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(54) Titre : FEUILLE D'ELASTOMERE THERMOPLASTIQUE A DEUX COUCHES
(54) Title: TWO-LAYER THERMOPLASTIC ELASTOMER SHEET

(57) **Abrégé/Abstract:**

Disclosed is a two-layer thermoplastic elastomer sheet comprising a skin layer [I] and a reverse surface layer [II], each layer being composed of a thermoplastic elastomer containing a polyolefin resin (A) and an α -olefin copolymer rubber (B), wherein a difference $[(I_B) - (II_B)]$ between the amount (I_B) of the α -olefin copolymer rubber (B) contained in the thermoplastic elastomer of the skin layer (I) and the amount (II_B) of the α -olefin copolymer rubber (B) contained in the thermoplastic elastomer of the reverse surface layer (II) is in the range of 5 to 85 parts by weight. The two-layer thermoplastic elastomer sheet of the invention is excellent in vacuum forming properties and can provide molded products excellent in the soft touch and having appearance of softness, appearance of flexibility and appearance of warmth. The sheet of the invention can be widely used for interior automotive trim such as an instrument panel.



ABSTRACT

Disclosed is a two-layer thermoplastic elastomer sheet comprising a skin layer [I] and a reverse surface layer [II], each layer being composed of a thermoplastic elastomer containing a polyolefin resin (A) and an α -olefin copolymer rubber (B), wherein a difference $[(I_B) - (II_B)]$ between the amount (I_B) of the α -olefin copolymer rubber (B) contained in the thermoplastic elastomer of the skin layer (I) and the amount (II_B) of the α -olefin copolymer rubber (B) contained in the thermoplastic elastomer of the reverse surface layer (II) is in the range of 5 to 85 parts by weight. The two-layer thermoplastic elastomer sheet of the invention is excellent in vacuum forming properties and can provide molded products excellent in the soft touch and having appearance of softness, appearance of flexibility and appearance of warmth. The sheet of the invention can be widely used for interior automotive trim such as an instrument panel.

TWO-LAYER THERMOPLASTIC ELASTOMER SHEETFIELD OF THE INVENTION

The present invention relates to a two-layer
5 thermoplastic elastomer sheet. More particularly, the
invention relates to a two-layer thermoplastic elastomer
sheet which is excellent in vacuum forming properties and
can provide molded products of excellent in the soft
touch..

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BACKGROUND OF THE INVENTION

Polyvinyl chloride (PVC) resins have been heretofore
widely used as materials for interior automotive trim.
However, the automotive trim made of the polyvinyl chloride
15 resins have problems in various properties such as heat
resistance, low-temperature resistance, heat aging
characteristics, light resistance, anti-fogging properties,
odor development, lack of the soft touch and cheap-looking
appearance. For this reason, polyolefin thermoplastic
20 elastomers excellent in those properties are paid much
attention as replacements of the polyvinyl chloride resins.

In the case of using the polyolefin thermoplastic
elastomer for a vacuum forming sheet, a rubber content in
the polyolefin thermoplastic elastomer needs to be reduced
25 from the viewpoint of vacuum forming properties. However,
if a sheet made of the polyolefin thermoplastic elastomer

having a low content of rubber is subjected to vacuum forming, the resulting molded product is rigid and lacking in soft touch (softness).

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OBJECT OF THE INVENTION

The present invention is to solve the above-mentioned problems existing in the prior arts, and it is an object of the invention is to provide a two-layer thermoplastic elastomer sheet which is excellent in vacuum forming properties and can produce molded products excellent in the soft touch.

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SUMMARY OF THE INVENTION

There is provided by the present invention a two-layer thermoplastic elastomer sheet comprising a skin layer [I] and a reverse surface layer [II], wherein:

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the skin layer is composed of a thermoplastic elastomer containing a polyolefin resin (A) in an amount of 1 to 85 parts by weight and an α -olefin copolymer rubber (B) in an amount of 99 to 15 parts by weight, total amount of (A) and (B) being 100 parts by weight;

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the reverse surface layer [II] is composed of a thermoplastic elastomer containing a polyolefin resin (A) in an amount of 6 to 90 parts by weight and an α -olefin copolymer rubber (B) in an amount of 94 to 10 parts by

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weight, total amount of (A) and (B) being 100 parts by weight; and

a difference $[(I_B) - (II_B)]$ between the amount (I_B) of the α -olefin copolymer rubber (B) contained in the

5 thermoplastic elastomer of the skin layer (I) and the amount (II_B) of the α -olefin copolymer rubber (B) contained in the thermoplastic elastomer of the reverse surface layer (II) is in the range of 5 to 85 parts by weight.

If a light stabilizer is added to the thermoplastic
10 elastomer constituting the skin layer [I] and a flame-retardant is added to the thermoplastic elastomer constituting the reverse surface layer [II], there can be obtained a two-layer thermoplastic elastomer sheet capable of producing a molded product which is excellent in light
15 resistance and flame retardance and is free from occurrence of bleedout.

At the same time the two-layer thermoplastic elastomer sheet can provide molded products having excellent vacuum forming properties and the soft touch.

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DETAILED DESCRIPTION OF THE INVENTION

The two-layer thermoplastic elastomer sheet of the present invention is concretely described below.

The two-layer thermoplastic elastomer sheet of the
25 invention comprises a skin layer [I] and a reverse surface layer [II], and these layers are composed of thermoplastic

elastomers (TPE) of different kinds which differ in the amounts of a polyolefin resin (A) and an α -olefin copolymer rubber (B) contained therein.

Examples of the polyolefin resins (A) include
5 homopolymers of ethylene or propylene, and copolymers of ethylene or propylene with a small amount of other polymerizable monomer (e.g., propylene-ethylene copolymer, propylene-1-butene copolymer, propylene-1-hexene copolymer, propylene-4-methyl-1-pentene copolymer). As the above-
10 mentioned other polymerizable monomers of a small amount, there can be mentioned vinyl acetate, ethyl acrylate and methacrylic acid. In the invention, the melt index (ASTM-D-1238-65T, 230 °C) of the polyolefin resin is preferably within the range of 0.1 to 100, more preferably 5 to 50.

15 As the polyolefin resin, a mixture of polyethylene (particularly, low-density polyethylene) and polypropylene having a mixing ratio of 10/90 to 70/30 (polyethylene/polypropylene) can be used for the purpose of enhancing forming properties (formability) and resistance
20 of damage of the resulting sheet.

The α -olefin copolymer rubber (B) employable in the invention is an amorphous elastomeric copolymer containing olefin as a host component, such as ethylene-propylene copolymer rubber, propylene-ethylene copolymer rubber,
25 ethylene-propylene non-conjugated diene copolymer rubber, propylene-ethylene non-conjugated diene copolymer rubber,

ethylene-butadiene copolymer rubber and propylene-butadiene copolymer rubber. Further, the α -olefin copolymer rubber is a rubber which is reduced in flowability or loses flowability by the crosslinking when it is mixed with organic peroxide and kneaded therewith under heating. The non-conjugated diene is a generic name to dicyclopentadiene, 1,4-hexadiene, dicyclooctadiene, methylene norbornene, ethylidene norbornene, etc. Of these copolymer rubbers, ethylene-propylene non-conjugated diene copolymer rubber, particularly ethylene-propylene-ethylidenenorbornene copolymer rubber, is preferably used in the invention, because a thermoplastic elastomer molded product excellent in heat resistance, tensile characteristics and impact resilience can be obtained. The Mooney viscosity [ML_{1+4} (100 °C)] of the copolymer rubber is preferably in the range of 10 to 120, more preferably 40 to 80. In the case of using a copolymer rubber having Mooney viscosity of the above range, a thermoplastic elastomer product having high tensile characteristics can be obtained. The iodine value (degree of unsaturation) of the copolymer rubber is preferably not more than 16. In the thermoplastic elastomer constituting the skin layer [I] of the two-layer thermoplastic elastomer sheet of the invention, the polyolefin resin (A) is used in an amount of 1 to 85 parts by weight, preferably 20 to 80 parts by weight, more preferably 30 to 50 parts by weight,

and the α -olefin copolymer rubber (B) is used in an amount of 99 to 15 parts by weight, preferably 80 to 20 parts by weight, more preferably 70 to 50 parts by weight, per 100 parts by weight of the sum of the polyolefin resin (A) and the α -olefin copolymer rubber (B).

In the thermoplastic elastomer constituting the reverse surface layer [II] of the two-layer thermoplastic elastomer sheet of the invention, the polyolefin resin (A) is used in an amount of 6 to 90 parts by weight, preferably 20 to 80 parts by weight, more preferably 30 to 50 parts by weight, and the α -olefin copolymer rubber (B) is used in an amount of 94 to 10 parts by weight, preferably 80 to 20 parts by weight, more preferably 70 to 50 parts by weight, per 100 parts by weight of the sum of the polyolefin resin (A) and the α -olefin copolymer rubber (B). The total amount of the polyolefin resin (A) and the α -olefin copolymer rubber (B) is 100 parts by weight. A difference $[(I_B) - (II_B)]$ between the amount (I_B) of the α -olefin copolymer rubber (B) contained in the thermoplastic elastomer of the skin layer (I) and the amount (II_B) of the α -olefin copolymer rubber (B) contained in the thermoplastic elastomer of the reverse surface layer (II) is in the range of 5 to 85 parts by weight, preferably 10 to 70 parts by weight, more preferably 15 to 50 parts by weight.

When two kinds of the thermoplastic elastomers having a difference of the above range in the content of the α -olefin copolymer rubber (B) are used, a two-layer sheet having high vacuum forming properties and capable of
5 producing a molded product especially soft in the touch

In the invention, the thermoplastic elastomers of the skin layer [I] and the reverse surface layer [II] constituting a two-layer sheet may contain a peroxide non-crosslinkable hydrocarbon gum rubber (C) and/or a mineral
10 oil softening agent (D) in addition to the polyolefin resin (A) and the α -olefin copolymer rubber (B).

The peroxide non-crosslinkable hydrocarbon gum rubber (C) employable in the invention is a gum rubber of hydrocarbon type which is not crosslinked and is not
15 reduced in flowability even when it is mixed with peroxide and kneaded therewith under heating. Examples of the gum rubber include polyisobutylene, butyl rubber (IIR), propylene-ethylene copolymer rubber having propylene content of not less than 70 % by mole, and atactic
20 polypropylene. Of these, polyisobutylene and butyl rubber are most preferred because of good performance and easy handling.

The peroxide non-crosslinkable hydrocarbon gum rubber (C) shows an effect to improve flowability of a
25 thermoplastic elastomer composition. In the invention, suitably employed is a peroxide non-crosslinkable

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hydrocarbon gum rubber having Mooney viscosity [ML₁₊₄ (100 °C)] of not more than 60.

The peroxide non-crosslinkable hydrocarbon gum rubber (C) is used in the invention in an amount of 5 to 100 parts by weight, preferably 10 to 50 parts by weight, more preferably 15 to 40 parts by weight, per 100 parts by weight of the sum of the polyolefin resin (A) and the α -olefin copolymer rubber (B).

The mineral oil softening agent (D) employable in the invention is a high-boiling petroleum cut which is generally used for mitigating intermolecular force of rubber to facilitate processing of rubber in the roll-processing procedure, assisting dispersibility of carbon black, white carbon, etc. added as a filler, or reducing rigidity of vulcanized rubber to increase flexibility and elasticity thereof. The mineral oil softening agent is classified into paraffin type, naphthene type, aromatic type, etc.

A molded product obtained from a thermoplastic elastomer composition containing the naphthene type mineral oil softening agent shows less surface tackiness as compared with a molded product obtained from a thermoplastic elastomer composition containing paraffin type mineral oil softening agent, so that the naphthene type mineral oil softening agent is more preferably used in

the invention than the paraffin type mineral oil softening agent.

In the invention, the mineral oil softening agent (D) is used in an amount of 5 to 100 parts by weight, preferably 10 to 80 parts by weight, more preferably 20 to 70 parts by weight, per 100 parts by weight of the sum of the polyolefin resin (A) and the α -olefin copolymer rubber (B).

The two-layer thermoplastic elastomer sheet of the invention may contain other additives, provided that the addition of the additives does not mar the object of the invention. Examples of the additives include polyolefin plastics such as high-density polyethylene, intermediate density polyethylene, low-density polyethylene, isotactic polypropylene and propylene- α -olefin copolymer; inorganic fillers such as calcium carbonate, calcium silicate, clay, kaolin, talc, silica, diatomaceous earth, mica powder, asbestos, alumina, barium sulfate, aluminum sulfate, calcium sulfate, basic magnesium carbonate, molybdenum disulfide, graphite, glass bulb and shirasu balloon; and colorants such as carbon black, titanium oxide, zinc white, blood red, ultramarine blue, Milori blue, azo pigment, nitroso pigment, lake pigment and phthalocyanine pigment.

Further, the two-layer thermoplastic elastomer sheet of the invention there may be used known heat stabilizers such as heat stabilizers of phenol type, sulfite type,

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phenylalkane type, phosphite type and amine type, aging-inhibiting agent, weathering stabilizer, antistatic agent, metallic soap, and lubricant such as wax. They can be added in such an amount as generally used for conventional polyolefin resins or α -olefin copolymer rubbers.

If a light stabilizer such as ultraviolet absorbing agent, light absorbing agent and hindered amines is added to the thermoplastic elastomer constituting the skin layer [I] of the two-layer thermoplastic elastomer sheet of the invention and a flame-retardant is added to the thermoplastic elastomer constituting the reverse surface layer [II] thereof, there can be obtained a two-layer thermoplastic elastomer sheet capable of providing a molded product which is excellent in light resistance and flame retardance and free from occurrence of bleedout that causes marked deterioration in merchandise value.

However, if the light stabilizer and the flame-retardant are together added to and allowed to present in the same thermoplastic elastomer according to the prior art, occurrence of bleedout could not be prevented.

There is no specific limitation on the light stabilizer and the flame-retardant employable in the invention, provided that they are generally used for conventional polyolefin thermoplastic elastomers.

Concrete examples of the light stabilizers preferably used in the invention include antioxidants of hindered

phenol type represented by pentaerythritol-tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] and octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate; and light stabilizers of hindered amine type represented by
5 bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate.

In the case of using the above-mentioned light stabilizers of hindered amine type, light stabilizers of benzotriazole type represented by 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole can be employed in
10 combination. The antioxidants of hindered phenol type and the light stabilizers of hindered amine type may be used singly or in combination.

The amount of the light stabilizer used in the invention is generally in the range of 0.01 to 0.3 phr,
15 preferably 0.05 to 0.2 phr.

Concrete examples of the flame-retardants preferably used in the invention include inorganic flame-retardants represented by antimony oxide and aluminum hydroxide; and halogen type flame-retardants represented by
20 decabromodiphenyl ether and chlorinated polyethylene.

The organic flame-retardant and the halogen type flame-retardant can be employed singly or in combination.

When the inorganic flame-retardant is used, the amount of the flame-retardant used in the invention is generally
25 in the range of 10 to 200 phr, preferably 5 to 150 phr.

When the halogen type flame-retardant was used, the amount

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of the flame-retardant used is generally in the range of 10 to 100 phr, preferably 25 to 55 phr.

The thermoplastic elastomer as mentioned above can be obtained, for example, by dynamically heat-treating a blend
5 of the above-mentioned components in the presence of organic peroxide to be partially crosslinked.

The expression "dynamically heat-treating a blend" means that a blend is kneaded in the molten state of dissolution.

10 Concrete examples of organic peroxides employable for preparing the thermoplastic elastomer in the invention include dicumyl peroxide, di-tert-butylperoxide, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexine-3, 1,3-bis(tert-
15 butylperoxyisopropyl)benzene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-bis(tert-butylperoxy)valerate, benzoyl peroxide, p-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, tert-butylperoxybenzoate, tert-butylperbenzoate, tert-
20 butylperoxyisopropyl carbonate, diacetyl peroxide, lauroyl peroxide and tert-butylcumyl peroxide.

Of these, from the viewpoints of odor development and scorching stability, preferred are 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-
25 butylperoxy)hexine-3, 1,3-bis(tert-butylperoxyisopropyl)benzene, 1,1-bis(tert-butylperoxy)-

3,3,5-trimethylcyclohexane and n-butyl-4,4-bis(tert-butylperoxy)valerate, and most preferred is 1,3-bis(tert-butylperoxyisopropyl)benzene.

The amount of the organic peroxide used in the invention generally is in the range of 0.05 to 3 % by weight, preferably 0.1 to 1 % by weight, more preferably 0.1 to 0.5 % by weight, based on the total amount of the above-mentioned components (A), (B) and (C). When the amount of the organic peroxide is within the above range, the obtained thermoplastic elastomer becomes excellent in properties required for rubbers such as heat resistance, tensile characteristics, elastic recovery and impact resilience as well as excellent in strength and formability.

As the kneading apparatus, an extruder is used in the invention. Particularly, an unopened extruder is preferably used. Kneading is preferably carried out in an atmosphere of inert gas such as nitrogen or carbonic acid gas. In the invention, kneading is carried out at such a temperature that the half-life of the used organic peroxide becomes shorter than 1 minute (generally at a temperature of 150 to 280 °C, preferably 170 to 240 °C), for 1 to 20 minutes, preferably 1 to 10 minutes. The shearing force applied in the kneading procedure is in the range of 10 to 10^4 sec^{-1} , preferably 10^2 to 10^3 sec^{-1} , in terms of a shear rate.

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In the aforementioned partially crosslinking processing using the organic peroxide in the invention, there can be added crosslinking assistants such as sulfur, p-quinonedioxime, p,p'-dibenzoylquinonedioxime, N-methyl-
5 N,4-dinitrosoaniline, nitrobenzene, diphenyl guanidine and trimethylolpropane-N,N'-m-phenylenedimaleimide; polyfunctional methacrylate monomers such as divinyl benzene, triallyl cyanurate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate,
10 polyethylene glycol dimethacrylate, trimethylolpropane trimethacrylate and allyl methacrylate; and polyfunctional vinyl monomers such as vinyl butyrate and vinyl stearate. By the use of these compounds, homogeneous and moderate crosslinking reaction can be expected. Of these compounds,
15 divinyl benzene is most preferably used in the invention, because it can be easily handled and is compatible with the α -olefin copolymer rubber and the polyolefin resin which are main components of the blend to be treated. Further, divinyl benzene has solvency action for the organic
20 peroxide and serves as a dispersing assistant of the peroxide, so that a composition having homogeneous crosslinking effect and good balance between flowability and physical properties can be obtained. In the invention, the crosslinking assistant or the polyfunctional vinyl
25 monomer is used in an amount of 0.1 to 2 % by weight, preferably 0.3 to 1 % by weight, based on the total amount

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of the blend to be treated. When they are used in such amount, obtainable is a composition which shows high flowability and brings about no change in physical properties caused by heating history in the molding
5 procedure.

Decomposition accelerators such as tertiary amines (e.g., triethylamine, tributylamine and 2,4,6-tris(dimethylamino)phenol) and naphthenic acid salts (e.g., aluminum, cobalt, vanadium, copper, calcium, zirconium,
10 manganese, magnesium, lead and mercury) can be used to accelerate decomposition of the organic peroxide.

As described above, the thermoplastic elastomer is partially crosslinked when it is dynamically heat-treated in the presence of the organic peroxide.

15 In the invention, the expression "the thermoplastic elastomer is partially crosslinked" means that the gel content measured by the following method is not less than 20 %, preferably in the range of 20 to 99.5 %, more preferably 45 to 98 %.

20 Measurement of gel content

100 mg of a specimen of the thermoplastic elastomer is weighed out, and it is cut into pieces having a size of 0.5 mm × 0.5 mm × 0.5 mm. The pieces of the specimen are immersed in 30 ml of cyclohexane at 23 °C for 48 hours in a
25 sealed container, then the residue is taken out of the container onto a filter paper, and dried at room

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temperature for 72 hours until the weight of the specimen becomes constant.

From the weight of the dried residue are subtracted the total weight of the cyclohexane-insoluble components (fibrous filler, filler, pigment, etc.) other than the polymer component and the weight of the polyolefin resin component contained in the specimen before immersing in cyclohexane, and the obtained value is "compensated final weight (Y)".

10 On the other hand, the weight of the α -olefin copolymer rubber contained in the specimen, namely, the value obtained by subtracting the weight of the cyclohexane-soluble component 1 (e.g., mineral oil and plasticizer) other than the α -olefin copolymer rubber, the
15 weight of the polyolefin resin component 2 and the weight of the cyclohexane-insoluble component 3 (e.g., fibrous filler, filler and pigment) other than the polymer component from the weight of the specimen, is "compensated initial weight (X)".

20 The gel content is determined by the following formula:

$$\text{Gel content (wt.\%)} = \frac{\text{Compensated final weight (Y)}}{\text{Compensated initial weight (X)}} \times 100$$

25

In the present invention, the light stabilizers and the flame-retardants are added at any steps, constituting the process for producing the thermoplastic elastomer composition. However, it is preferred that the flame-
5 retardant is added to the thermoplastic elastomer by using an extruder or Banbury mixer intermediately or with an elapse of time after the dynamically heat-treatment in the presence of the organic peroxide.

In the invention, the skin layer [I] composed of the
10 thermoplastic elastomer constitutes a skin layer of a vacuum forming molded product. The thickness of the skin layer [I] constituting a skin layer of the vacuum forming molded product is generally in the range of 0.01 to 50 mm, preferably 0.10 to 20 mm, while the thickness of the other
15 layer [II] constituting the inner layer of the vacuum forming molded product is generally in the range of 0.01 to 100 mm, preferably 0.10 to 50 mm.

The two-layer thermoplastic elastomer sheet of the invention can be obtained by fusing the above-mentioned two
20 kinds of the thermoplastic elastomers to each other utilizing, for example, conventionally known extrusion laminating method or injection molding method.

Otherwise, the two-layer thermoplastic elastomer sheet of the invention can be also obtained by fusing two kinds
25 of sheets having been beforehand molded, which constitutes the skin layer [I] and the reverse surface layer [II] of

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the two-layer sheet, at a temperature not lower than the temperature at which at least one of the two sheets is melted using a calender roll molding machine, a compression molding machine, etc.

5 Further, the two-layer thermoplastic elastomer sheet of the invention can be also obtained by fusing a beforehand molded sheet which constitutes the skin layer [I] or the reverse surface layer [II] of the two-layer sheet to a sheet which constitutes the reverse surface
10 layer [II] or the skin layer [I] of the two-layer sheet at the time when the latter sheet is prepared by extrusion molding or calendering.

 The two-layer thermoplastic elastomer sheet of the invention is generally subjected to vacuum forming with
15 other core materials to produce a molded product being particularly soft in the touch.

EFFECT OF THE INVENTION

 The two-layer thermoplastic elastomer sheet of the
20 invention is excellent in vacuum forming properties and can provide a molded product excellent in the soft touch.

 Further, the two-layer thermoplastic elastomer sheet of the invention also shows softness, flexibility and warmth in its appearance.

25 The two-layer thermoplastic elastomer sheet of the invention having the above-mentioned effects can be widely

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employed for various interior automotive trim such as instrument panel.

The present invention is further described by the following examples, but the examples are given by no means to
5 restrict the invention.

At first, methods for evaluating vacuum forming properties (formability) and the soft touch of two-layer thermoplastic elastomer sheets obtained by an example and comparative examples and single-layer sheets produced using
10 the components of the two-layer sheets are described below.

[Evaluation Method]

(1) Evaluation on vacuum forming properties (formability)

The sheet is subjected to vacuum forming using a drape
15 forming mold until the extensibility of the sheet becomes 250 % and 400 %, and then occurrence of sheet break is observed.

Condition of drape forming: upper and lower heaters are operated so that the surface temperature of the sheet
20 is 150 °C.

(2) Evaluation on the soft touch

The surface of the vacuum forming molded product is touched with fingers, and the touch is classified into 5 levels.

25 5: very soft
 4: soft

- 3: normal
- 2: hard
- 1: very hard

5

EXAMPLE 1

In the first place, pellets of two kinds of thermoplastic elastomers (referred to hereinafter as TPE (I) and TPE (II)) were prepared as follows.

10

[Preparation of pellet of TPE (I)]

37 parts by weight of an isotactic polypropylene resin (i) [melt flow rate: 13 g/10 min (230 °C)], 63 parts by weight of an ethylene-propylene-ethylidenenorbornene terpolymer rubber (ii) [ethylene unit / propylene unit (molar ratio): 78/22, iodine value: 15, Mooney viscosity ML₁₊₄ (121 °C): 61], and 30 parts by weight of a naphthene type process oil (iii) were kneaded at 180 °C for 5 minutes in a nitrogen atmosphere using Banbury mixer. Then, the obtained kneadate was cut into angular pellets using a sheet cutter.

20

Thereafter, with 100 parts by weight of the angular pellets was kneaded 1 part by weight of a mixture (iv) of 20 wt.% of 1,3-bis(tert-butylperoxyisopropyl)benzene, 30 wt.% of divinyl benzene and 50 wt.% of a paraffin mineral oil in Henschel mixer. Then, the obtained kneadate was extruded at 220 °C in a nitrogen atmosphere using an

25

extruder, to prepare pellets of a thermoplastic elastomer [TPE (1)].

[Preparation of pellet of TPE (II)]

5 The above procedure for preparing the pellets of TPE (I) was repeated except for using the isotactic polypropylene resin (i) in an amount of 50 parts by weight and the ethylene-propylene-ethylidenenorbornene terpolymer rubber (ii) in an amount of 50 parts by weight, to prepare
10 pellets of a thermoplastic elastomer [TPE (II)].

Then, a skin layer sheet of a two-layer sheet was prepared from the above pellets of TPE (I) in the following manner.

15

[Preparation of TPE (I) sheet]

The pellets of TPE (I) were melted at 220 °C and subjected to calendering using a calendering molding machine (produced by NIPPON Roll, Co., Ltd.), to obtain a
20 thermoplastic elastomer [TPE (I)] sheet having a thickness of 0.3 mm.

[Preparation of two-layer sheet]

The pellets of TPE (II) were melted at 220 °C, and the
25 obtained molten TPE (II) was coated on the reverse surface of the above TPE (I) sheet using a calendering molding

machine (produced by NIPPON Roll, Co., Ltd.), to obtain a two-layer thermoplastic elastomer sheet having a thickness of 0.9 mm.

The obtained two-layer thermoplastic elastomer sheet
5 was evaluated on the vacuum forming properties and the soft touch according to the aforementioned evaluation methods.

The results are set forth in Table 1.

COMPARATIVE EXAMPLE 1

10 A thermoplastic elastomer [TPE (I)] sheet having a thickness of 9 mm was prepared in the same manner as that for preparing the TPE (I) sheet in Example 1.

Thus prepared sheet was evaluated on the vacuum forming properties and softness according to the
15 aforementioned evaluation methods.

The results are set forth in Table 1.

COMPARATIVE EXAMPLE 2

The procedure for preparing the TPE (I) sheet in
20 Example 1 was repeated except that pellets of TPE (II) was used instead of the pellets of TPE (I), to prepare a thermoplastic elastomer [TPE (II)] sheet having a thickness of 0.9 mm.

Thus prepared sheet was evaluated on the vacuum
25 forming properties and softness according to the aforementioned evaluation methods.

The results are set forth in Table 1.

COMPARATIVE EXAMPLE 3

[Preparation of pellet of TPE (III)]

5 The procedure for preparing the pellets of TPE (I) in
Example 1 was repeated except for using the isotactic
polypropylene resin (i) in an amount of 10 parts by weight
and the ethylene-propylene-ethylidenenorbornene terpolymer
rubber (ii) in an amount of 90 parts by weight, to prepare
10 pellets of a thermoplastic elastomer [TPE (III)].

[Preparation of pellet of TPE (IV)]

 The procedure for preparing the pellets of TPE (I) in
Example 1 was repeated except for using the isotactic
15 polypropylene resin (i) in an amount of 97 parts by weight
and the ethylene-propylene-ethylidenenorbornene terpolymer
rubber (ii) in an amount of 3 parts by weight, to prepare
pellets of a thermoplastic elastomer [TPE (IV)].

20 Then, a skin layer sheet of a two-layer sheet was
prepared from the above pellets of TPE (III) in the
following manner.

[Preparation of TPE (III) sheet]

25 The pellets of TPE (III) were melted at 220 °C and
subjected to calendering using a calendering molding

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machine (produced by NIPPON Roll, Co., Ltd.), to obtain a thermoplastic elastomer [TPE (III)] sheet having a thickness of 0.3 mm.

5 [Preparation of two-layer sheet]

The pellets of TPE (IV) were melted at 220 °C, and the obtained molten TPE (IV) was coated on the reverse surface of the above TPE (III) sheet using a calendering molding machine (produced by NIPPON Roll, Co., Ltd.), to obtain a
10 two-layer thermoplastic elastomer sheet having a thickness of 0.9 mm.

The obtained two-layer thermoplastic elastomer sheet was evaluated on the vacuum forming properties and the soft touch according to the aforementioned evaluation methods.

15 The results are set forth in Table 1.

COMPARATIVE EXAMPLE 4

[Preparation of pellet of TPE (V)]

20 The procedure for preparing the pellets of TPE (I) in Example 1 was repeated except for using the isotactic polypropylene resin (i) in an amount of 40 parts by weight and the ethylene-propylene-ethylidenenorbornene terpolymer rubber (ii) in an amount of 60 parts by weight, to prepare
25 pellets of a thermoplastic elastomer [TPE (V)].

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[Preparation of two-layer sheet]

The pellets of TPE (V) were melted at 220 °C, and the obtained molten TPE (V) was coated on the reverse surface of the TPE (I) sheet of Example 1 using a calendering
5 molding machine (produced by NIPPON Roll, Co., Ltd.), to obtain a two-layer thermoplastic elastomer sheet having a thickness of 0.9 mm.

The obtained two-layer thermoplastic elastomer sheet was evaluated on the vacuum forming properties and softness
10 according to the aforementioned evaluation methods.

The results are set forth in Table 1.

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Table 1

	Ex. 1	Com. Ex. 1	Com. Ex. 2	Com. Ex. 3	Com. Ex. 4
Structure of vacuum forming molded product	skin layer of TPE (I), reverse surface layer of TPE (II)	single layer of TPE (I)	single layer of TPE (II)	skin layer of TPE (III), reverse surface layer of TPE (IV)	skin layer of TPE (I), reverse surface layer of TPE (V)
Difference of rubber content [part by weight]	13	-	-	87	3
Vacuum forming properties					
Extensibility of 250 %	break is not observed	break is not observed	break is not observed	break is observed	break is not observed
Extensibility of 400 %	break is not observed	break is observed	break is not observed	break is observed	break is observed
Softness					
Extensibility of 250 %	5	5	3	5	5
Extensibility of 400 %	5	5	3	5	5

Note: Difference of rubber content in Table 1 is obtained by the formula of [(rubber content of skin layer) - (rubber content of reverse surface layer)].

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CLAIMS:

1. A two-layer thermoplastic elastomer sheet comprising a skin layer [I] and a reverse surface layer [II], wherein:

5 said skin layer is composed of a thermoplastic elastomer containing a polyolefin resin (A) in an amount of 1 to 85 parts by weight and an α -olefin copolymer rubber (B) in an amount of 99 to 15 parts by weight, total amount of (A) and (B) being 100 parts by weight;

10 said reverse surface layer [II] is composed of a thermoplastic elastomer containing a polyolefin resin (A) in an amount of 6 to 90 parts by weight and an α -olefin copolymer rubber (B) in an amount of 94 to 10 parts by weight, total amount of (A) and (B) being 100 parts by
15 weight; and

 a difference $[(I_B) - (II_B)]$ between the amount (I_B) of the α -olefin copolymer rubber (B) contained in the thermoplastic elastomer of the skin layer (I) and the amount (II_B) of the α -olefin copolymer rubber (B) contained
20 in the thermoplastic elastomer of the reverse surface layer (II) is in the range of 5 to 85 parts by weight.

2. The two-layer thermoplastic elastomer sheet as claimed in claim 1, wherein the thermoplastic elastomer
25 constituting the skin layer [I] contains a peroxide non-

crosslinkable hydrocarbon gum rubber (C) and/or a mineral oil softening agent (D).

3. The two-layer thermoplastic elastomer sheet as claimed in claim 1 or claim 2, wherein the thermoplastic elastomer constituting the reverse surface layer [II] contains a peroxide non-crosslinkable hydrocarbon gum rubber (C) and/or a mineral oil softening agent (D).

4. The two-layer thermoplastic elastomer sheet as claimed in any of claim 1 to claim 3, wherein the thermoplastic elastomer constituting the skin layer [I] contains a light stabilizer and the thermoplastic elastomer constituting the reverse surface layer [II] contains a flame-retardant.

5. The two layer thermoplastic elastomer sheet as claimed in claim 1 or 2, wherein:

the polyolefin resin (A) is a homopolymer of ethylene or propylene or is a copolymer of ethylene/propylene or of a major amount of ethylene or propylene and a small amount of another polymerizable monomer selected from the group consisting of 1-butene, 1-hexene, 4-methyl-1-pentene, vinyl acetate, ethyl acrylate and methacrylic acid and the polyolefin resin (A) has a melt index (ASTM-D 1238-65T at 230 °C) of 0.1 to 100;

the α -olefin copolymer rubber (B) is an amorphous elastomeric copolymer containing an α -olefin as a host component and being selected from the group consisting of ethylene/propylene copolymer rubber, propylene/ethylene copolymer rubber, ethylene/propylene/non-conjugated diene copolymer rubber, propylene/ethylene/non-conjugated diene copolymer rubber, ethylene/butadiene copolymer rubber and propylene/butadiene copolymer rubber; the α -olefin copolymer rubber (B) has been partially crosslinked by kneading the rubber under heat in a molten state in the presence of an organic peroxide to reduce its flowability; and

the α -olefin copolymer rubber (B) has a Mooney viscosity [ML₁₊₄ (100°C)] of 10 to 120 before being subjected to the kneading under heat.

6. The two layer thermoplastic elastomer sheet as claimed in claim 5, wherein the polyolefin resin (A) is polypropylene resin having a melt index (ASTM-D 1238-65T at

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230°C) of 5 to 50.

7. The two layer thermoplastic elastomer sheet as claimed in claim 5 or 6, wherein the α -olefin copolymer rubber (B) is ethylene/propylene/non-conjugated diene copolymer rubber
5 having a Mooney viscosity $[ML_{1+4} (100^\circ C)]$ of 10 to 80 before being subjected to the kneading under heat.

8. The two layer thermoplastic elastomer sheet as claimed in any one of claims 1 to 4, wherein at least one of the thermoplastic elastomers of the skin layer and the reverse
10 surface layer is partially crosslinked.

9. The two layer thermoplastic elastomer sheet as claimed in claim 8, wherein only the thermoplastic elastomer of the skin layer is partially crosslinked.

10. The two layer thermoplastic elastomer sheet as
15 claimed in claim 8, wherein the thermoplastic elastomers of both the skin and reverse surface layers are partially crosslinked.

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