

# **AUTO-CRUSTING MICROPOROUS ELASTOMER COMPOSITION FOR USE IN POLYURETHANE FOAM-FILLED TIRE**

## **FIELD OF THE INVENTION**

- 5 The invention belongs to the field of polyurethane elastomers, involving in particular a auto-crusting microporous elastomer composition for use in polyurethane foam-filled tire.

## **BACKGROUND OF THE INVENTION**

- 10 The integral skin microcellular polyurethane elastomer is a PU foam elastomer material with surface and core once formed in the foaming process. As a new material between foam and elastomer, it combines the good mechanical properties of elastomer and the comfort of foams with many advantages such as high strength, good toughness, light weight, smooth compression stress conductivity, oil or water-resistant  
15 and excellent fatigue resistance. Its excellent buffer damping property enables it to gradually replace the traditional rubber materials and to be widely used in automotive soft parts, such as the preparation of the tires.

- At present, B material used in the preparation of polyurethane foam tires is mostly polyester semi-prepolymer, ie. the common polyurethane sole resin. The microcellular  
20 elastomer made from polyester type B material has excellent mechanical properties. The foam material shows high hardness and good elasticity. However, the polymer molecular structure contains a large number of polar ester groups. Under the action of the alternating stress, its endogenous heat increases. A high accumulation of heat easily leads to burning and loss of applicability. Therefore, the low temperature  
25 performance and dynamic mechanical properties of the polyester-based polyurethane foam tires are relatively not very good. In addition, due to the easy hydrolysis of the ester groups in the polyester polyols, the tires in hot and humid conditions are prone to molecular chain scission and decomposition. For polyester elastomer materials, the resistance to hydrolysis and fungal is pretty low.

- 30 Using polyether semi-prepolymer to prepare PU microcellular elastomer can effectively solve those problems. But the mechanical properties of the PU microcellular elastomer prepared by using conventional polyether semi-prepolymer are too low. Under the same density conditions, the skin hardness is also too low, making it difficult to achieve the surface hardness and mechanical properties  
35 requirements of polyurethane foam tires. Many patents have reported the microcellular elastomer prepared from a new low unsaturated polyether polyols has better performance. Patent CN 1341132A has reported PU microcellular elastomer used for the sole and insoles. Patent CN 1341132A has reported PU microcellular elastomer used for car armrest, car steering wheel, sole and insole. CN 1986592A has  
40 reported a way to improve the mechanical properties of the polyether type

polyurethane microcellular elastomer. But the vast majority of the microcellular elastomer material mentioned in these patents can be used only for polyurethane soles or insoles and not for polyurethane foam tires. Patent CN 101857670A claimed to use polycarbonate polyols made from carbon dioxide and epoxide in the preparation of microcellular elastomer with good mechanical properties. But it only applies to the preparation of polyurethane insole material. The polyether microcellular elastomer combination used in polyurethane tires is rarely reported in the literature.

## SUMMARY OF THE INVENTION

The technical problem to be solved by this invention is to provide a polyether-based microcellular elastomer combination used in polyurethane foam tires. The polyurethane foam tires prepared by using this composition have excellent mechanical properties, good elasticity, high skin hardness and excellent resistance to hydrolysis and fungal.

The technical solution of the present invention is: An integral skin microcellular elastomer composition used for the polyurethane foam tires. The composition consists of A and B components, of which:

(1) The A component contains polyether polyols, polymer polyols, cross-linking agent and / or chain extender, foam stabilizers, catalysts and foaming agents. Take the total mass of polyether polyols and polymer polyols as 100%, the polyether polyols content is 60 ~ 90% while the polymer polyols content is 10 ~ 40%. The percentage of other components as compared to the total weight of polyether polyols and polymer polyols are: cross-linking agent or / and chain extender 10 to 25%, foam stabilizer 0.2 to 2.5%, catalyst 0.03 to 1.0%, and foaming agent 0.01 to 10%.

(2) B component is the alcohol-modified isocyanate. -NCO content is between 18.0% and 20.0%. The raw material composition by weight percentage is: Polyether Polyol, 20~40%; Small molecule alcohols, 0~10%; Isocyanate, 50~70%.

(3) Mix component A and B by the weight ratio of 100:70 ~ 100 for the preparation of PU foam tires.

The optimal technical solutions are as follows:

The polyether polyol contained in component A is the high primary hydroxyl content and low unsaturated polyether polyol. The number average molecular weight is 5000 to 8000. The functionality is 2 to 3. The content of the primary hydroxyl is  $\geq 65\%$ . And the degree of unsaturation is  $\leq 0.008\text{meq/g}$ .

The polymer polyol contained in component A is the styrene-acrylonitrile graft modified polyether polyol. The optimal choice is one or more Dongda Chemical production of the POP36/28 POP93/28 and POP40 (commercial product).

The cross-linking agents contained in component A are glycerol, trimethylolpropane, pentaerythritol, triethanolamine, diethanolamine or the mixture of those above. The

chain extenders are 3,3 - dichloro, 4,4 - diphenyl toluene diamine, 3,5 - bis toluene diamine, 3,5 - diethyl toluene diamine, ethylene glycol, propylene glycol, 1,4 - butanediol, diethylene glycol, dipropylene glycol, 1,3 - pentanediol or the mixture of those above. The optimal choice is 1,4 - butanediol. Both cross-linking agents and chain extenders can be chosen to use in component A. One or more of the material described above can be chosen.

Foam stabilizer in component A is silicone surfactant. The optimal choice is DC3043 (commercial product) of the Air Products and Chemicals Co., Ltd. in the U.S. or 8444 (commercial product) of Goldschmidt Chemical Co., Ltd. in Shanghai.

The catalyst is organic tin catalyst and / or tertiary amine catalyst. The optimal choice is one or more of the dilaurate dibutyltin, triethyldiamine, bis (dimethyl aminoethyl) ether, and the delay equilibrium catalyst. The foaming agent is HCFC-14B.

The polyether polyols contained in component B have the following properties: The number average molecular weight is 6000 to 8000; The functionality is 3; The content of the primary hydroxyl is  $\geq 75\%$ ; And the degree of unsaturation is  $\leq 0.008\text{meq/g}$ .

The small molecule alcohols contained in component B are 1,4 - butanediol, 2 - methyl 1,3 - propylene glycol, diethylene glycol, dipropylene glycol, 1,3 - pentanediol or a mixture of those above. The optimal amount is 5% to 10% of the raw material in component B.

The isocyanate contained in component B is 4,4 - diphenyl methane diisocyanate or carbonized carbodiimide modified isocyanate.

The advantages of this invention: The polyurethane foam tires prepared from the composition of this invention have excellent mechanical properties, good elasticity and high epidermal hardness.

## DETAILED DESCRIPTION/PREFERRED EXAMPLE

The following examples further illustrate the present invention.

Example 1:

Take polyether polyols (EP-330NG by Shandong Dongda Chemical Co., Ltd.) 85kg, polymer polyols (POP36/28 by Shandong Dongda Chemical Co., Ltd.) 15kg, 1,4 - D diol 12kg, glycol 7kg, glycerol 1kg, silicone foam agent 8444 (Goldschmidt Chemical Co., Ltd. Shanghai) 0.2kg, and tertiary amines and organic tin catalyst (A-33 and T-12) 0.20kg and 0.18 kg respectively, and foaming agent of HCFC-141B 12kg. Put them in the reactor. Fully mix at 25 °C. Take out the material, Seal and store.

Take polyether polyols (EP-3600 by Shandong Dongda Chemical Co., Ltd.) 33.45kg and dipropylene glycol 1.76kg. Place them in the reactor. Heat to 100 ~ 110 °C. Dehydrate in vacuum (-0.09MPa) for 1.5 to 2 hours. Then cool to 30 to 50 °C. Add 61.62kg 4,4 - diphenyl methane diisocyanate (pure MDI). Slowly heat

to 80 ~ 85 °C. Maintain temperature and react for 1.5 to 2 hours. Add 3.17kg carbonized carbodiimide-modified MDI. Stir for 0.5 hours. Sample and test until -NCO content reaches 19.8%. Cool to 40 °C. Take out the material, Seal and store.

When used, the temperature of component A is maintained at 25 to 30 °C while component B is maintained at 30 ~ 40 °C. Rapidly mix and stir A and B microcellular material according to the weight ratio of 100:90. Centrifugal cast to mold to obtain PU microcellular elastic tire.

#### Example 2:

Take polyether polyols (EP-3600 by Shandong Dongda Chemical Co., Ltd.) 70kg, polymer polyols (POP36/28 by Shandong Dongda Chemical Co., Ltd.) 30kg, 1,4 - D diol 10kg, ethylene glycol 7kg, dipropylene glycol 2kg, glycerol 1kg, silicone foam agent DC3043 (U.S. Air Products and Chemicals Co., Ltd) 0.2kg, and tertiary amines and organic tin catalyst (A-33 and T-12) 0.3kg and 0.08kg respectively, and physical foaming agent of HCFC-141B 12kg. Put them in the reactor. Fully mix at 25 °C. Take out the material, Seal and store.

Take polyether polyols (EP-3600 by Shandong Dongda Chemical Co., Ltd.) 33.67kg and dipropylene glycol 2.53kg. Place them in the reactor. Heat to 100 ~ 110 °C. Dehydrate in vacuum (-0.09MPa) for 1.5 to 2 hours. Then cool to 30 to 50 °C. Add 60.54kg 4,4 - diphenyl methane diisocyanate (pure MDI). Slowly heat to 80 ~ 85 °C. Keep the temperature and react for 1.5 to 2 hours. Add 3.26kg carbonized carbodiimide-modified MDI. Stir for 0.5 hours. Sample and test until -NCO content reaches 19.0%. Cool to 40 °C. Take out the material, Seal and store.

When used, the temperature of component A is maintained at 25 to 30 °C while component B is maintained at 30 ~ 40 °C. Rapidly mix and stir A and B microcellular material according to the weight ratio of 100:90. Centrifugal cast to mold to obtain PU microcellular elastic tire.

#### Contrasting example 1:

A material uses the formula in Example 1. B material uses the Asahikawa chemical sole resin B8090.

#### Contrast example 2:

A material uses the formula in Example 1. B material uses Huntsman sole resin B8090.

Physical properties of the products in both examples and contrasting examples are shown in the table below:

|                               | Example 1: | Example 1: | Example 2: | Contrasting example 1: | Contrasting example 2: |
|-------------------------------|------------|------------|------------|------------------------|------------------------|
| Density/<br>Kg/m <sup>3</sup> | 850        | 500        | 500        | 500                    | 500                    |
| Shore A<br>Hardness           | 86         | 72         | 71         | 73                     | 65                     |
| Tensile<br>strength /<br>MPa  | 9.53       | 4.55       | 4.98       | 4.26                   | 4.03                   |
| Tear<br>strength /<br>KN / m  | 39.56      | 20.65      | 21.85      | 16.25                  | 16.56                  |
| Elongation /%                 | 240        | 200        | 225        | 150                    | 180                    |

The table above shows that the microcellular elastomer combination prepared by the present invention is of high performance and can replace the polyester sole resin in preparation of polyurethane microcellular elastomer tires.

## CLAIMS

1. An integral skin microcellular elastomer composition used for polyurethane foam (PU) tires, characterized in that the composition comprises (i) component A obtained  
5 by mixing polyether polyols, polymer polyols, cross-linking agent and / or chain extender, foam stabilizers, catalysts and foaming agents, wherein the total weight of polyether polyols and polymer polyols as 100%, the polyether polyols content is 60 ~ 90%, the polymer polyols content is 10 ~ 40%, and other components in percentage based on the total weight % of polyether polyols and polymer polyols are:  
10 cross-linking agent or / and chain extender: 10 to 25%, foam stabilizer: 0.2 to 2.5%, catalyst: 0.03 to 1.0%, and foaming agent 0.01 to 10%; and (ii) component B being alcohol-modified isocyanate, wherein the content of -NCO is between 18.0% and 20.0%, and the raw material composition by weight percentage is:

|    |                         |        |
|----|-------------------------|--------|
| 15 | Polyether polyol        | 20~40% |
|    | Small molecule alcohols | 0~10%  |
|    | Isocyanate              | 50~70% |

20 thereby, by mixing component A and B with the weight ratio of 100:70 – 100 for the preparation of PU foam tires.

2. The integral skin microcellular elastomer composition used for the polyurethane foam tires as claimed in claim 1, characterized in that the polyether polyol of component A is high primary hydroxyl content and low unsaturated polyether polyol,  
25 and the average molecular weight is 5000 to 8000, and the functionality is 2 to 3, and the content of the primary hydroxyl is  $\geq 65\%$ , and the degree of unsaturation is  $\leq 0.008\text{meq/g}$ .

3. The integral skin microcellular elastomer composition used for the polyurethane foam tires as claimed in claim 1, characterized in that the polymer polyol of component A is styrene-acrylonitrile graft modified polyether polyol.  
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4. A The integral skin microcellular elastomer composition used for the polyurethane foam tires as claimed in claim 1, characterized in that the cross-linking agents of component A are glycerol, trimethylolpropane, pentaerythritol, triethanolamine, diethanolamine or the mixture thereof, and the chain extenders are 3,3 – dichloro, 4,4 - diphenyl toluene diamine, 3,5 - bis toluene diamine, 3,5 - diethyl toluene diamine, ethylene glycol, propylene glycol, 1,4 - butanediol, diethylene glycol, dipropylene glycol, 1,3 – pentanediol or the mixture thereof.  
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40 5. The integral skin microcellular elastomer composition used for the polyurethane foam tires as claimed in claim 1, characterized in that the foam stabilizer of component A is silicone surfactant, and the catalyst is organic tin catalyst and / or tertiary amine catalyst and the foaming agent is HCFC-141B.

6. The integral skin microcellular elastomer composition used for the polyurethane foam tires as claimed in claim 5, characterized in that the catalyst is selected from the group consisting of dilaurate dibutyltin, tri-ethyl-diamine, bis (dimethyl aminoethyl) ether, and the delay equilibrium catalyst or the mixture thereof.

7. The integral skin microcellular elastomer composition used for the polyurethane foam tires as claimed in claim 1, characterized in that the polyether polyols of component B has average molecular weight being 6000 to 8000, and the functionality being 3, and the content of the primary hydroxyl being  $\geq 75\%$ , and the degree of unsaturation being  $\leq 0.008\text{meq/g}$ .

8. The integral skin microcellular elastomer composition used for the polyurethane foam tires as claimed in claim 1, characterized in that the small molecule alcohols of component B are 1,4 - butanediol, 2 - methyl 1,3 - propylene glycol, diethylene glycol, dipropylene glycol, 1,3 - pentanediol or the mixture thereof.

9. The integral skin microcellular elastomer composition used for the polyurethane foam tires as claimed in claim 1, characterized in that the amount of the small molecule alcohols of component B is 5-10%.

10. The integral skin microcellular elastomer composition used for the polyurethane foam tires as claimed in claim 1, characterized in that the isocyanate of component B is 4,4 - diphenyl methane diisocyanate or carbonized carbodiimide modified isocyanate.

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