

RTFL 접착제를 이용한 SBR과 폴리에스테르의 접착 연구

정 경 호
수원대학교 고분자공학과

The Adhesion Study of SBR and Polyester Using RTFL Adhesive

Kyung Ho Chung

Department of Polymer Engineering, The University of Suwon, Suwon 445-743, Korea

요 약

폴리에스테르와 SBR 1502 고무의 접착을 위해 RTFL(resorcinol-tannin-formaldehyde-latex) 접착제를 사용하였다. T-peel geometry를 이용하여 접착력을 평가한 결과 접착제 조성에서 레소시놀과 탄닌이 4대 6의 중량비로 합성된 접착제를 사용한 경우 뛰어난 접착력을 보였다. 폴리에스테르 표면의 소수성과 활성기의 부족에도 불구하고 SBR 고무와 높은 접착력을 보인 이유는 RTFL 접착제 자체의 일정 조성에서 나타나는 toughness 때문이었다. 또한 폴리에스테르와 고무 접착을 위한 single dip 시스템인 N-3형 접착제와 RTFL 접착제를 사용하여 폴리에스테르와 SBR 고무를 접착시킨 후 $-20^{\circ}\text{C}\sim 100^{\circ}\text{C}$ 의 온도 범위와 0.2cm/min \sim 50 cm/min의 박리속도 조건아래서 박리 실험하여 얻은 mastercurve들을 비교한 결과 전 범위에서 RTFL 접착제는 기존의 N-3형 접착제와 거의 필적할만한 접착 결과를 나타내었다.

I. Introduction

Resorcinol-formaldehyde-latex(RFL) dip systems are the preferred adhesive since 1935 for reinforced rubber products. These aqueous dips have the advantage of low viscosity and thus good wetting-out in the beginning of the rubber curing process. When cured, they change to an insoluble system. The elastomer latex gives the adhesive necessary flexibility and reactivity to bonded rubber, while the part of resorcinol-formaldehyde resin provides the desired heat and fatigue resistance by forming a 3-dimensional network. Also, the presence of unreacted methylol groups in the resin offers reactivity to hydroxyl,

amine, or amide groups on the surface of the reinforcing fibers. The mole ratio of resorcinol to formaldehyde, type of catalyst, and type of latex, as well as the ratio of resin to latex are varied in different RFL systems.^{1,2)}

The RFL dips were originally introduced for rayon cords and the bonding could be ascribed to the reaction between rayon hydroxyl groups and RF methylol groups. Similarly, the amide groups of nylon can undergo a reaction with these methylol groups,³⁾ although physical forces resulting from interpenetration and interlocking of the RF resin with the fiber have also been claimed to be a factor.⁴⁾ However, it was so difficult to obtain satisfactory

adhesion to polyester that their introduction in tires was delayed for many years. That is, the surface of fiber itself plays the most important role. The use of polyester as a rubber reinforcing material was greatly expanded when new methods for bonding the polyester to rubber were discovered. Due to the lack of reactive hydrogen in the polyester molecule and its hydrophobic nature, ordinary RFL type cord adhesives would not bond to the polyester surface. Thus, other methods were found to adhere the adhesive to the surface of the polyester. The following methods have been used for bonding polyester to rubber.⁵⁻⁹⁾ 1) A two-step adhesive process in which the first step activates the surface of the fiber followed by a standard RFL dip. 2) A one-step dipping process in which both the activating materials as well as the RFL are included in a single-step dip. 3) Chemical activation of the fiber surface during fiber spinning. 4) Modification of the fiber surface by grafting or plasma treatment. By using above methods, polyester can be bonded well to rubber. However, the high cost and scarcity of resorcinol which is required for the synthesis of most adhesives has prompted the use of condensed tannins. The properties and chemistry of condensed tannin were described well in the previous publication.¹⁰⁾

The objective of this experiment is to examine the potential of RTFL(resorcinol-tannin-formaldehyde-latex) adhesive for bonding polyester to SBR.

II. Materials and Experimental

The following materials were used in this experiment.

1. Materials

- 1) SBR 1502 : Polysar Co., 23.5% bound styrene
- 2) Dicumyl peroxide : Hercules Inc., 40% dicumyl peroxide supported on calcium carbonate
- 3) Polyethylene terephthalate(Mylar) : Cadillac Plastic & Chemical Co., 0.13mm film
- 4) Resorcinol : Sigma Chemical Co.
- 5) Triallyl cyanurate : Fluka Co.
- 6) 37% Formalin solution : Fisher Scientific Co.
- 7) Sodium hydroxide : Fisher Scientific Co.
- 8) Gentac 118 latex : Gencorp Co.(Styrene : Butadiene : Vinyl pyridine = 15 : 70 : 15)

2. Experimental

2.1 Adhesive Preparation

The compositions of standard RFL and RTFL adhesives were given in the previous publication.¹⁰⁾ In adhesive preparation, all ingredients except the latex were mixed and allowed to react at room temperature for 2 hours. Any insolubles were then filtered out, and the appropriate quantity of latex was added. Generally, a further reaction time of 24 hours was allowed before the adhesive was applied.

2.2 Preparation of N-3 Adhesive Dip¹¹⁾

As a conventional single dip system for polyester bonding, an N-3 dip was prepared as follows : 100 parts by weight of resorcinol and 24 parts by weight of triallylcyanurate were placed in a glass flask and heated until melted. Then, 0.4 part by weight of sodium metal was added in small pieces and the flask heated to 250°C. At this time, some allyl alcohol was slowly given off. The flask was then cooled to 110°C and connected to a reflux condenser. Then, 28 parts by weight of 37% aqueous formaldehyde were added slowly through the condenser over a

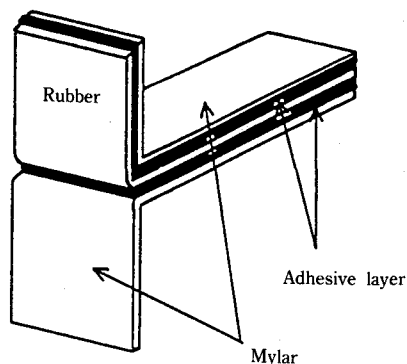


Fig. 1. Geometry of T-peel test.

period of 10 minutes. The contents of the flask were refluxed for an additional 10 minutes. Then, a solution containing 400 parts by weight of water and 28 parts by weight of 28% aqueous ammonium hydroxide was added. The product was a clear liquid of dark brown color which tended to turn blue on long exposure to air. The N-3 dip was combined with the conventional RFL dip in a 1:1 weight ratio to complete the single dip system for polyester.

2.3 T-peel Test

The T-peel geometry was shown in Fig. 1. Specimens were prepared as follows: 1) SBR 1502 was mixed with 1 phr of dicumyl peroxide in a Brabender Plasticorder. Then, the rubber was sheeted on a mill. 2) The adhesive dip was applied onto a Mylar sheet, which had been cleaned with solvent. 3) The coated sheet was heat treated in an oven at 220°C for 30 seconds. 4) T-peel testpieces were prepared by pressing a flat sheet of rubber between two layers of Mylar. A spacer was used to keep the rubber thickness at about 0.7mm. 5) The sandwich was cured for 30 minutes at 150°C. 6) T-peel specimens were cut. The peel rate was varied in the range of 0.2 to 50cm/min. The test temperature was varied in the range of -20 to 100°C. The average peel

force per centimeter width was calculated. The peel force fluctuated, either randomly or in a stick-slip fashion. Initiation, arrest, and mean values were considered.

III. Results and Discussion

Peel tests are commonly used to determine the strength of adhesion of a flexible adhering layer. The strength of adhesion between the polyester (Mylar) and the SBR using RTFL adhesive was examined using the T-peel geometry. Based on the control RFL dip,¹⁰ the portions of resorcinol were replaced by tannin to give various adhesive compositions. The change of the peel strength as function of percent resorcinol was shown in Fig. 2. The peel strength increased with increasing level of tannin substitution and passed through a maximum at about 60% substitution of tannin for resorcinol, except for the two lower peel rates. Failure took place at the interface between Mylar and the adhesive in all cases. It is well-known 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

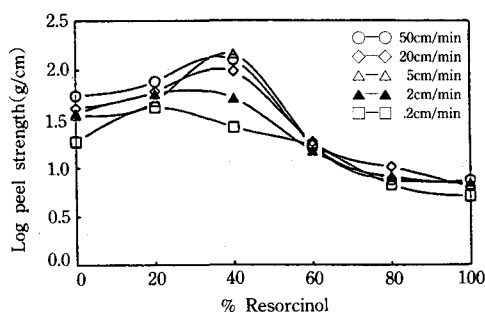


Fig. 2. Change of peel strength as a function of percent resorcinol.

energy into heat. If large amounts of mechanical energy are dissipated while stressing an adhesive joint, then this will be reflected by an enhancement in the energy that must be supplied to fracture the joint. Hamed¹²⁾ showed that a substantially greater detachment energy was required to strip Mylar film from a styrene-butadiene-styrene(SBS) triblock copolymer compared to that for peeling from a random SBR copolymer. He proposed that the higher detachment work was a consequence of the higher dissipative capacity of the triblock copolymer. In this system, the increase of peel strength with increasing tannin substitution level could be explained to a consequence of increasing dissipative capacity of the RTFL adhesive layer with the level of tannin substitution. The results could be obtained by comparing the area under stress-strain curves of various RTFL adhesive films shown in the previous publication.¹⁰⁾ According to the previous tensile results, the maximum toughness of adhesive film was obtained by the about 60% tannin substitution for resorcinol in the adhesive composition and the result affected the maximum peel strength.

Peel strength for rubbery adhesives depends strongly upon the rate of detachment and test temperature, because these materials are viscoelastic. Thus, the adhesive composition of R40T60 was chosen as a basic composition, which showed the maximum peel strength, in order to investigate rate and temperature effect on adhesion strength between SBR and polyester. The number after R and T was the weight percent of resorcinol and tannin in RTFL adhesive composition, respectively. Results were shown in Fig. 3. Each point represented an average of the peel force over a peeled distance of about 10cm, averaged for at least three test strips. Above

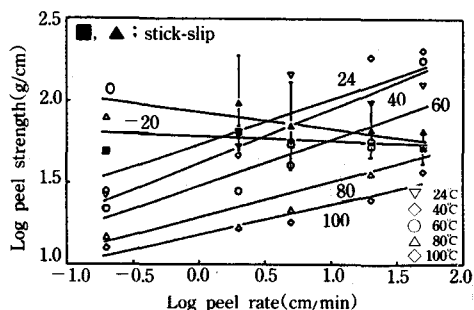


Fig. 3. Peel strength of R40T60 system with peel rate and temperature.

Table 1. The change of peeling mode with peel rate and temperature

Temp.(°C)	peeling rate (cm/min)	Mode	W(cm)
Above 24	all	I	—
0	0.2	I	—
	2	II	0.28
	5	III	0.22
	20	III	0.18
	50	III	0.16
-20	0.2	III	0.10
	2	III	0.10
	5	I	—
	20	I	—
	50	I	—

Note 1. I ; random fluctuation

II ; mixing of random and stick-slip

III ; stick-slip

2. W; average distance between initiation and arrest in stick-slip fashion

24°C, the peel strength increased with increasing peel rate and decreasing temperature. At the highest temperature used, 100°C, and at the lowest rate of peel, 0.2cm/min, the peel strength was low. On the other hand, the peel strength decreased with increasing peel rate at 0°C and -20°C. Also, failure pattern was stick-slip with the peel force oscillating between high and low values. Values of initiation and arrest

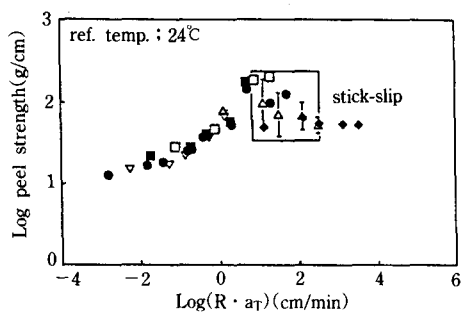


Fig. 4. Mastercurve for peel strength versus peel rate, Ra_T , reduced to 24°C for R40T60 system.

were indicated with error bars in Fig. 3. Failure loci were at the interface between the Mylar and the adhesive layer in all cases. The peeling modes for various rates and temperatures were summarized in Table 1. Stick-slip behavior occurred below 0°C , and the distance between initiation and arrest narrowed with decreasing temperature and increasing peel rate. Then, stick-slip behavior disappeared. Peel strengths at various peel rates and temperatures were replotted against reduced rate Ra_T at 24°C and all data fell on a single curve (Fig. 4). In Fig. 4, the blocked portion indicated the region which showed stick-slip behavior. Gent and Petrich¹³⁾ contributed a great deal to the understanding of peel behavior. Peel forces for a Mylar adherend and rubbery interlayer versus peel rates at three different temperatures were presented in Fig. 5(a). There was a steady rise in peel force with peel rate up to a critical rate, then an abrupt transition to much lower peel forces. At the same time, the locus of failure changed abruptly from cohesive failure of the adhesive layer to interfacial failure at the adhesive-adherend interface. This transition shifted to higher rates as the temperature was increased. The entire force-rate curves at different temperatures

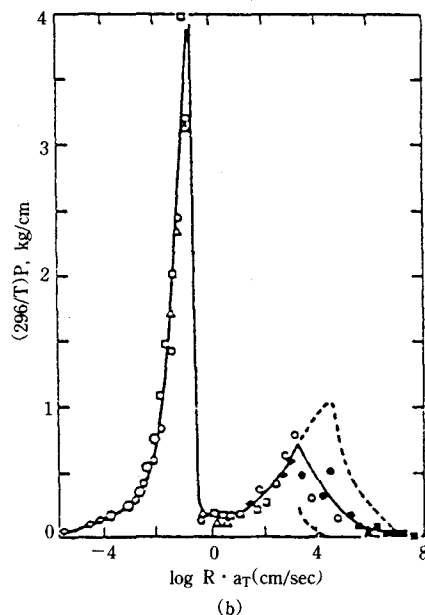
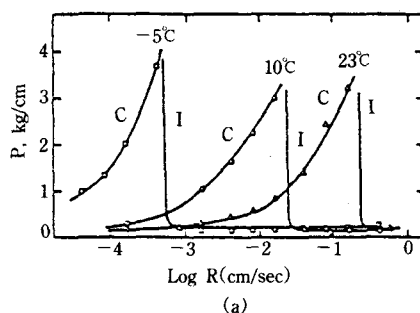


Fig. 5. (a) Average peel force P against rate of peel R for an uncrosslinked butadiene-styrene rubber adhering to Mylar. (b) Mastercurve for peel force P against rate of peel R , reduced to 23°C , for an uncrosslinked butadiene-styrene rubber adhering to Mylar.

could be superimposed to give a single mastercurve by horizontal shifting, using the universal form of the WLF shift factor (Fig. 5(b)).¹³⁾ Generally, the peel force should be increased with rate of peel as long as the locus of failure remains the same (either cohesive or adhesive) for elastomeric adhesives. However, they found that the low peel rate transition in peel strength was associated with the

transition from liquid-like to rubber-like behavior of the polymer and the high peel rate phenomenon appeared to be associated with the onset of the transition from rubber-like to glass-like behavior at high rates of deformation. In the present system, the loci of failure were the same and there was no transition from liquid-like to rubber-like behavior of the adhesive, because it was already cured. Therefore, the peel strength should be increased with increasing peel rate. However, there was a transition at the region of high peel rate as shown in Fig. 4. It might be related to the transition from rubber-like to glass-like response of the RTFL adhesive. In this region, a small amount of work was expended in the adhesive due to its stiffness and there was a severe increase in stress concentration at the interface. Thus, the peel strength decreased with increasing peel rate.

A conventional single dip system(N-3) for polyester to rubber bonding also was compared with the RTFL system. T-peel tests were performed at five different peel rates and seven different temperatures. The peel strength with peel rate and their mastercurve were shown in Fig. 6 and 7, respectively. Peel strength increased with increasing peel rate and decreasing temperature, but eventually reached a plateau. With the N-3 system, the failure loci were mixed interfacial and cohesive failure between the adhesive and the rubber unlike the RTFL system. Generally, rubber coverage of the stripping member at high peel rate and low temperature was higher than that at low peel rate and high temperature. High rubber coverage was correlated with high peel strength. In the region of mixed failure, where peel strength was strongly dependent on peel rate, separation occurred within the bulk of the adhesive and

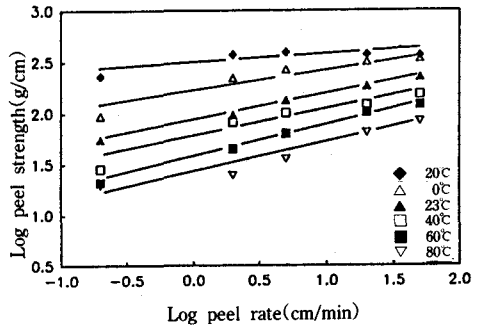


Fig. 6. Peel strength of N-3 system with peel rate and temperature.

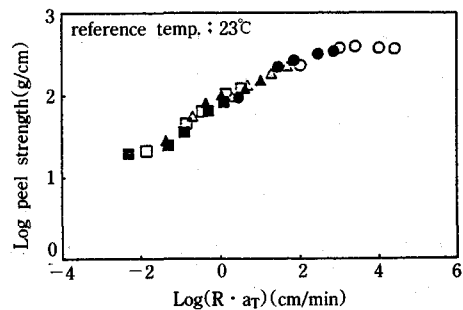


Fig. 7. Mastercurve for peel strength versus peel rate, Ra_T , reduced to 23°C for N-3 system.

rubber. When cohesive failure occurred, the peel strength increased with peel rate. Peel strength can be correlated with the area under the stress-strain curve of an adhesive.¹³⁾ Because the ultimate stress and elongation increased with strain rate, the area under the stress-strain curve increased with strain rate. Consequently, the peel strength increased with peel rate. Mastercurves with the N-3 system and the RTFL adhesive system were compared in Fig. 8. At the region of low temperatures and high peel rates, the N-3 system gave higher peel strength than the RTFL system. However, the values were similar at the region of lower peel rates and higher temperatures. For the R40T60 system, the lower peel st-

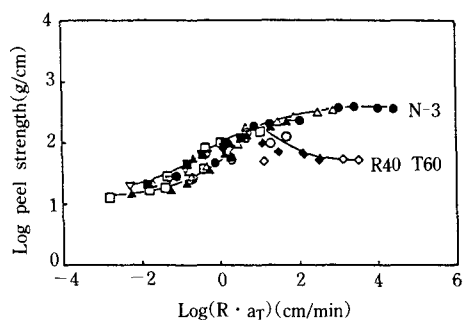


Fig. 8. Comparison of mastercurves of R40T60 and N-3 system.

length than that of the N-3 system was accompanied by apparent interfacial failure at the adhesive-Mylar interface.

IV. Conclusion

From this experiment, the following results were obtained.

1. Peel strength of rubber to polyester bonding passed through a maximum at 60% replacement of tannin for resorcinol in the RFL adhesive system. High dissipative capacity of the adhesive film was the cause of this maximum.

2. The R40T60 system had a transition region which was characterized by stick-slip behavior, while the N-3 system reached a plateau region in peel strength with increasing peel rate and decreasing temperature. Both systems showed similar peel strengths at low peel rates and high temperatures, while the N-3 system showed higher peel strengths at high peel rates and low temperatures. Also, both systems had different failure loci. The R40T60 system showed interfacial failure between adhesive and Mylar, while the N-3 system showed mixed interfacial and cohesive failure between the adhesive and

the rubber.

3. The results with polyester are particularly encouraging, since the simple RFL control dip is not that well suited for polyester. Thus, it is expected that the tannin based adhesive will be a good adhesive for polyester if the polyester is modified to prevent interfacial failure between adhesive and polyester. This additional work will hopefully allow a better understanding of the bonding properties that will lead to improved strength.

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