*Journal of Mechanical Engineering Research and Developments*
*ISSN: 1024-1752*
*Website: http://www.jmerd.org*
*Vol. 39, No. 1, 2016, pp. 217-225*

# Optimized Design of Adhesive Formations for Tennis Ball

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ABSTRACT: By studying the effects of reinforcing system, tackifier, vulcanization system and solvent on properties of tennis ball adhesive (of which the main material is NR), the purpose of this article is to achieve the optimized design for adhesive formulations of tennis ball. Optimized formulation is: NR100, carbon black N220 of 30, zinc oxide of 8.3, stearic acid of 2.2, phenolic tackifying resin of 3, accelerator CZ/D of 1.5/1 and sulfur of 3. Using this formulation could make the obtained adhesive with good properties, and accordingly make the finished balls with excellent adhesive properties and air-tightness as well as meet the design requirements.

KEYWORDS: Tennis ball; NR; Adhesives; Formulation design; Adhesive properties; Material properties; Air-tightness.

## INTRODUCTION

The excellent elasticity of tennis ball is because that its interior is filled with a certain amount of gas, and the gas retention property of tennis ball therefore becomes an important factor which influences its performance. This gas retention property does not only relate to the air-tightness of the bladder of tennis ball but also more closely associates with its adhesion.

The vulcanization molding of tennis ball is rather special. First, compound has to be vulcanized into two hemispheres, filled with inflatable agent, and then the two hemispheres will be bonded into a whole ball and the second vulcanization molding will be finished. So the adhesion of tennis ball is actually the adhesion of vulcanized rubber, which is more difficult than the adhesion between unvulcanized rubbers. First of all, vulcanized rubber is the network polymer shaped by material like sulfur, lacking of activity on its surface; secondly, the adhesion is a process, in which the adhered surface also as the bonding interface, including the flowing of adhesives, the infiltration and the forming of stable interface between adhesives and adherends. Therefore, it is necessary to conduct experiments to study adhesive formulation for making the adhesion strong, so as to obtain qualified adhesives for tennis ball.

In this paper, by studying the effects of reinforcing system, tackifier, vulcanization system and solvent on properties of tennis ball adhesive (of which the main material is NR), the optimal design for adhesive formulations of tennis ball can be obtained.

## EXPERIMENTAL PROCEDURE

### Raw Materials

NR, trademark SIR20, Indonesia products; carbon black N220 and N550, Shandong Luhua Co., Ltd. products; zinc oxide, stearic acid, accelerator D and CZ and sulfur, Rhein Chemie (Qingdao) Co., Ltd. products; phenolic tackifying resin, Henan Open Chemical Co., Ltd. products.

### The Main Equipments and Instruments

*XK-160 open mill*

XK-160 open mill is the product of Shanghai Rubber Machinery Factory. XR-160 could monitor and record the parameter of horizontal pressure, auxiliary temperature, stick speed and its ratio, power and energy consumption and has the function of data storage, data processing and so on. They can also automatically feed material, control the distance, temperature, speed and speed ratio, turn adhesive and prepare the needed material. The appearance of XK-160 experimental platform is shown in the Figure 1.

DOI: 10.7508/jmerd.2016.01.030

**Figure 1.** XK-160 open mill.

*GT-M2000 curometer and GT-AI-2000 tensile testing machine*

GT-M2000 curometer (Figure 2) and GT-AI-2000 tensile testing machine (Figure 3) are the products of Taiwan GaoTie detecting instrument CO. LTD. GT-M2000 curometer which is made according to the standard to ASTM-D5289 is an engineering management instrument which can detect the most proper rubber and sulfur by the method of compulsory vibration. Due to the change of viscosity the rubber make model produce torque induction that the torque signal is transferred to the computer in order to be processed and the change curve of torsion and time, induction time, the most proper time of adding sulfur (T90), the lowest elasticity value of adding sulfur (ML), the highest elasticity value of adding sulfur (MH), the lowest and the highest viscosity value and the curve of viscoelastic ratio which are the basis and guidance for the judgment of rubber curing characteristics, study of physical nature, material proportioning and actual production are all listed.

**Figure 2. GT-M2000 curometer.**

**Figure 3.** GT-AI-2000 tensile testing machine.

*Flat vulcanizing machine*

Flat vulcanizing machine, as is shown in the Figure 4, is a product of East Asian rubber machine CO. LTD. in the city of Qingdao. Flat vulcanizing, a press machine with hot plates, is the important equipment of the rubber manufacturing industry. It has the following merits such as its simple structure, high pressure, wide adaptability and so on.

**Figure 4.** Flat vulcanizing machine.

*Thickness gauge MI-1000*

Thickness gauge (Figure 5) is a product of Shanghai Movie Machinery Factory.

Sample Preparation

Compound was mixed in the open mill, after being mixed uniformly, thin-passing was batched out six times with a part of the rubber compound vulcanizing on the plate vulcanization machine, under vulcanization condition of 145 $^{o}$C × t90; another part of the mix was dissolved in a solvent (mucilage) for peeling test.

Peeling sample preparation: The mucilage was spread evenly over the two 180mm × 11mm vulcanization rubber strips, and the spread length of sample should be longer than 100mm, bonded firmly. Then, it was vulcanized on the plate vulcanization machine, removed the spared.

Performance Testing

All the performance tests were conducted according to relevant national standards.

RESULTS AND DISCUSSION


**Figure 5.** Thickness gauge MI-1000.

Reinforcing System

*Filler Varieties*

Effects of nanometer calcium carbonate, silica as well as carbon black N220 and N550 on the adhesive properties are listed in Table 1.

**Table 1.** Effects of filler varieties on the adhesive properties.

| project | nanometer calcium carbonate | silica | carbon black N220 | carbon black N550 |
|---|---|---|---|---|
| curemeter data [145℃] | | | | |
| $t_{S2}$/[min] | 1.4 | 2.3 | 1.5 | 1.6 |
| $t_{90}$/[min] | 19.9 | 11.7 | 8.9 | 9.2 |
| shore A hardness/[degree] | 60 | 63 | 72 | 70 |
| 200% stretching stress/[MPa] | 3.1 | 5.3 | 5.7 | 5.8 |
| tensile strength/[MPa] | 16.6 | 20.5 | 21.8 | 20.5 |
| breaking elongation/[%] | 590 | 699 | 559 | 563 |
| tear strength/[kN·m-1] | 30 | 62 | 57 | 55 |
| peeling strength/[kN·m-1] | 5.0 | 6.2 | 7.3 | 6.9 |

As Table 1 shows, vulcanized rubber filled with carbon black N220 has the maximum hardness, tensile strength and peeling strength; vulcanized rubber filled with silica has the highest tear strength; the reinforcing effect of carbon black N550 is between that of carbon black N220 and silica; while vulcanized rubber filled with nanometer calcium carbonate has the worst vulcanized property. Based on the analysis, it is considered that carbon black N220 has a higher structure, which could provide better tensile properties for vulcanized rubber; furthermore, the particle surface

of carbon black N550 is smooth, so its reinforcing effect is worse than carbon black N220. According to comprehensive consideration, carbon black N220 should be selected as the suitable reinforcing agent for the adhesive.

*The Amount of Carbon Black N220*

**Table 2.** Effects of the amount of carbon black N220 on the adhesive properties.

| Project | the amount of carbon black N220/[phr] | | | | |
|---|---|---|---|---|---|
| | 15 | 20 | 25 | 30 | 35 |
| curemeter data [145℃] | | | | | |
| $t_{S2}$/[min] | 1.6 | 1.5 | 1.6 | 1.6 | 1.6 |
| $t_{90}$/[min] | 7.5 | 8.3 | 9.6 | 9.6 | 9.4 |
| shore A hardness/[degree] | 63 | 67 | 71 | 74 | 76 |
| 200% stretching stress/[MPa] | 3.8 | 4.4 | 5.3 | 6.0 | 7.0 |
| tensile strength/[MPa] | 22.3 | 22.8 | 22.0 | 21.4 | 21.8 |
| breaking elongation/[%] | 635 | 610 | 571 | 542 | 514 |
| tear strength/[kN·m-1] | 44 | 48 | 55 | 70 | 74 |
| peeling strength/[kN·m-1] | 4.5 | 5.7 | 5.8 | 6.4 | 5.7 |

As can be seen from Table 2, along with the increasing amount of carbon black N220, the hardness, 200% stretching stress and tear strength will all gradually increase. However, both the tensile strength and peeling strength will reduce after the first increase. And moreover, when the amount of carbon black N220 is 20 or 30, the tensile strength and peel strength of the vulcanized rubber will respectively reach the maximum. It is indicated that with the increasing amount of carbon black, the reinforcing function and each property of vulcanized rubber will be increased and improved. But when excessive use of carbon black, its rubber content will decrease with reducing of bounding points between rubber and the adherend, and the peel strength will therefore also decrease. Thus, as a reinforcing agent in adhesives, the amount of carbon black should not be too large; otherwise rubber would become rigid, stiff and brittle because of too large stiffness as well as decreasing of adhesive properties. Peel strength is an important property of the adhesive, and therefore the optimum amount of carbon black N220 are 30 portions.

Tackifier

The main role of the tackifier is to increase the viscosity of adhesive surface, and the diffusion-ability of adhesives and the interaction between contact surfaces will be both improved by putting the tackifier. Impacts of tackifier varieties to adhesives properties are given in Table 3.

**Table 3.** Impacts of tackifier varieties to adhesives properties.

| project | Blank | rosin | coumarone resin | petroleum resin | phenolic resin |
|---|---|---|---|---|---|
| curemeter data [145℃] | | | | | |
| $t_{S2}$/[min] | 1.7 | 1.5 | 1.4 | 1.6 | 1.6 |
| $t_{90}$/[min] | 9.2 | 7.5 | 6.9 | 7.7 | 7.9 |
| shore A hardness/[degree] | 65 | 60 | 59 | 55 | 58 |

| | | | | | |
|---|---|---|---|---|---|
| 200% stretching stress/[MPa] | 5.4 | 5.7 | 5.7 | 5.3 | 5.6 |
| tensile strength/[MPa] | 25.7 | 25.5 | 25.1 | 22.5 | 26.5 |
| breaking elongation/[%] | 530 | 550 | 550 | 530 | 580 |
| tear strength/[kN·m-1] | 56 | 58 | 52 | 47 | 61 |
| peeling strength/[kN·m-1] | 4.9 | 5.7 | 5.5 | 5.3 | 6.6 |

Table 3 shows that adding rosin, coumarone resin or phenolic resin can increase both 200% stretching stress and peeling strength of vulcanized rubber, which indicates that these three kinds of resins are more suitable for tackifying effect and among them phenolic resin is the best choice. This may be due to the infiltration of resin molecules into molecular chain of rubber, which makes the latter more active and easier to spread. But the tackifying effect of petroleum resin is a little worse, which may be related to its molecular structure and adhesive in bonding and so on. Taken together, phenolic resin should be selected as the tackifier for adhesives.

Vulcanization System

*Accelerator*

The bonding of the bladder of the tennis ball is actually the bonding between two hemispheres as well as the bonding between vulcanized rubbers. In order to ensure the full decomposition and aeration of inflated agent during the adhesion of the bladder of the tennis ball, before curing reaction occurs, the adhesive should have sufficiently long time to fulfill diffusion and infiltration in the bonding interface. Therefore, the use of accelerator CZ/D is appropriate. Impacts of blending ratio of accelerator CZ/D to adhesives properties are listed in Table 4.

**Table 4.** Impacts of blending ratio of accelerator CZ/D to adhesives properties.

| project | blending ratio of accelerator CZ/D | | | | |
|---|---|---|---|---|---|
| | 0.5 /1 | 1 /1 | 1.5 /1 | 2 /1 | 2.5 /1 |
| curemeter data [145℃] | | | | | |
| $t_{S2}$/[min] | 1.4 | 1.7 | 1.7 | 1.9 | 2.1 |
| $t_{90}$/[min] | 8.5 | 8.1 | 7.9 | 7.7 | 7.6 |
| shore A hardness/[degree] | 57 | 59 | 60 | 60 | 64 |
| 200% stretching stress/[MPa] | 5.5 | 5.8 | 6.3 | 6.7 | 6.6 |
| tensile strength/[MPa] | 21.5 | 23.9 | 25.9 | 26.3 | 25.9 |
| breaking elongation/[%] | 765 | 628 | 584 | 475 | 491 |
| tear strength/[kN·m-1] | 55 | 58 | 57 | 60 | 61 |
| peeling strength/[kN·m-1] | 6.0 | 6.4 | 7.1 | 6.7 | 5.8 |

As can be seen from Table 4, along with the increasing blending ratio of the accelerator CZ/D, the $t_{S2}$ will be overall extended while the $t_{90}$ is shortened; and all the hardness, 200% stretching stress and tear strength have generally increasing tendency. However, both the tensile strength and peeling strength will reduce after the first increase. And moreover, when the accelerator CZ/D is with blending ratios of 1.5/1 and 2/1, the tensile strength and peeling strength of the vulcanized rubber will respectively reach the maximum. It is indicated that the accelerator CZ/D using system can improve the curing degree of vulcanized rubber, and thereby products of excellent hardness, tensile modulus, tensile strength, elasticity and dynamic Performance can be obtained. Therefore, under the presupposition of

guaranteed performance of rubber, the amount of accelerator CZ/D should not be too large and it would be best with suitable blending ratio of 1.5/1.

*Sulfur*

**Table 5.** Effects of the amount of sulfur on the adhesive properties.

| project | amount of sulfur/[phr] | | | | | |
|---|---|---|---|---|---|---|
| | 2 | 2.5 | 3 | 3.5 | 4 | 4.5 |
| curemeter data [145℃] | | | | | | |
| $t_{S2}$/[min] | 1.8 | 1.7 | 1.7 | 1.6 | 1.5 | 1.6 |
| $t_{90}$/[min] | 7.5 | 7.8 | 8.4 | 9.5 | 9.9 | 10.9 |
| shore A hardness/[degree] | 52 | 54 | 60 | 60 | 63 | 63 |
| 200% stretching stress/[MPa] | 4.3 | 4.7 | 5.7 | 5.6 | 6.7 | 6.6 |
| tensile strength/[MPa] | 27.3 | 27.7 | 29.9 | 28.5 | 24.5 | 24.4 |
| breaking elongation/[%] | 746 | 656 | 596 | 536 | 469 | 488 |
| tear strength/[$kN \cdot m^{-1}$] | 55 | 60 | 57 | 58 | 54 | 56 |
| peeling strength/[$kN \cdot m^{-1}$] | 5.5 | 6.0 | 7.6 | 6.5 | 6.2 | 5.8 |

Table 5 shows that, with the increasing amount of sulfur, the $t_{S2}$ does not change too much while the $t_{90}$ will be gradually extended; the hardness of vulcanized rubber have generally increasing tendency. However, both the tensile strength and peeling strength will reduce after the first increase. And moreover, when the sulfur is of 3phr, the tensile strength and peeling strength of the vulcanized rubber will respectively reach the maximum. Taken together, the optimal amount of sulfur should be of 3 phr.

Solvent

Mucilage refers to a kind of pulp made by the mixture of rubber compound and organic solvent. Solvent molecules diffuse into the rubber molecule chain, which enlarge its volume and enter a swelling state. After a certain period the interstices of rubber molecule chain become larger and the gravity of it become smaller. The result is the dissolution. This is the whole process of rubber dissolution. Therefore according to the principle of dissolution in the similar material structure the consistency of the rubber material and solvent should be considered while the solvent is preferred.

Respectively using toluene, petrol and toluene/petrol mix (volume ratio of 1:1) as solvent to dissolve the compounded rubber (of the formulation: NR100, carbon black N220 of 30, zinc oxide of 8.3, stearic acid of 2.2, phenolic tackifying resin of 3, accelerator CZ/D of 1.5/1 and sulfur of 3). The peeling strength of the obtained glues are respectively 6.7, 7.8 and 5.5kN • $m^{-1}$. It is indicated that petrol as the solvent has the best adhesion effect; toluene takes the second place, followed by toluene / petrol with the worst result.

According to analysis, the solubility parameter of the rubber, petrol and toluene are 7.9, 7.8~8.1 and 8.97. According to the principle of dissolution in the similar material structure the closer the solubility parameter of the rubber and the solvent are, the better mutual solubility could be achieved. This is due to the large interval between molecular chains of rubber, which makes the diffusion and infiltration effect of adhesive on the interface of the two hemispheres clearer. Therefore, the best solvent for adhesive should be petrol.

Optimized Formulation and Property

Under the comprehensive consideration, the optimized formulation is: NR100, carbon black N220 of 30, zinc oxide of 8.3, stearic acid of 2.2, phenolic tackifying resin of 3, accelerator CZ/D of 1.5/1 and sulfur of 3. Under this formulation is obtained adhesive with following physical properties: Shore A hardness of 59 degrees, 200% stretching stress of 5.8MPa, tensile strength of 29.6MPa, breaking elongation of 612%, tear strength of 60 $kN \cdot m^{-1}$, peeling strength of 7.8 $kN \cdot m^{-1}$.

Application Effects

Using the prepared adhesive with optimized formulation in the production of tennis ball, all performances of the finished ball were tested in tennis court, and then stored for 6 months; finally its performances were tested one more time. The results of experiment pointed out that the finished balls with excellent adhesive properties and air-tightness as well as meet the design requirements.

## THE CONCLUSION

By studying the effects of reinforcing system, tackifier, vulcanization system and solvent on properties of tennis ball adhesive (of which the main material is NR) the optimized design for adhesive formulations of tennis ball is achieved. Optimized formulation is: NR100, carbon black N220 of 30, zinc oxide of 8.3, stearic acid of 2.2, phenolic tackifying resin of 3, accelerator CZ/D of 1.5/1 and sulfur of 3. The study shows that using this formulation could make the obtained adhesive with good properties, and accordingly make the finished balls with excellent adhesive properties and air-tightness, and meet the design requirements of tennis, and make obtained tennis ball with good production and use value and finally meet the demand of the research.

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