am. Chem. Soc.*, **74**, 2937 (1952).

5. Freeman, J. H., and C. W. Lewis, *J. Am. Chem. Soc.*, **76**, 2080 (1954); G. R. Sprengling and J. H. Freeman, *ibid.*, **72**, 1982 (1950).

6. Granger, F. S., *Ind. Eng. Chem.*, **24**, 442 (1932); *ibid.*, **29**, 860, 1125, 1305 (1937).

7. Jones, T. T., *J. Soc. Chem. Ind. (London)*, **65**, 264 (1946).

8. Sprengling, G. R., *J. Am. Chem. Soc.*, **76**, 1190 (1954).

Synopsis

Nitrile rubbers have often been used together with phenolic resins in molding materials to produce an impact-resistant product. These mechanical mixtures may react during final cure. Acrylonitrile–butadiene rubbers containing residual unsaturation can, however, be coreacted with phenolic resins during the early stages of polymerization if appropriate conditions are adopted. The coreaction probably occurs via formation of a chroman from a double bond in the rubber and an o-methylol phenol. The coreaction products are completely soluble in alcohol, whereas the rubbers are not. Laminates made from these coreaction products are flexibilized to the point at which they lend themselves well to cold punching. Yet the rubber, being tightly bound, cannot be extracted with solvents nor lead to blistering on heating.

Résumé

On a souvent employé des caoutchoucs nitriliques ensemble avec des résines phénoliques dans des matériaux moulables afin d'obtenir un produit à impact élevé. Ceci donne des mélanges mécaniques qui peuvent réagir durant le traitement final. Des caoutchoucs d'acrylonitrile-butadiène, contenant une insaturation résiduelle, peuvent cependant réagir avec des résines phénoliques pendant les premières étapes de la polymérisation, si les conditions sont appropriées. Une coréaction probable peut survenir par suite de formation de chromane à partir d'une double liaison de la molécule du caoutchouc avec un phénol o-méthylolique. Les produits de réaction sont entièrement solubles dans l'alcool, ce qui n'est pas de las pour les caoutchoucs. Les laminés préparés au départ de ces produits sont rendus souples, à tel point qu'ils sont facilement percés à froid. Cependant le caoutchouc, étant fortement lié, ne peut être extrait au moyen de solvants, ni donner lieu à des boursouflements par chauffage.

Zusammenfassung

Nitrilkautschuke wurden oft zusammen mit Phenolharzen bei Pressmassen zur Erzeugung eines schlagfesten Produktes verwendet. Es sind das mechanische Mischungen, welche während der Aushärtung noch reagieren können. Acrylnitril-Butadienkautschuke, die noch restliche Doppelbindungen enthalten, können jedoch mit Phenolharzen bei Einhaltung geeigneter Bedingungen schon im Anfangsstadium der Polymerisation zur Reaktion gebracht werden. Diese Reaktion verläuft wahrscheinlich über die Bildung eines Chromans aus einer Kautschukdoppelbindung und einem o-Methylolphenol. Im Gegensatz zu den Kautschuken sind diese Reaktionsprodukte in Alkohol vollständig löslich. Aus diesen Reaktionsprodukten erzeugte dünne Blätter zeigen eine so stark erhöhte Biegsamkeit, dass sie sich gut in der Kälte stanzen lassen. Da aber der Kautshuk fest gebunden ist, kann er weder mit Lösungsmitteln extrahiert werden noch führt er beim Erhitzen zur Blasenbildung.