<table>
<thead>
<tr>
<th>Title</th>
<th>Method for manufacturing a composite tire of polyurethane tread and radial carcase</th>
</tr>
</thead>
<tbody>
<tr>
<td>B29D 30/66 (2006.01)</td>
<td></td>
</tr>
<tr>
<td>Application No:</td>
<td>2006203253</td>
</tr>
<tr>
<td>Date of Filing:</td>
<td>2006.07.28</td>
</tr>
<tr>
<td>Number</td>
<td>Date</td>
</tr>
<tr>
<td>200510101982.4</td>
<td>2005.12.05</td>
</tr>
<tr>
<td>Publication Date:</td>
<td>2007.06.21</td>
</tr>
<tr>
<td>Publication Journal Date:</td>
<td>2007.06.21</td>
</tr>
<tr>
<td>Accepted Journal Date:</td>
<td>2008.03.06</td>
</tr>
<tr>
<td>Applicant(s)</td>
<td>Guangzhou Scut Bestry Auto Co., Ltd.</td>
</tr>
<tr>
<td>Inventor(s)</td>
<td>Zhang, Hai; Ma, Tiejun; Yi, Yuhua</td>
</tr>
<tr>
<td>Agent / Attorney</td>
<td>Hubert Chan, 39 Canberra Street St Johns Park, Sydney, NSW, 2176</td>
</tr>
<tr>
<td>Related Art</td>
<td>JP 2006-264637</td>
</tr>
<tr>
<td>US 2005/092424</td>
<td></td>
</tr>
<tr>
<td>US 5462617</td>
<td></td>
</tr>
</tbody>
</table>
ABSTRACT

The invention refers to a manufacturing technology for composite tire. Detailedly speaking it refers to a manufacturing method for polyurethane-rubber composite tire. Adopt the composite structure of polyurethane tread and rubber carcase and modify and optimize low polymer polyol/butylene oxide-propylene epoxide copolyether-p-diisocyanate and polybutadiene glycol-diphenylmethane diisocyanate. Treat an outer surface of an internal rubber body and cast. It owns good property of low temperature and high heating-resisitant. So it can be used in high-speed condition and also it has long lifetime. Besides, its manufacturing method is easy and its cost is low, so it can be easily put into industrialization.
METHOD FOR MANUFACTURING A COMPOSITE TIRE OF POLYURETHANE TREAD AND RADIAL CARCASE

BACKGROUND

The present invention relates to a method for manufacturing a composite rubber tire, and more particularly to a composite rubber that has a polyurethane tread to achieve an environmentally friendly tire with excellent mechanical efficiency.

Polyurethane is a kind of material with excellent synthesis properties. After the development of over sixty years, it has owned special synthesis properties which are wide range of hardness, strength and modulus, high elongation wide usage range of temperature, good property of oil-resistance, low temperature and ozone aging. And also it owns excellent abrasion resistance. Its wearing-resistant property is better than that of natural rubber by 2-10 times and it can be called wear-resisting rubber. Besides, its molding technology and equipment are simple and can be recycled completely. It is an ideal rubber material of tire tread.

Since 1960s, many countries in the world have begun the research of polyurethane applied to the tire manufacturing such as the Lim Corporation of Austria, Phoenix of Germany and UTI of Britain and so on. They mainly research the polyurethane entire casting tire, namely that both the tire body and tread are made of polyurethane material. At the beginning of molding, put the cord, belted and ring traveler etc. into the die and fix each position, and then adopting the method of centrifugal pouring, cast the polyurethane into the die. After the solidification demolding, the tire articles come out. The molding of entire casting
polyurethane tire is very convenient and fast. And its cost is very low and is one-fifth of rubber tire manufacturing equipment investment. However, because its strong polarity and acute acting of intermolecular linkage and inner molecular hydrogen bond, its the rigid of molecular chain is big, in the dynamic condition, the internal heat generation is also big. And the resist heat of polyurethane is poor and its long period of time usage temperature is below 80°C. So all these tires are only applied to low-speed vehicles the drive speed is below 50km/hour such as bicycle fun vehicle cutting-grass vehicle golf vehicle and sliding vehicle etc. Recently Amerityre corporation in the USA has researched developed a kind of spare tire for bus, Although its properties meat the NO.109 safe standard of America federal motor vehicles, the tires are solid tires which are made from plugging polyurethane foam, the drive speed is still 50km/hour and its drive mileage is only 2000 miles. To sun up, because of the particularity of polyurethane material, at present, the polyurethane tires in the marker are the low-speed tires.

**SUMMARY**

The main objective of the present invention is to overcome the shortcomings of the above-mentioned polyurethane tires, we adopt the polyurethane tread/rubber tire body composite structure, and optimize and modify the polyurethane composition so as to make it have low development of heat and high heat resistance, so we provide a method for manufacturing polyurethane-rubber composite tire which has long lifetime, simple technology, low cost and easy industrialization.

The invention includes the following procedures and technology requirements:
Step 1: Treating an outer surface of an internal rubber body:

(1) the preparation of finishing agent

A solution was obtained by adding N,N-di-chloro-p-toluene sulfonamide (weight content in the range of 5 to 15) to anhydrous acetone solvent (weight content range from 85 to 95), which was dehydrated by molecular sieves, then benzoyl peroxide (weight content range from 3 to 10) was dissolved in this solution.

(2) Preparation of a polyurethane adhesive

A polyurethane pre-polymer with isocyanate group content range from 7 to 8 percent was prepared by using a diol with a molecular weight of 1000 to 2000 (such as polyoxytetramethylene glycol or polycaprolactone diol) and methylene diphenyl diisocyanate with a novel method, then a final adhesive was obtained by using 1,4-butanediol/triethanolamine mixing chain extender after the polyurethane pre-polymer had been diluted to a solution of 40 to 60 weight content with ethyl acetate.

(3) Surface treatment process of rubber tire body

A rubber radical tire was polished on the surface where the polyurethane tread should be applied. After trimmed clearly, the rubber tire was sprayed or coated uniformly with surface treatment agent [made in step 1 (1)] and placed for 0.5 to 1 hours or treated by plasma and placed for 0.1 to 1 hours, then the surface was sprayed or coated with the polyurethane adhesive [made in step 1 (2)] and placed for 0.5 to 3 hours, the tire body can be used to be casted a polyurethane tread.

Step 2: preparation of polyurethane pre-polymer for tire tread
(1) a low polymerized polyol (tetramethylene-propylene oxide copolyethol) -p-phenyl-diisocyanate polyurethane system

This polyurethane system was prepared by a novel method, in which the low polymerized polyol was polyoxytetramethlyene glyol or polycaprolactone diol with a molecular weight of 1000 to 2000. The quantity of the tetramethylene-propylene oxide copolyethol was 30 to 50 percent of the system total weight, wherein the propylene oxide contend range is from 20 to 40 percent. The pre-polymer isocyanate content range is from 3.5 to 5 percent.

(2) a low polymerized polyol(polybutadiene diol)- diphenylmethanediiisocyanate polyurethane system

This polyurethane system was prepared by a novel method, in which the low polymerized polyol was polyoxytetramethylene glyol or polycaprolactone diol with a molecular weight of 1000 to 2000. The quantity of the polybutadiene diol was 15 to 30 percent of the system total weight. The pre-polymer isocyanate content range is from 5.0 to 7.0 percent.

(3) Preparation of modified silicon whisker

After silicon whisker powder (100 weight content) was heated and activated, polyisocyanate (50 to 60 weight content) and anhydrous toluene (150 to 250 weight content) was added in and reacted for 1 to 2 hours at 80 ±2°C, then the mixture was heated to 220 to 240°C and dried for 4 to 6 hours under a less than 500Pa vacuum atmosphere to obtain a solid, the solid was cooled and pulverized to obtain a polyisocyanate modified silicon whisker.

(4) preparation of nano-montmorillonite
Montmorillonite (5 to 10 weight content) was added in distilled water (90 to 95 weight content) to obtain a mixture. The mixture was added in tetradecyl to octadecyl trimethyl ammonium chloride (14 to 16 weight content) at 80 ± 2 °C. After 1 to 2 hour reaction with stirring, a montmorillonite suspension was obtained. Then a solid was achieved after filtration and water washing and drying. A powdered nano- montmorillonite of 50 to 90 nm was obtained by pulverizing the solid.

(5) Preparation of polyurethane pre-polymer for tire tread

The modified silicon whisker [made in step 2 (3)] or the nano-montmorillonite [made in step 2 (4)] was added into the reactive system [made in step 2 (1) or (2)], then the polyurethane pre-polymer for tire tread can be obtained by a novel method, it also can be obtained by dispersing the modified silicon whisker [made in step 2 (3)] or the nano-montmorillonite [made in step 2 (4)] (1 to 7 weight content) into the polyurethane pre-polymer (100 weight content) [made in step (1) or (2)].

Step 3 manufacture of the composite tire

(1) materials

The pre-polymer [made in step 2 (5)] was transferred into A tank of a casting machine and heated to 70 to 80 °C and deaerated for 15 to 30 minutes under a less than 500Pa vacuum atmosphere; the low molecular diol chain extender was transferred into B tank. The isocyanate content of pre-polymer was tested according to the standard method and the ratio of pre-polymer VS chain extender was calculated by the set chain extending coefficient, the metering pump of the polyurethane elastomer casting machine was adjusted according to the proportion and the preferable low molecular weight diol chain extender was 1,4-
butanediol or hydroquinone-di-(β-hydroxyethyl) ether or/and resorcinol-di-(β-hydroxyethyl) ether with a chain extending coefficient of 0.95 to 0.98.

(2) casting

The tire body (treated in step 1) was placed into a mold which been heated to 110 to 130 °C, then the casting machine was applied to mold a polyurethane tread. The mold was kept at a pressure of 200 to 300 kpa and a temperature of 110 to 130 °C. after 30 to 80 minutes, the internal rubber body casted with a polyurethane tread was detached from the mold and moved into an oven or a baking channel with an inner-temperature of 110 to 130 °C and stayed for 12 to 24 hours to achieve a final tire.

Compared to the known entire polyurethane tire, the composite tire of polyurethane tread and radical carcass has the following advantages:

1. The composite rubber tires with a polyurethane treacle not only have low distortion good flexibility and excellent wear-resistance polyurethane tread, but also have low heat generation, friendly environmental characteristic, therefore it is suitable for them to be used as high-speed tires.

2. The formulation of polyurethane tire tread is reasonable and the characteristic is excellent. The temperature on the surface of the polyurethane tread is laver 5 degree C than that of a normal rubber tire. At the same time, the normal stability of the polyurethane tread is good, and the strength reservation rate at 120 degree C is more than 30 percent.

3. Therefore the composite rubber tires with a polyurethane tread like suitable for high-speed tire usage and the speed can be 80 to 100 Km per hour. The service life of the tires is so long that it is two times than that of rubber tires.
4. Investment of equipment is low and molding processing is simple, so it is fit for industrial manufacture.

**DETAILED DESCRIPTION OF THE INVENTION**

To further clarify this invention, following operational examples were shown.

5 Example 1

Step 1: Surface treatment of an internal rubber body:

A combinative method of painting surface treating agent and coating polyurethane adhesive was using as a method for surface treatment of an internal rubber body.

10 (1) preparation of a surface treatment agent.

A solution was obtained by adding N,N-di-chloro-p-toluene sulfonamide (6.8 weight content) into anhydrous acetone solvent (93.2 weight content) and dispersing uniformly with string than benzoyl peroxide (2 weight content) was dissolved in this solution.

15 (2) preparation of a polyurethane adhesive

A reactive pot was charged with polyoxytetramethylene glycol of a molecular weigh of 1000 (100 content by weigh) and heated to $120 \pm 10^\circ \text{C}$. The reactant was dehydrated for 2 hours at a less than 500Pa vacuum atmosphere, then cooled to $80^\circ \text{C}$ and added in MDI(59 weigh content) under protection of N2 for 2 hours. The isocyanate content (NCO%) was tested and reaction could be stopped if the isocyanate content of the mixture was 7.2 percent. Before application, the mixture (45 weight content) should be diluted uniformly by ethyl acetate (55 weight content), then 1,4-butanediol/tirethanolamine mixing chain extender(3.32 weight content) was adding into the mixture to obtain a final
adhesive, wherein 1,4-butanediol weight content is 2.96, trithanolamine weight content is 0.36.

(3) Surface treatment process of rubber tire body

A rubber radical tire was polished on the surface where the polyurethane tread should be applied. After trimmed clearly, the rubber tire was sprayed or coated uniformly with surface treatment agent [made in step 1(1)], and staged for 20 minutes, the surface was sprayed or coated with the polyurethane adhesive [made in 1(2)] and placed for 30 minutes, the tire body can be used to cast a polyurethane tread.

Step 2 preparation of polyurethane pre-polymer for tire tread.

In this example, a polyoxytetramethylyene glyol/ tetramethylene-propylene oxide copolyethol -p-phenyl-diisocyanate system was applied, wherein the molecular weight for poly-diol is 2000, the propylene oxide content is 20 percent and silicon whisker was used as a modifier before polymerization.

(1) preparation of modified whisker

Silicon whisker powder (100 weight content) was heated to 240 to 250°C and activated for 6 hours. MDI (60 weight content) was dissolved into anhydrous toluene solvent (225 weight content) and added into activated silicon whisker powder to obtain a mixture. The mixture was heated to 80°C ± 2°C for 1.5h, then the mixture was heated to 230°C ± 10°C and dried for 4h at a less than 500Pa vacuum atmosphere to achieve a solid. The modified silicon whisker was produced by cooling and pulverizing the solid.

(2) preparation of polyurethane pre-polymer for tire tread
A reactive pot was charged with polyoxytetramethyleylene glyol of an average molecular weigh of 2000 (70 weight content), tetramethylene-propylene oxide copolyethol of a molecular weight of 2000 (30 weight content) and modified silicon whisker [made in step 2(1)] (3 weight content). The mixture was heated to 120 ± 10°C and dehydrated for 2 hours at a less than 500Pa vacuum atmosphere then added in p-phenyl-diisocyanate (18.2 weight content) after cooled to 90 ± 5°C and dissolved it with strong stirring. The mixture was heated to 100 to 105°C and reacted for 2 hours to obtain a silicon whisker modified polyurethane pre-polymer.

Step 3 manufacture of the composite tires

(1) materials

The pre-polymer [made in step (2)] was transferred into A tank of a casting machine and heated to 75 ± 2°C, then deaerated for 15 minutes under a less than 500Pa vacuum atmosphere, resorcinol-di-(β-hydroxyethyl) ether was transferred into B tank. The quality of chain extender and the ratio of pre-polymer VS resorcinol-di-(β-hydroxyethyl) ether were calculated by a traditional method, the detail was shown as follow:

The quality of chain extender per 100 weight content polyurethane pre-polymer is:

\[ B = 0.045 \times 2.36 \times 0.97 \times 100 \]

\[ = 10.3 \]

Wherein, 0.045 equals the isocyanate content theoretical value of polyurethane pre-polymer;
2.36 equals the constant of the chain extender when it is resorcinol-di-(β-hydroxyethyl) ether. 0.97 equals the chain extending coefficient in this example i.e. every 100 part polyurethane pre-polymer is corresponding to 10.3 part chain extender of resorcinol-di-(β-hydroxyethyl) ether. The A and B component metering pumps of polyurethane elastomer casting machine were adjusted according to the proportion.

(2) casting

The tire body which had been treated and coated with polyurethane adhesive was placed into a mold at a temperature of 110 °C, then the casting machine was applied to cast a polyurethane tread. The pressure was kept at 270 ±10 kpa and the mold temperature was retained at 110 °C. After 60 minutes, the internal rubber body casted with a polyurethane tread was detached from the mold and moved into an oven or a baking channel with an inner-temperature of 110 °C and stayed for 16 hours to achieve a final tire.

Example 2

Step 1: surface treatment of the rubber tire body

The rubber tire body surface treatment method is combined with plasma surface treatment and coating with a polyurethane adhesive.

(1) Preparation of a polyurethane adhesive

A reactive pot was charged with polyoxytetramethylene glycol of a molecular weigh of 2000 (100 content by weigh) and heated to 120 ±10 °C, The reactant was dehydrated for 2 hours at a less than 500Pa vacuum atmosphere, then cooled to 80 ±2 °C and added in MDI(47.6 weigh content) under protection of
N2 for 2 hours. The isocyanate content (NCO%) was determined and reaction could be ceased if the isocyanate content of the mixture was 8 percent. Before application, the mixture (55 weight content) should be diluted uniformly by ethyl acetate (45 weight content), then 1,4-butanediol/tirethanolamine mixing chain extender (4.51 weight content) was adding into the mixture to obtain a final adhesive, wherein 1,4-butanediol weight content is 4.02, trithanolamine weight content is 0.49.

(2) Surface treatment process of rubber tire body

After trimmed clearly, the rubber tire was treated by plasma and placed for 0.5 hours, then the surface was sprayed or coated with the polyurethane adhesive [made in step 1 (1)] and placed for 2 hours, the tire body can be used to be casted a polyurethane tread.

Step 2: preparation of polyurethane pre-polymer for tire tread

In this example, a polyoxytetramethlyene glyol/ tetramethylene-propylene oxide copolyethol -p-phenyl-diisocyanate system was applied, wherein the molecular weight for tetramethylene-propylene oxide copolyethol is 2000, the propylene oxide content is 20 percent and nano-montmorillonite was used as a modifier before polymerization.

(1) preparation of nano-montmorillonite

Montmorillonite (5 weight content) was added into distilled water (95 weight content) to obtain a mixture. The mixture was added in octadecyl trimethyl ammonium chloride (16 weight content) at 80 ± 2 °C. After 3 hours reaction with stirring, a montmorillonite suspension was obtained. Then a solid was achieved
after filtration and water washing and drying. A powdered nano- montmorillonite of 50 to 90 nm was obtained by pulverizing the solid.

(2) preparation of polyurethane pre-polymer for tire tread

A reactive pot was charged with polyoxytetramethyleneglyol of an average molecular weigh of 2000 (50 weight content), tetramethylene-propylene oxide copolyethol of a molecular weight of 2000 (50 weight content) and nano-montmorillonite [made in step 2(1)] (5 weight content). The mixture was heated to 120 ±10°C and dehydrated for 2 hours at a less than 500Pa vacuum atmosphere then added in p-phenyl-diisocyanate (15.7 weight content) after cooled to 90 ±5°C and dissolved it with strong stirring. The mixture to 100 to 105°C and reacted for 2 hours to obtain a nano-montmorillonite modified polyurethane pre-polymer.

Step 3 manufacture of the composite tire

(1) materials

The pre-polymer [made in step (2)] was transferred into A tank of a casting machine and heated to 80 ±2°C, then deaerated for 15 minutes under a less than 500Pa vacuum atmosphere, the mixing chain extender was composed of hydroquinone-di-(β-hydroxyethyl) ether and resorcinol-di-(β-hydroxyethyl) ether with a mass proportion of 7:3 and was transferred into B tank. The quality of chain extender and the ratio of pre-polymer VS chain extender were calculated by a traditional method, the detail was shown as follow:

The quality of chain extender per 100 weight content polyurethane pre-polymer is:

\[ B = 0.035 \times 2.36 \times 0.97 \times 100 \]
Wherein,

0.035 equals the isocyanate content theoretical value of polyurethane pre-polymer;

2.36 equals the constant of the chain extender when it was composed of hydroquinone-di-(β-hydroxyethyl) ether and resorcinol-di-(β-hydroxyethyl) ether;

0.95 equals the chain extending coefficient in this example

i.e. every 100 part polyurethane pre-polymer is corresponding to 7.847 part chain extender. The A and B component metering pumps of polyurethane elastomer casting machine were adjusted according to the proportion.

(2) casting

The tire body which had been treated and coated with polyurethane adhesive was placed into a mold at a temperature of 110 °C, then the casting machine was applied to cast a polyurethane tread. The pressure was kept at 220 ± 10 kpa and the mold temperature was retained at 110 °C. After 80 minutes, the internal rubber body casted with a polyurethane tread was detached from the mold and moved into an oven or a baking channel with an inner-temperature of 110 °C and stayed for 15 hours to achieve a final tire.

Example 3

Step 1: surface treatment of the rubber tire body

The rubber tire body surface treatment method is combined with plasma surface treatment and coating with a polyurethane adhesive.

(1) Preparation of a polyurethane adhesive
A reactive pot was charged with polyoxytetramethylene glycol of a molecular weight of 1000 (100 content by weight) and heated to 120±10°C. The reactant was dehydrated for 2 hours at a less than 500Pa vacuum atmosphere, then cooled to 70±5°C and added in MDI (47.6 weight content) under protection of N2 for 2 hours. The isocyanate content (NCO%) was determined and reaction could be ceased if the isocyanate content of the mixture was 7.9 percent. Before application, the mixture (60 weight content) should be diluted uniformly by ethyl acetate (40 weight content), then 1,4-butanediol/tirethanolamine mixing chain extender (5.02 weight content) was adding into the mixture to obtain a final adhesive, wherein 1,4-butanediol weight content is 4.47, trithanolamine weight content is 0.55.

(2) Surface treatment process of rubber tire body

After trimmed clearly, the rubber tire was treated by plasma and placed for 0.2 hours, then the surface was sprayed or coated with the polyurethane adhesive [made in step 1 (1)] and placed for 2 hours, the tire body can be used to be casted a polyurethane tread.

Step 2: preparation of polyurethane pre-polymer for tire tread

In this example, a polyoxytetramethylene glycol/polybutadiene diol-diphenylmethane diisocyanate system was applied, wherein the molecular weight for polybutadiene diol is 2000 and nano-montmorillonite was used as a modifier after polymerization.

(1) preparation of nano-montmorillonite

Montmorillonite (9 weight content) was added into distilled water (91 weight content) to obtain a mixture. The mixture was added in octadecyl trimethyl
ammonium chloride (27 weight content) at $80 \pm 2$ °C. After 2 hour reaction with stirring, a montmorillonite suspension was obtained. Then a solid was achieved after filtration and water washing and drying. A powdered nano-montmorillonite of 50 to 90 nm was obtained by pulverizing the solid.

(2) preparation of polyurethane pre-polymer for tire tread

A reactive pot was charged with polyoxytetramethylene glyol of an average molecular weigh of 2000 (80 weight content), polybutadiene diol of a molecular weight of 2000 (20 weight content). The mixture was heated to $120 \pm 10$ °C and dehydrated for 2 hours at a less than 500Pa vacuum atmosphere then added in diphenylmethanediisocyanate (3 weight content) after cooled to $70 \pm 5$ °C and dissolved it with strong stirring. The mixture was heated to $80 \pm 2$ °C and reacted for 2 hours to obtain a polyurethane pre-polymer.

(3) A powdered nano-montmorillonite (2 weight content) was dispersed with a powerful high-speed dispersing machine into the polyurethane pre-polymer (100 weight content) to obtain a nano-montmorillonite modified polyurethane pre-polymer.

Step 3 manufacture of the composite tire

(1) materials

The pre-polymer [made in step (2)] was transferred into A tank of a casting machine and heated to $80 \pm 2$ °C, then deaerated for 15 minutes under a less than 500Pa vacuum atmosphere, 1,4-butanediol was transferred into B tank. The quality of chain extender and the ratio of pre-polymer VS chain extender were calculated by a traditional method, the detail was shown as follow:
The quality of chain extender per 100 weight content polyurethane pre-polymer is:

\[ B = 0.065 \times 1.07 \times 0.95 \times 100 \]
\[ = 6.61 \]

Wherein,

- 0.065 equals the isocyanate content theoretical value of polyurethane pre-polymer;
- 1.07 equals the constant of the chain extender when it was composed of hydroquinone-di-(β-hydroxyethyl) ether and resorcinol-di-(β-hydroxyethyl) ether;
- 0.95 equals the chain extending coefficient in this example i.e. every 100 part polyurethane pre-polymer is corresponding to 6.61 part chain extender. The A and B component metering pumps of polyurethane elastomer casting machine were adjusted according to the proportion.

(2) casting

The tire body which had been treated and coated with polyurethane adhesive was placed into a mold at a temperature of 120 °C, then the casting machine was applied to cast a polyurethane tread. The pressure was kept at 250 ± 10 kpa and the mold temperature was retained at 120 °C. After 70 minutes, the internal rubber body casted with a polyurethane tread was detached from the mold and moved into an oven or a baking channel with an inner-temperature of 110 °C and stayed for 20 hours to achieve a final tire.

Example 4

Step 1: Surface treatment of an internal rubber tire body:
A combinative method of painting surface treating agent and coating
Polyurethane adhesive was used as a method for surface treatment of an internal rubber body.

(1) Preparation of a surface treatment agent

A solution was obtained by adding N,N-di-chloro-p-toluene-sulfonamide (12PHR) into anhydrous acetone-solvent (88PHR) and dispersing uniformly with trimming, then benzoyl peroxide (7.2PHR) was dissolved in this solution.

(2) Preparation of polyurethane adhesive

A reactive pot was charged with polyoxytetramethylene glycol of a molecular weight of 2000 (100PHR) and heated to 120 ± 10°C. The reactant was dehydrated for 2 hours at a less than 500Pa vacuum atmosphere, then cooled to 70 ± 5°C and added in MDI (55PHR) under protection of Nitrogen atmosphere for 1-2 hours. The isocyanate content (Nco%) was tested, and the reaction could be stopped if the isocyanate content of the mixture was 7%, before application, the mixture (55PHR) should be diluted uniformly by ethyl acetate (45PHR), then 1,4-butanediol/triethanolamine mixing chain extender (3.94PHR) was added into the mixture to obtain a final adhesive, among which, the PHR of the 1,4-butanediol is 3.51, the PHR of the triethanolamine is 0.43.

(3) Surface treatment process of rubber tire body:

A rubber radial tire was polished on the surface where the polyurethane tread should be applied, after trimmed clearly, the rubber tire was sprayed or coated uniformly with surface treatment agent (made in step 1) and stayed for 45 minutes, the surface was sprayed or coated with the polyurethane adhesives
{made in step 1 2} and placed for 2 hours, the tire body can be used to cast the polyurethane tread.

Step 2 preparation of polyurethane pre-polymer for tire tread

In this example, choose the ploycaprolactone diol molecular weight is 2000/polybutadiene glycol-diphenylmethane diisocyanate, among which, the molecular weight of polybutadiene glycol is 2000, And silicon whisker was used to be modifier.

(1) preparation of modified silicon whisker

Silicon whisker powder (100PHR) was heated to 230 to 250°C and activated for 4 hours. MDI (0PHR) was dissolved into anhydrous toluene solvent(250PHR) and added into activated silicon whisker powder to obtain a mixture. The mixture was heated to 80±2°C for 2 hours, then the mixture was heated to 230±10°C and dried for 6 hours at a less than 500Pa vacuum atmosphere to achieve a solid, the modified silicon whisker was produced by and pulverizing the solid.

(2) Preparation of polyurethane pre-polymer for the treacle

A reactive pot was charged with an average molecular weight of 2000: ploycaprolactone glycol(75PHR), a molecular weight of 2000 polybutadiene glycol(25PHR) and modified silicon whisker, the mixture was heated to 120±10°C and dehydrated for 1 hour at a less than 500Pa vacuum atmosphere, then added diphenylmethane diisocyanate(37PHR) after cooled to 60-65°C and dissolved it with strong stirring, the mixture was heated to 80±2°C and reacted for 2 hours to obtain a silicon whisker modified polyurethane pre-polymer.
(3) Disperse the modified silicon whisker (5PHR)\{made in step 1\} into pre-polymer(100PHR)\{made in step 2\}, so we can obtain the modified silicon whisker polyurethane pre-polymer for tire tread.

Step 3 manufacturing for the polyurethane composite tire

5 (1) Materials:

The pre-polymer \{made in step 3\} was transferred into a tank of a casting machine and heated to 80±°C, then deaerated for 10-15 minutes under a less than 500Pa vacuum atmosphere, resorcinol-di-(β-hydroxyethyl ether was transferred into B tank, the quality of chain extender and the ratio of pre-polymer VS resorcinol-di-(β-hydroxyethyl were calculated by a traditional method, the details was shown as follows:

the quantity of chain extender per 100(PHR)polyurethane pre-polymer is:

\[ B = 0.060 \times 2.36 \times 0.95 \times 100 \]

\[ = 13.45 \]

Above 0.060 equals the isocyanate content theoretical value of polyurethane pre-polymer;

2.36 equals the constant of the chain extender when it is resorcinol-di-(β-hydroxyethyl) ether;

0.95 equals value of chain extender.

i.e. every 100 part polyurethane pre-polymer is corresponding to 13.45 part chain extender. The A and B component metering pumps of polyurethane elastomer casting machine were adjusted according to the proportion.

(2) Casting
The tire body which had been treated and coated with polyurethane adhesive was placed into a mold at a temperature of 110°C, then the casting machine was applied to cast a polyurethane tread. The pressure was kept at 200-300 kpa and the mold temperature was retained at 110°C. After 80 minutes, the internal rubber body casted with a polyurethane tread was detached from the mold and moved into an oven or a baking channel with an inner-temperature of 110°C, and stayed for 18 hours to achieve a final tire.
Claims

1. A manufacturing method for polyurethane-rubber composite tire, its characteristics are as follows:

Step 1: Treating an outer surface of an internal rubber body:

5 (1) the preparation of finishing agent

A solution was obtained by adding N,N-di-chloro-p-toluene sulfonamide (weight content in the range of 5 to 15) to anhydrous acetone solvent (weight content range from 85 to 95), which was dehydrated by molecular sieves, then benzoyl peroxide (weight content range from 3 to 10) was dissolved in this solution;

10 (2) Preparation of a polyurethane adhesive

A polyurethane pre-polymer with isocyanate group content range from 7 to 8 percent was prepared by using a diol with a molecular weight of 1000 to 2000 (such as polyoxymethylene glycol or polycaprolactone diol) and methylene diphenyl diisocyanate with a novel method, then a final adhesive was obtained by using 1,4-butanediol/triethanolamine mixing chain extender after the polyurethane pre-polymer had been diluted to a solution of 40 to 60 weight content with ethyl acetate;

15 (3) Surface treatment process of rubber tire body

A rubber radical tire was polished on the surface where the polyurethane tread should be applied; After trimmed clearly, the rubber tire was sprayed or coated uniformly with surface treatment agent [made in step 1 (1)] and placed for 0.5 to 1 hours or treated by plasma and placed for 0.1 to 1 hours, then the surface was sprayed or coated with the polyurethane adhesive [made in step 1 (2)] and
placed for 0.5 to 3 hours, the tire body can be used to be casted a polyurethane tread;

Step 2: preparation of polyurethane pre-polymer for tire tread

(1) a low polymerized polyol (tetramethylene-propylene oxide copolyethol)-p-phenyl-diisocyanate polyurethane system

   this polyurethane system was prepared by a novel method, in which the low polymerized polyol was polyoxytetramethylene glyol or polycaprolactone diol with a molecular weight of 1000 to 2000; The quantity of the tetramethylene-propylene oxide copolyethol was 30 to 50 percent of the system total weight, wherein the propylene oxide contend range is from 20 to 40 percent; The pre-polymer isocyanate content range is from 3.5 to 5 percent;

(2) a low polymerized polyol(polybutadiene diol)- diphenylmethane diisocyanate polyurethane system

   this polyurethane system was prepared by a novel method, in which the low polymerized polyol was polyoxytetramethylene glyol or polycaprolactone diol with a molecular weight of 1000 to 2000; The quantity of the polybutadiene diol was 15 to 30 percent of the system total weight; The pre-polymer isocyanate content range is from 5.0 to 7.0 percent;

(3) preparation of modified silicon whisker

After silicon whisker powder (100 weight content) was heated and activated, polyisocyanate (50 to 60 weight content) and anhydrous toluene (150 to 250 weight content) was added in and reacted for 1 to 2 hours at 80±2°C, then the mixture was heated to 220 to 240°C and dried for 4 to 6 hours under a less than 500Pa
vacuum atmosphere to obtain a solid, the solid was cooled and pulverized to obtain a polyisocyanate modified silicon whisker;

(4) preparation of nano-montmorillonite

Montmorillonite (5 to 10 weight content) was added in distilled water (90 to 95 weight content) to obtain a mixture; The mixture was added in tetradecyl to octadecyl trimethyl ammonium chloride (14 to 16 weight content) at 80 ± 2 °C. After 1 to 2 hour reaction with stirring, a montmorillonite suspension was obtained; Then a solid was achieved after filtration and water washing and drying; A powdered nano-montmorillonite of 50 to 90 nm was obtained by pulverizing the solid;

(5) preparation of polyurethane pre-polymer for tire tread

The modified silicon whisker [made in step 2 (3)] or the nano-montmorillonite [made in step 2 (4)] was added into the reactive system [made in step 2 (1) or (2)], then the polyurethane pre-polymer for tire tread can be obtained by a novel method, it also can be obtained by dispersing the modified silicon whisker [made in step 2 (3)] or the nano-montmorillonite [made in step 2 (4)] of 1 to 7 weight content into the polyurethane pre-polymer of 100 weight content [made in step (1) or (2)];

Step 3 manufacture of the composite tire

(1) materials

The pre-polymer [made in step 2 (5)] was transferred into A tank of a casting machine and heated to 70 to 80 °C and deaerated for 15 to 30 minutes under a less than 500 Pa vacuum atmosphere; the low molecular diol chain extender was transferred into B tank; The isocyanate content of pre-polymer was tested according to the standard method and the ratio of pre-polymer VS chain...
extender was calculated by the set chain extending coefficient, the metering pump of the polyurethane elastomer casting machine was adjusted according to the proportion and the preferable low molecular weight diol chain extender was 1,4-butanediol or hydroquinone-di-(β-hydroxyethyl) ether or/and resorcinol-di-(β-hydroxyethyl) ether with a chain extending coefficient of 0.95 to 0.98;

(2) casting

The tire body (treated in step 1) was placed into a mold which been heated to 110 to 130°C, then the casting machine was applied to mold a polyurethane tread; The mold was kept at a pressure of 200 to 300kpa and a temperature of 110 to 130°C. after 30 to 80 minutes, the internal rubber body casted with a polyurethane tread was detached from the mold and moved into an oven or a baking channel with an inner-temperature of 110 to 130°C and stayed for 12 to 24 hours to achieve a final tire.

2. According to the above manufacturing method for polyurethane-rubber composite tire, the 1,4-dihydroxybutane or hydroquinone-(β-ethylol)/resorcin (β-ethylol), whose coefficient of chain extender is 0.95-0.98, are used in the course of tire casting.