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SBR과 폴리에스테르 코드의 접착에 탄닌 접착제의 응용

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Application of Tannin Based Adhesive for Bonding SBR to Polyester Cord

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요 약: 레소시놀-포름알데히드-라텍스(RFL) 접착제의 레소시놀 대체 물질로서 탄닌을 사용하여 접착제를 합성한 후 SBR과 폴리에스테르간의 접착을 시도하였다. 탄닌이 약 70% 이상 대체되거나, 접착제에서 라텍스/수지의 비가 3 이하에서 접착제의 점도는 크게 증가하였다. 탄닌이 약 60% 대체된 조성에서 접착제 자체가 가장 강인한 물성을 나타냈고, 타이어코드 접착실험(TCAT)으로부터 SBR과 폴리에스테르간의 접착력을 평가한 결과 가장 우수한 접착력을 나타냈다. 또한 TCAT에 의한 파단면의 분석결과 폴리에스테르 코드와 접착제의 계면에서 파단이 일어난 것으로 보아 SBR과 폴리에스테르간의 접착력에 영향을 끼치는 주된 접착기구는 접착제 자체의 강인성이었다.

ABSTRACT: The adhesion between SBR and polyester was done by using tannin as replacement for resorcinol in Resorcinol-Formaldehyde-Latex (RFL) adhesive. The viscosity of adhesive solution was greatly increased by the about 70% replacement of tannin for resorcinol and at the below 3 of latex/resin ratio. From the tensile test of adhesive itself it was found that the composition of 60% replacement of tannin for resorcinol showed the highest toughness among the all compositions. Also, the maximum adhesion strength between SBR and polyester could be obtained by using the adhesive containing that composition. The failure mode by the TCAT (Tire Cord Adhesion Test) was mainly interfacial failure between polyester and adhesive. The results indicated that the major factor affecting adhesion between SBR and polyester was the toughness of adhesive itself.

Keywords: RFL, tannin, pull-out force, failure locus, toughness.

INTRODUCTION

The properties of common rubbers and textiles are quite different. Textiles are polar and have high moduli, while rubbers typically are nonpolar and have high elasticity. Composites of the two do not have good mechanical properties, if the components are not intimately bonded.

In 1938, Charch and Maney of DuPont disclosed the original resorcinol-formaldehyde-latex (RFL) adhesive,[1] which cured rapidly without heat and gave durable adhesion betweenrubbers and textiles. RFL adhesives usually are prepared by reacting resorcinol and formaldehyde under alkaline conditions in the presence of a synthetic latex. When the adhesive is properly applied to a cord and cured by application of heat, it provides excellent adhesion to many kinds of rubber compounds. The resorcinol(R) and formaldehyde(F) react to form a product that reinforces the rubbery major portion.[2] It is also the RF part of the adhesive that is thought to be principally responsible for the adhesive's strong interaction with the cord.[3] During the vulcanization of a cord-RFL-rubber composite, co-curing across the rubber-adhesive interface is expected. The polymeric latex is usually chosen for its compatability with the rubber to be bonded. Styrene-butadiene-vinylpyridine latex is probably the most widely used aqueous polymer system for tire applications today. One function of the pyridine moiety of the styrene-butadiene-vinylpyridine latex is to increase the interaction between this latex rubber and the RF, thereby enhancing the cohesive strength of the adhesive.[4] The RFL adhesive first was applied primarily to rayon fibers and later to nylon and glass fibers.

Although the RFL adhesive has been successfully used for bonding of rubber to fiber, the use of condensed tannin obtained from pine tree has been considered as an alternative due to the high cost and scarcity of resorcinol. The condensed tannins in loblolly pine bark are polymeric procyanidins that are composed predominantly of 2,3-cis-procyanidin units terminated with the 2,3-trans-flavan-3-ol (+)-catechin(Fig. 1).[5] Condensed tannins are phenolic in nature and undergo reaction with formaldehyde to form resins. Thus, these renewable phenolic polymers will be a good candidate to try as a resorcinol replacement. Indeed, condensed tannins from wattle and pine bark extracts have been successfully used in cold-setting, wood-laminating adhesives, and the former are used extensively in the commercial production of laminated timbers in South Africa.[6,7] Also, the tannin based adhesive was applied successfully for bonding SBR to nylon cord.[8] However, RFL or tannin based systems are not suitable for bonding rubber to polyester due to a lack of reactive sites in the polyester as well as its hydrophobic nature. Thus, several adhesive systems for polyester bonding have been developed.[9,10] In this study, tannin based adhesive applied for polyester bonding and its properties were examined. The main objective of this study is to examine the potential of condensed tannin as an adhesive for bonding rubber to polyester.

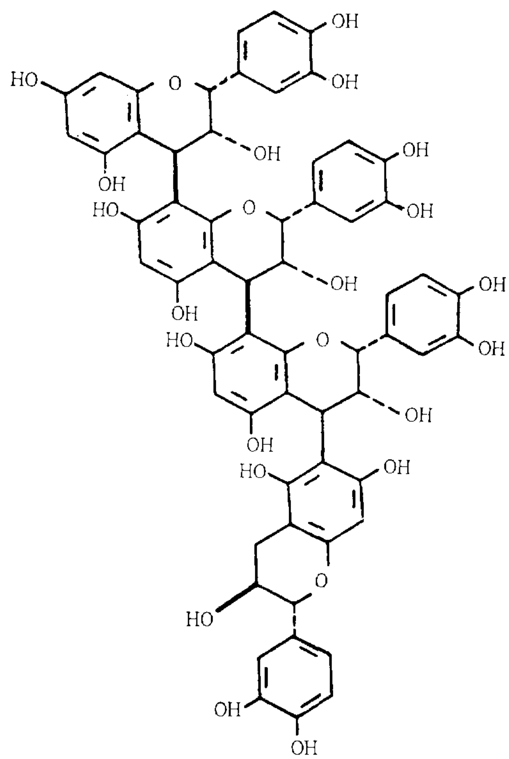

Fig. 1. Structure of polymeric procyanidins.

EXPERIMENTAL

Materials.

Rubber Stock: Rubber compound which used in this study was supplied by Kumho Tire Co. The ingredients are SBR1502, N330 carbon black, zinc oxide, sulfur, 2-morpholinothiobenzothiazole, and stearic acid.

Adhesive Solution: Adhesive solution was prepared with pine bark tannin, resorcinol, formaldehyde, sodium hydroxide. Also, styrenebutadiene-vinylpyridine latex was supplied by Kolon Co.

Tire Cord: A 1000/3 polyester tire cord was supplied by Dong Yang Nylon Co.

Experimental.

Compounding: SBR1502 and other ingredients (carbon black, zinc oxide, stearic acid) were mixed in a Brabender Plasticorder at 60 rpm. During mixing, the temperature was maintained below 200 ℃ to prevent degradation of the rubber. The vulcanization agent and accelerator were added on a cool, 12″ wide laboratory two-roll mill. Cold water was run through the rolls, because the rubber becomes sticky if it becomes too hot. The rubber composition is given in Table 1. After the rubber was sheeted off the mill, it was relaxed for 1 day at room temperature before using.

Cure Characteristics: A Monsanto Rheometer was used to obtain cure characteristics. ASTM D2084 gives the method. A rubber specimen of about 10 g was placed on a biconical rotor which is embedded in a cylindrical cavity. The rotor oscillated sinusoidally through a small amplitude by means of a motor-driven eccentric. The cavity and specimen were maintained at a temperatures of 140, 150, and 160 ℃ by electric heaters regulated by thermistor controllers, while the dies, which form the cavity, were held together by a force of about 1.5 MPa.

Table 1. Composition of Rubber Stock

Ingredients	phr
SBR1502	100.0
N330 Carbon Black	50.0
ZnO	5.0
Stearic Acid	0.5
Sulfur	1.7
2-morpholinothiobenzothiazole	2.0

Preparation of Adhesive Solution and Dipping of Polyester Cord: A typical RFL adhesive contains : resorcinol, 11 g ; 37% formalin solution, 16.4 mL ; 10% NaOH solution, 3 g ; distilled water, 236 g.[11] The above mixture was allowed to react for 2 hours at room temperature before adding the latex. After 2 hours, any insolubles were filtered out using a vacuum distillation apparatus and medium fast filter paper. Then, latex of 244 g was added and the adhesive solution was allowed to react for 24 hours at room temperature before using. Pine bark tannin was used as a replacement for resorcinol.

The dip procedure of polyester cord is as follows : a) cut cord to about 8 cm length, b) stir adhesive solution before dipping, c) dip cord into adhesive solution for 30 seconds then remove, d) allow to dry at room temperature for 5 hours before embedding into rubber stock. Dip pickup was determined by the following method ; a) weigh cords before dipping(to the nearest 0.0001 g), b) dip 2 cm of cord length, c) dry the cord for 5 hours, d) weigh cords again to the nearest 0.0001 g, e) record increase in weight of the dipped cord.

Tensile Test of Adhesive: Tensile test of dried adhesive was performed with an Universal Testing Machine(Lloyd LR50K). Adhesive solutions were cast on Teflon sheets in order to make adhesive film. All tensile tests were performed at a cross-head speed of 20 cm/min at room temperature, the nominal strain rate was about 6.67 min^{-1}.

Tire Cord Adhesion Test (TCAT): TCAT geometry is shown in Fig. 2. The exposed part of the cord was clamped in an UTM. Upon pulling

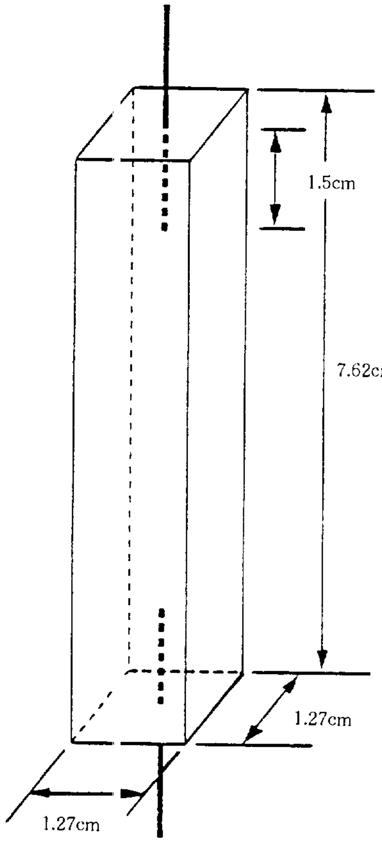

Fig. 2. Tire cord adhesion test geometry.

at the rate of 5 cm/min, failure occurred, resulting in the pull-out of one cord. The maximum force required to pull-out the cord is the pull-out force and the area under the force-deflection curve is the pull-out energy. The adhesion strength between SBR and polyester was examined by this method. Also, the effect of latex solid to resin solid ratio of adhesive on adhesion was investigated by using TCAT geometry. In this test, the latex solid to resin solid(resorcinol, tannin, and formaldehyde) ratio was changed at a fixed weight ratio of resorcinol/tannin of 40/60 in the adhesive formulation.

RESULTS AND DISCUSSION

Cure Characteristics. The cure characteristics of the rubber compound used are summarized in Table 2. The cure curves were an equilibrium type. Scorch time(t_{s2}), which is generally defined as premature vulcanization, was taken as the time after which the torque increased 0.226 Nm (2 lb. in) above minimum torque and 90% cure time($t_{c(90)}$) was taken as time to 90% of maximum minus minimum torque. As shown in Table 2, the t_{s2} and $t_{c(90)}$ decreased with increasing cure temperature and cure time reduced by a factor of about 2 for each 10 ℃ increase in cure temperature.

Adhesive Solution.

Mixing Order: During this experiment, it was found that the mixing order of ingredients for making the adhesive solution affected the viscosity of the adhesive solution and its adhesion. When the adhesive solution was made in the mixing order of resorcinol, tannin, NaOH solution, formalin solution, and water, which was designated by post-dilution method, there was incomplete dissolution of tannin. Before the water was added, some precipitation between resorcinol, tannin, and formaldehyde took place. These portions were not dissolved when the water was added. They were removed through filtering. However, tannin was dissolved completely when the NaOH and formalin solutions were added to water first, and then

Table 2. Cure Characteristics of the Rubber Compound

Temperature / Properties	140 ℃	150 ℃	160 ℃
$T^{a)}$(N.m)	3.83	4.03	4.18
$t_{s2}^{b)}$(min.)	23.38	12.15	6.13
$t_{c(90)}^{c)}$(min.)	45.53	25.17	14.09

[a] Maximum torque-minimum torque.
[b] Scorch time.
[c] 90% cure time.

the tannin and resorcinol were added to the solution with vigorous stirring. Thus, the mixing order of water, NaOH solution, formalin solution, resorcinol, and tannin, which was designated by pre-dilution method, was used for preparing the adhesive solution.

Viscosity Measurement: After 1 day aging of the adhesive solution, the viscosities with the different mixing orders and the weight ratio of R/T in adhesive are compared in Table 3. All readings were taken after the controlled shearing time because the cases of composition numbers of 8-11 showed typical thixotropic behavior which decreases viscosity with shearing time. As expected, the viscosity increased with increasing amounts of tannin reflecting its relatively high initial molecular weight. Since tannin molecules are generally large, the rate of molecular growth in relation to the rate of linkage formation is high, so the viscosity increases with increasing the tannin content. In the case of post-dilution, the viscosity changed slightly because some portions, which were precipitated by the reaction of resorcinol, tannin, and formaldehyde, were removed by filtering. However, the viscosities of the adhesives made by predilution method increased markedly after composition 8. Also, the viscosity changed with varying resin solid (resorcinol, tannin, and formaldehyde) amount as shown in Table 4. The viscosity increased as the resin content increased. The viscosity of control 1 (100 parts latex solid/100 parts resin solid) was beyond the measurable range of the Brookfield viscometer. After this adhesive solution was aged for 1 day, it became solid-like.

Table 3. The Change of Viscosity with the Different Mixing Order and the Weight Ratio of R/T in Adhesive

Composition number	R/T[a] Ratio	Viscosity(cp) by post-dilution	Viscosity(cp) by pre-dilution
1	100/0	23.7	39.5
2	90/10	45.8	43.4
3	80/20	50.8	59.2
4	70/30	50.8	57.4
5	60/40	69.0	63.2
6	50/50	71.1	94.8
7	40/60	94.8	300.0
8	30/70	103.0	1340.0
9	20/80	118.0	2760.0
10	10/90	190.0	2710.0
11	0/100	356.0	2765.0

[a] R/T ; resorcinol/tannin.

Tensile Test of Adhesive: Adhesive solutions with the weight ratio of R/T were prepared without change of the amounts of other ingredients in adhesive composition . After making thin films of adhesive solutions, tensile tests of the cast films were performed. In order to simulate cure, dried adhesives were molded at 160 ℃ for 15 minutes. The results are shown in Figs. 3 and 4.

In many cases, tensile samples could not be prepared, because, when the adhesive had dried, it became very brittle and cracked into many pieces. Even if the molding was tried with the crumbs, a coherent sheet could not be obtained because flow of the adhesive did not occur during molding. Thus, it was expected that the films, for which samples could not be obtained, had higher moduli than those of other adhesive compositions. As shown in Fig. 3, tensile strength of the adhesive decreased as the content of tannin was increased. Because of the molecular size and shape of tannin, it becomes immobile at a low level of condensation with formaldehyde so that the available reactive sites are too far apart for further methy-

Table 4. Viscosity of Adhesives Formulated with the Various Ratio of Latex to Resin Solid

Latex/Resin Solids Ratio	Viscosity(cp)
1	gelled
3	350.0
6	63.2
9	45.0
12	45.0
15	45.0

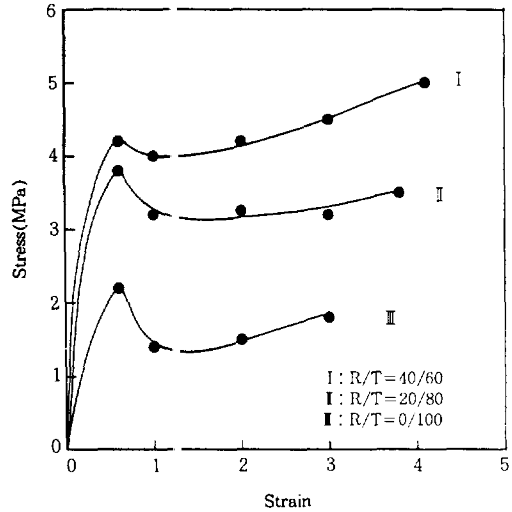

Fig. 3. Stress-strain curves with different weight ratios of resorcinol/tannin.
(I ; R/T=40/60, II ; R/T=20/80, III ; R/T=0/100).

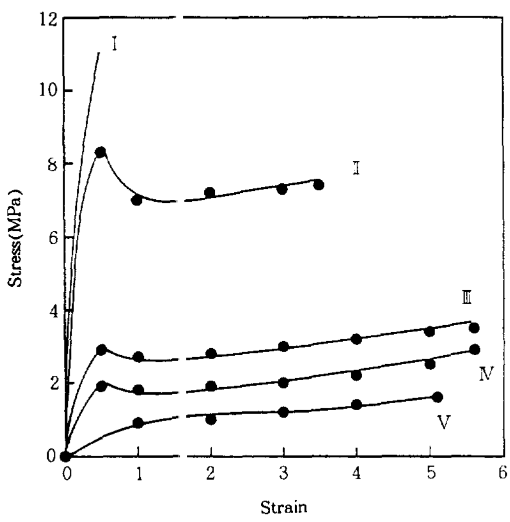

Fig. 4. Stress-strain curves with different weight ratios of latex solid to resin solid.
(I ; 3, II ; 6, III ; 9, IV ; 12, V ; 15).

lene bridge formation. It causes incomplete crosslinking and weakness. During the tensile test, necking was observed. For composition I, strain hardening was sufficient to result in a breaking stress that exceeded the yield stress. However, this was not true for compositions II and III, they showed ductile drawing. Therefore, it was expected that the composition I would be a composition shows the best adhesion strength for bonding rubber to polyester because it showed the most tough character as shown in Fig. 3. The results will be discussed more detail in the next section.

When the weight ratio of R/T was fixed to 40/60, the effect of latex solid to resin solid ratio of adhesive on adhesion was shown in Fig. 4. The numbers of I to V indicate that the ratios of latex /resin are 3, 6, 9, 12, and 15, respectively. As shown in Fig. 4, the tensile strength increased with increasing resin solid content. If the latex alone is employed as an adhesive, good rubber to fiber adhesion cannot be obtained because of a lack of active groups in the latex and the weak tensile properties of the latex film. As the amounts of resin are increased, the viscosity of the adhesive solution also increased, resulting in a hard gel at high resin content as shown in Table 4. Thus, testing of the control 1 of latex to resin ratio could not be done. As the resin solid content increased, it was expected that the methylol concentration increased in the adhesive. This resulted in more complete crosslinking, and gave high values of tensile strength. However, too much resin was detrimental since less latex rubber caused lack of adhesion to the rubber compound. As shown in Fig. 4, the composition II showed the most tough character among the all compositions. Consequently, the optimum compositions of adhesive obtained from tensile results was 60% replacement of tannin for resorcinol and 6 of latex to resin ratio. The corroborative of it were shown in other publications.[12] The reason was that the strength of an adhesive joint depends not only on the intrinsic interaction across the interface, but also on the ability of the joint members to dissipate mechanical energy into heat.[13] As shown in Figs. 3 and 4, the compositions of

R40T60 and 6 of latex to resin ratio showed the highest energy at break, which could be calculated from the area under the stress-strain curve. Therefore, the maximum adhesion between rubber and polyester can be obtained by using adhesive with these compositions because the interfacial interaction of rubber-adhesive and adhesive-polyester is not different with the adhesive compositions.

Tire Cord Adhesion Test. The adhesion between SBR and polyester cord was estimated by using TCAT geometry shown in Fig. 2. In making TCAT specimens, the embedment depth is an important factor because the pull-out force increases with increasing embedment depth. According to Livingston and co-workers,[14] the pull-out force increased as the embedment depth was increased upto 1.8 cm. They found that there was a slight dependence of the pull-out force on embedment depth at depths above about 1.8 cm. The results of this study were in good agreement with this. However, the following result was found occasionally during this work. When the embedment depth was longer than about 1.5 cm, failure occurred in the polyester cord instead of it pulling out from the rubber block. Thus, the embedment depth was fixed to 1.5 cm. As shown in Fig. 5, the pull-out force and pull-out energy passed through the maximum at about 60% replacement of tannin for resorcinol. Although the tannin was replaced for resorcinol in adhesive, the interactions at interfaces between adhesive and rubber, adhesive and polyester are same because the major chemical nature was not varied. Therefore, the adhesion strength could be attributed to the toughness of adhesive itself.

The pull-out force increased with an increasing amount of resin solid up to a latex to resin ratio of about 3 in the adhesive, but it decreased with further increasing of resin amounts. The results are shown in Fig. 6. Generally, it is expected that adhesion increases with an increasing amount of

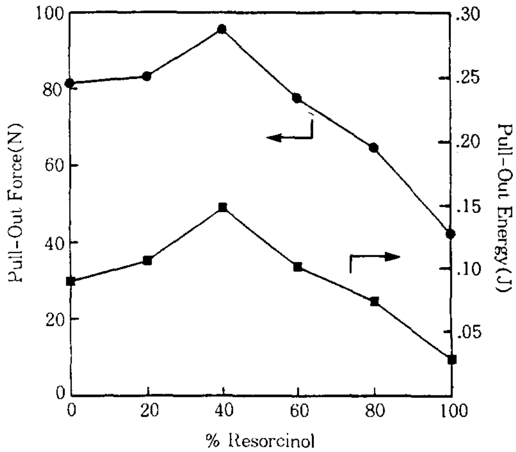

Fig. 5. Pull-out force and pull-out energy with varing of resorcinol/tannin weight ratio.

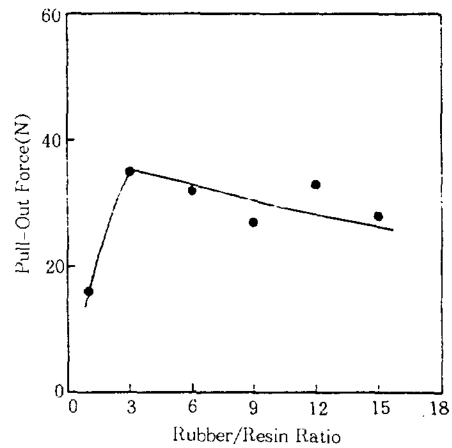

Fig. 6. Effect of rubber to resin ratio on adhesion.

resin. As the amount of resin increase, active methylol groups on the resin increase; this is expected to result in strong adhesive film strength and good adhesion to the rubber compound. However, too much resin is detrimental since less latex rubber causes lack of adhesion to the rubber compound. As shown in Fig. 6, the pull-out force was low when the rubber to resin ratio was 1, which was a hard solid after drying the solution, resulting in a low pull-out force. Above the ratio of 3, the pull-out force decreased slightly as the resin content was decreased. If only the latex is used, then the bonding force is low because of unsatisfactory film strength and the lack of interaction with the fiber.

Therefore, the toughness of adhesive played an important role for bonding rubber to polyester because the adhesive layer also experienced the applied stress during fracture.

Dip Pick Up and Failure Locus.

Dip Pick Up: Dip pick up (DPU) on the cord surface might be affect the adhesion. Table 5 showed DPU amounts with the adhesive compositions. From general experience, the joint strength increases with increasing adhesive pick up. It is, however, important to consider not total pick up, but effective pick up since penetrated RFL does not contribute to adhesion.[15]

Pick up level changed little up to 60% replacements with tannin. However, the viscosities of the adhesive solutions increased markedly after about 80% or more replacements with tannin, so the pick up level was high. Here, the DPU level could have played an important role. However, the adhesion strength was low be cause the strength of adhesive layer was low as shown in Fig. 3. Thus, the major effect on adhesion was not due to DPU level, but the rôle of tannin.

Failure Locus: In the TCAT, the failure locus was very important in understanding rubber to cord bonding. In the simple case, the failure may occur at four possible places(Fig. 7). In Table 6, interpretation of each failure loci is considered. However, the actual failure locus often was not exactly at any one of these, but usually mixed interfacial cohesive failure.

If the interfacial diffusion between adhesive and two bulk phases(rubber, polyester) is sufficient, the interface will be diffused. In this case, clear interfacial separation is not feasible. On the other hand, if little or no interfacial diffusion occurs, the

Table 5. Dip Pick Up Level for Polyester Cord

Dip Composition (weight % of R/T)[a]	DPU[b] (g/2cm of cord)
R100	0.0011
R80T20	0.0014
R6040	0.0013
R40T60	0.0011
R20T80	0.0038
T100	0.0042

[a] R/T : resorcinol/tannin.
[b] DPU : dip pick up.

Table 6. Interpretation of Failure Locus

Failure Locus	Comparison of Strength
1	D,[a] D-R[b]>C-D[c]
2	C-D, D-R>D
3	C-D, D>D-R
4	C-D, D, D-R>R[d]

[a] D : dip.
[b] D-R : interface of dip and rubber.
[c] C-D : interface of cord and dip.
[d] R : rubber.

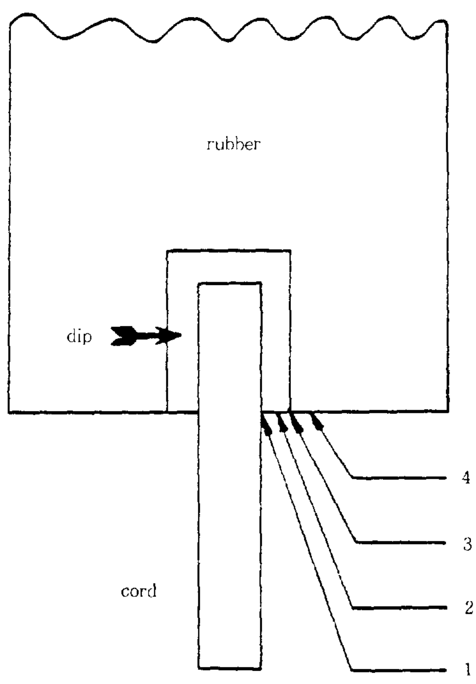

Fig. 7. Failure loci of TCAT block.

interface will be sharp, so true interfacial separation may occur. When the reaction mechanism between adhesive and two bulk phases is considered, it is believed that there is no chemical bonds at the interface of polyester cord and adhesive. Thus, it was expected that the failure would be occurred at the cord-adhesive interface which had the weakest links. Actually, failure occurred mainly in region I.

CONCLUSION

From this work, the following results were obtained.

1) The mixing order of adhesive ingredients affected to the viscosity of adhesive solution, and the pre-dilution method gave the best results.

2) The viscosity of adhesive solution markedly increased with the above 70% tannin replacement for resorcinol and the below 3 of latex/resin ratio.

3) The optimum compositions of adhesive obtained from tensile results was 60% replacement of tannin and 6 of latex/resin ratio.

4) From the TCAT results, it was found that the toughness of adhesive itself contributed to the final adhesion strength.

5) DPU was not a major factor on adhesion between rubber and polyester.

6) Failure loci in this system were mainly at the interface between polyester cord and adhesive.

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