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(54) Title: CYCLIC BLOCK COPOLYMER COMPOSITIONS AND ARTICLES OF MANUFACTURE FABRICATED THEREFROM

(57) Abstract: Convert cyclic block copolymer compositions into mono-layer sheets or multi-layer sheets that have at least one cyclic block copolymer composition layer and transform the sheets into articles of manufacture such as orthodontic appliances.



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CYCLIC BLOCK COPOLYMER COMPOSITIONS AND ARTICLES OF
MANUFACTURE FABRICATED THEREFROM

This application is a non-provisional application claiming priority from the U.S.
Provisional Patent Application No. 61/122,931, filed on December 16, 2008, entitled

5 "CYCLIC BLOCK COPOLYMER COMPOSITIONS AND ARTICLES OF
MANUFACTURE FABRICATED THEREFROM," the teachings of which are
incorporated by reference herein, as if reproduced in full hereinbelow.

This invention relates to cyclic block copolymer (CBC) compositions, mono-layer
sheets fabricated from such compositions, multi-layer sheets having at least one layer
10 fabricated from such compositions, and articles of manufacture (e.g. an orthodontic
appliance) fabricated, at least in part, from a mono-layer sheet, a multi-layer sheet or both a
mono-layer sheet and a multi-layer sheet.

A growing trend exists that focuses on use of clear, transparent plastic orthodontic
devices to align human teeth. Growth stems, at least in part, from ease of use and relative
15 aesthetic beauty relative to conventional orthodontic braces or devices based upon metal.

Manufacturers of plastic orthodontic devices desire a plastic material that allows for
or promotes movement of human teeth in a controlled, uniform and safe manner for as large
a portion of the human population as possible. In attempts to satisfy this desire,
manufacturers currently use transparent, thermoplastic resins or materials such as rigid,
20 thermoplastic polyurethane (TPU), polycarbonate (PC) or saturated polyester. Devices
fabricated from PC resins tend to undergo environmental stress cracking when exposed to
human saliva. Devices fabricated from rigid TPU or polyester resins often show undesirable
levels of creep when exposed to human saliva, possibly due in part to a tendency of such
resins toward plasticization when immersed in water.

25 United States Patent (US) 6,964,564 (Phan et al.) discloses improved devices,
systems and methods for repositioning teeth from an initial tooth arrangement to a final
tooth arrangement. The system comprises a series of polymeric shell appliances configured
to receive teeth and incrementally reposition individual teeth in a series of incremental steps.
See also related USP 6,454,565 (Phan et al.) and USP 6, 424,101 (Phan et al.).

30 United States Patent Application Publication (USPAP) 2006/0078841 (DeSimone et
al.) teaches forming a polymeric shell of a removable dental positioning appliance from
transparent polymeric materials having a tensile strength at yield of greater than 6,000

pounds per square inch (psi), an elongation at yield of greater than 4%, an elongation at break of greater than 80%, a tensile modulus greater than 200,000 psi, a flexural modulus greater than 200,000 psi, stress relaxation over time of not more than 50%, and a transmissivity of light between 400 nm and 800 nm greater than 75%.

5 In some aspects, this invention is a CBC composition, the composition comprising a CBC that is a substantially fully hydrogenated vinyl aromatic-conjugated diene block copolymer, said substantially fully hydrogenated block copolymer having an elongation strain at break of more than 30% and a modulus that is within a range of from greater than or equal to 150,000 pounds per square inch (psi) (1034 megapascals (MPa) to less than
10 270,000 psi (1862 MPa). Determine both elongation strain at break and modulus in accord with American Society for Testing and Materials (ASTM) Test D638-02a.

In some aspects, the CBC is a functionalized CBC. Examples include but not restricted to, silane-grafted CBCs, maleic anhydride grafted CBCs, acrylate-grafted CBCs, methacrylate-grafted CBCs and siloxanes-grafted CBCs. Silane-grafted CBCs employ a
15 grafting moiety such as vinyl trimethoxy silane (VTMS) or vinyl triethoxy silane (VTES) which crosslinks upon hydrolysis. Siloxane grafted CBCs employ a grafting moiety such as a vinyl terminated polydimethyl siloxane that does not undergo crosslinking upon hydrolysis.

In some aspects, the aforementioned CBC composition further comprises an amount
20 of at least one other polymer or copolymer selected from a group consisting of a non-hydrogenated vinyl aromatic-conjugated diene block copolymer or random copolymer, a hydrogenated vinyl aromatic homopolymer, a cyclic olefin polymer, or a cyclic olefin copolymer.

The CBC compositions disclosed above have utility in that they may readily be
25 formed (e.g. extruded, or injection molded) into a sheet, either mono-layer or multi-layer. The sheet, in turn, has utility in that it can be thermoformed into a shaped article such as an orthodontic appliance. In view of these utilities, additional aspects follow in succeeding paragraphs.

In some aspects, this invention is a multi-layer, thermoformable, polymeric sheet, the
30 sheet comprising at least one hard layer and at least one soft layer, the hard layer comprising the CBC composition described in the immediately preceding two paragraphs and the soft layer comprising an elastomeric, substantially fully hydrogenated CBC composition, the

elastomeric CBC composition comprising a substantially fully hydrogenated vinyl aromatic-conjugated diene block copolymer composition, said composition having a prehydrogenated vinyl aromatic content of less than 50 percent by weight (wt%), based upon total vinyl aromatic-conjugated diene block copolymer weight prior to hydrogenation, and a number
5 average molecular weight (Mn) within a range of from 30,000 grams per mole (g/M) to 250,000 g/M.

In some aspects, this invention is a multi-layer, thermoformable, polymeric sheet having a hard layer as described above, but with a soft layer that comprises a polymer composition other than the elastomeric CBC composition, such other polymer composition
10 comprising at least one of a cyclic vinyl aromatic-conjugated diene block copolymer in which only the diene block is substantially fully hydrogenated and the vinyl aromatic block is substantially free of hydrogenation (e.g. styrene-ethylene-propylene-styrene (SEPS) or styrene-ethylene-butylene-styrene (SEBS)), an olefin elastomer and a thermoplastic polyurethane (TPU).

15 In some aspects, this invention is a mono-layer sheet, preferably an extruded mono-layer sheet or an injection molded sheet comprising the CBC composition described hereinabove. A "mono-layer sheet" has a thickness of at least 20 mils (0.51 millimeters (mm)). The thickness preferably lies within a range of from 20 mils (0.5 mm) to 60 mils (1.5 mm) and more preferably within a range of from 25 mils (0.6 mm) to 40 mils (1 mm).

20 In some aspects, this invention is a process for preparing a thermoformed sheet, the process comprising subjecting a sheet selected from the multi-layer sheet and the mono-layer sheet, each of which is described hereinabove, to thermoforming conditions, the thermoforming conditions including use of a thermoforming device, and a thermoforming temperature within a range of from the cyclic block copolymer composition's glass
25 transition temperature (Tg) to a temperature 100 degrees centigrade (°C) in excess of the Tg, preferably within a range of from Tg + 5 °C to Tg + 50 °C. The thermoforming conditions preferably include a pressure sufficient to effect, in conjunction with the thermoforming device and the thermoforming temperature, a change in shape from sheet form to a desired shape, e.g. that of an orthodontic appliance when the thermoforming device includes a die
30 that facilitates forming the desired shape.

When ranges are stated herein, as in a range of from 2 to 10, both end points of the range (e.g. 2 and 10) and each numerical value, whether such value is a rational number or an irrational number, are included within the range unless otherwise specifically excluded.

Expressions of temperature may be in terms either of degrees Fahrenheit (°F) together with its equivalent in °C or, more typically, simply in °C.

Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight.

A thermoformed sheet in a form such as an orthodontic appliance has certain property advantages relative to a thermoformed sheet fabricated solely from rigid TPU. The advantages include an improved creep resistance and a slightly lower modulus, both relative to rigid TPU.

The CBC compositions of various aspects of this invention have certain processing advantages over rigid TPU compositions, especially when such compositions are destined for use in an orthodontic appliance. One may, for example, feed CBC composition pellets to an extruder as is when forming a sheet without resort to a drying step commonly required for rigid TPU pellets. A CBC sheet similarly need not be dried before thermoforming into a device such as an orthodontic appliance. A rigid TPU sheet typically requires a drying step at an elevated temperature (e.g., 80°C) for at least 12 hrs. Elimination of drying steps translates to energy savings and reduction in manufacturing costs.

The CBC is a substantially fully hydrogenated vinyl aromatic-conjugated diene block copolymer with an elongation strain at break, determined in accordance with American Society for Testing and Materials (ASTM) D638 that is preferably at least ($\geq$) 30%, more preferably $\geq$ 50%, and even more preferably at least 100%. The cyclic block copolymer also preferably has a modulus, determined in accord with ASTM D638, that is $\geq$ 150,000 psi (1034 MPa) but less than ($<$) 270,000 psi (1862 MPa).

“Substantially fully hydrogenated” means that at least 90 percent (%) of vinyl aromatic double bonds and at least 95% of conjugated diene double bonds are hydrogenated.

The substantially fully hydrogenated vinyl aromatic-conjugated diene block copolymers preferably have, prior to hydrogenation, a pentablock architecture with alternating styrene (S) blocks and either butadiene (B) blocks or isoprene (I) blocks. Representative prehydrogenation pentablock copolymers include SBSBS pentablock copolymers and SISIS pentablock copolymers. The styrene (S) blocks may, but need not be

of equal length. Similarly, the butadiene (B) blocks and isoprene (I) blocks may, but need not be of equal length.

The SBSBS-based and SISIS-based CBC pentablock copolymers have a pre-hydrogenation styrene content that is preferably greater than 50 percent by weight (wt%) to less than 70 wt%, more preferably within a range of from 55 wt% to 65 wt%, each wt% being based upon total pentablock copolymer weight prior to hydrogenation. The pentablock copolymers have a pre-hydrogenation Mn that is preferably within a range of from 40,000 g/M to 150,000 g/M, more preferably within a range of from 50,000 g/M to 120,000 g/M, and even more preferably within a range of from 60,000 g/M to 90,000 g/M. Following hydrogenation, at least 90 percent (%) of vinyl aromatic (e.g. styrene) unsaturation (double bonds) present prior to hydrogenation and at least 90 % of conjugated diene (e.g. butadiene or isoprene) unsaturation (double bonds) present prior to hydrogenation are hydrogenated or converted to saturated bonds. The percentage more preferably equals or exceeds 95 %.

While sequentially polymerized pentablock copolymers may be preferred, satisfactory results also occur with use of triblock, multi-armed or coupled block copolymers. The multi-armed and coupled block copolymers contain a residue from a coupling agent. Such coupled block copolymers may be represented as, for example, $X(BS)_n$ where n is ≥ 1 and X represents a chain coupling agent. The coupled block copolymers preferably have the same styrene content and hydrogenation percentage as the sequential SBSBS and SISIS pentablock copolymers but a broader Mn range that is preferably from 40,000 g/M to 250,000 g/M, more preferably from 50,000 g/M to 200,000 g/M and even more preferably from 60,000 g/M to 160,000 g/M.

The CBC compositions of at least some aspects of this invention may be modified by one or more procedures, one of which is silane-grafting. USP 5,266,627 and USPAP 20060199914A1 teach suitable procedures for silane grafting using a silane compound such as vinyltrimethoxysilane and a catalyst such as 2,5-di-tert-butylperoxy-2,5-dimethylhexane.

See Patrice Lucas and Jean-Jacques Robin, "Silicone-Based Polymer Blends: An Overview of the Materials and Processes", Advanced Polymer Science (2007), volume 209, pages 111-147, for a discussion of siloxane and silane technology in general and blending and grafting in particular.

See Kuk Young Cho et al., "Grafting of Glycidyl Methacrylate onto High-Density

Polyethylene with Reaction Time in the Batch Mixer”, Journal of Applied Polymer Science, Volume 108, pages 1093-1099 (2008), for general teachings relative to methacrylate grafting. *See also* Shenglong Ding et al., “The Study of Melt Grafting Mechanism of Acrylic Acid and Butyl Acrylate onto Low Density Polyethylene and Its Application as Internal Plasticizer”, Journal of Applied Polymer Science, Volume 108, pages 423-430 (2008) for general teachings relative to acrylate grafting. In addition, *see* K. E. Russell, “Free radical graft polymerization and copolymerization at higher temperatures”, Progress in Polymer Science, Volume 27 (2002), pages 1007-1038, for teachings relative to graft addition of vinyl monomers to polyolefins.

10 The CBC compositions of at least some aspects of this invention yield optically transparent, thermoformable sheets or films. Optical transparency makes such sheets and the compositions that form the sheets very desirable from an aesthetic point of view in orthodontic appliances, especially those used for tooth alignment (otherwise known as “braces”).

15 While orthodontic appliances represent a preferred end use application for CBC compositions of some aspects of this invention and thermoformable sheets of other aspects of this invention, the compositions and sheets have utility in other end use applications. Such other end use applications include, but are not limited to, display films, signage sheets, and medical/pharmaceutical vials and bottles.

20 The CBC compositions of at least some aspects of this invention further comprise any one or more members of three groups of polymers. The groups are: a) hydrogenated vinyl aromatic-conjugated diene block copolymers; b) hydrogenated random vinyl aromatic-conjugated diene copolymers; c) hydrogenated vinyl aromatic homopolymers; d) cyclic olefin polymers; e) and cyclic olefin copolymers.; f) non-hydrogenated vinyl aromatic-conjugated diene block copolymers; and g) non-hydrogenated random vinyl aromatic-conjugated diene copolymers.

25 Conversion of CBC compositions of some aspects of this invention into thermoformable sheets of other aspects of this invention employs conventional processes. Such conventional processes include extrusion, injection molding and compression molding. Any of these processes readily forms a plaque suitable for thermoforming into an article of manufacture, such as an orthodontic appliance of some aspects of this invention.

30 Compositions of some aspects of this invention have utility as a layer of a multi-

layer structure, especially as a hard outer layer of a multi-layer structure such as a coextruded multi-layer structure. The hard outer layer provides creep resistance. A softer, relative to the hard outer layer, inner layer provides a degree of wearer comfort in an orthodontic appliance wherein the inner layer is in contact with the wearer's teeth and the
5 hard outer layer is spaced apart from the wearer's teeth by the inner layer. Materials suitable for use in fabricating the inner or soft layer include, but are not limited to, styrene-ethylene-butylene-styrene copolymers, styrene-ethylene-propylene-styrene copolymers, olefin elastomers, and thermoplastic polyurethanes.

Extruded sheets, either mono-layer or multi-layer, of some aspects of this invention
10 lend themselves to thermoforming into various structures, one of which is an orthodontic appliance. Suitable thermoforming temperatures satisfy a relationship wherein thermoforming temperature (T) lies within a range that has a lower limit established by glass transition temperature (T_g) of CBCs of some aspects of this invention and an upper limit of 100° C greater than the T_g. The range is preferably from T_g + 5°C to T_g + 50°C.

15 Compositions of some aspects of this invention may include one or more conventional additives. Illustrative additives include antioxidants, mold release agents, ultraviolet light stabilizers, processing aids, lubricants, anti-static agents, antimicrobial agents (e.g. ALPHASAN™ RC2000 or MICROBAN™), colorants, coloring agents, and dyes.

20 Examples

The following examples illustrate, but do not limit, the present invention. All parts and percentages are based upon weight, unless otherwise stated. All temperatures are in °C. Examples (Ex) of the present invention are designated by Arabic numerals and Comparative Examples (Comp Ex or CEx) are designated by capital alphabetic letters. Unless otherwise
25 stated herein, "room temperature" and "ambient temperature" are nominally 25°C.

Table 1 below lists three pentablock (SBSBS-based) CBCs (CBC-1, CBC-2 and CBC-3), and one TPU (ISOPLAST™ 2530, commercially available from The Dow Chemical Company). For the CBCs, Table 1 includes their respective Mn, wt% styrene (based on total CBC weight before hydrogenation) and wt% 1,2-vinyl (based on total
30 butadiene (B) content before hydrogenation) content. Table 1 also includes physical performance data in terms of strain at break and modulus (thousand psi or kpsi and MPa), both determined in accord with ASTM D638.

Table 1

Material	Mn (g/M)	Styrene content (wt%)	1,2-vinyl content (wt%)	Strain@break (%)	Modulus (kpsi/MPa)
CBC-1	72,800	60	8	240	220/1517
CBC-2	69,000	55	8	300	155/1069
CBC-3	70,500	70	11	20	244/1682
TPU	N/A	N/A	N/A	160	270/1862

Determine T_g of hydrogenated vinyl aromatic block copolymers by dynamic mechanical analysis using a rheometer (e.g., ARES rheometer manufactured by TA Instruments). Define T_g by its $\tan \delta$ peak measured from a solid state temperature ramp of linear viscoelastic spectrum data (storage modulus G' , loss modulus G'' and $\tan \delta = G''/G'$) between room temperature and 160°C at a temperature ramp rate of 3°C/min and an oscillatory frequency of 1 radian per second (rad/s). Use a solid rectangular shaped specimen of approximate 45 millimeter (mm) length, 12.5 mm width and 3.2 mm thickness for testing. Compression mold test specimens at a temperature of 250°C and a pressure of approximately 500 pounds per square inch (psi) (3447 kilopascals (KPa) using a standard compression molder (e.g., Tetrahedron™ 1401 from Tetrahedron Associates Inc., San Diego, CA).

Conduct molecular weight analysis of a hydrogenated vinyl aromatic-conjugated diene block copolymer by subjecting the block copolymer, prior to its hydrogenation, to gel permeation chromatography (GPC) using tetrahydrofuran (THF) as a solvent for the block copolymer. Calibrate GPC columns using narrow molecular weight polystyrene standards from Polymer Labs, Inc. The M_n of the standards ranges from 580 g/M to 3,900,000 g/M. Prepare six standard cocktails that have three or four standards per cocktail, each standard in the cocktail differing in molecular weight from others in the cocktail by a factor of approximately ten. Determine peak elution volume of each standard and generate a column calibration of molecular weight versus elution volume by fitting the narrow standard data with a 5th order polynomial fit. Report M_n of pre-hydrogenated block copolymers as polystyrene-equivalent values.

Test Methods

A. Determination of Resistance to Stress Cracking

Use ASTM D638 Type IV (dog bone type) microtensile test specimens and a clamp equipped with a strain jig that applies a five percent (5%) strain deformation to each specimen for stress crack testing. Place a clamped specimen into a container that holds a volume of water sufficient to allow complete sample immersion and fully immerse the clamped specimen in the water for one week at a set point temperature of 37°C.

Following the one week immersion, remove each clamped specimen from the water and then remove each specimen from the strain jig, then pat the sample specimen dry using paper towels before subjecting it to tensile testing.

Prescreen specimens for tensile testing by inspecting each dried specimen for visual defects such as craze lines, stress marks and breakage. Set aside any test specimens that contain a visual defect. Mount each specimen that lacks visual defects in an Instron machine and subject it to ASTM D638 tensile testing. Record strain at break for each tested specimen and compare it to an untreated sample (no strain or immersion in water).

A reduction in elongation strain at break, relative to the untreated sample, of less than 25% merits a pass rating, with values that approach a reduction of 0% being very desirable.

B. Determination of Creep Resistance

Using test specimens measuring 4 inches (in) (10.2 centimeter (cm)) x 0.5 in (1.3 cm) x 0.030 in (0.08 cm), conduct a three point bending test to characterize a material's resistance to creep. Die cut the test specimens from compression molded plaques that measure five (5) inches (in.) (12.7 centimeters (cm)) x 5 in. (12.7 cm) x 0.030 in. (0.08 cm). Before loading a test specimen onto the testing fixture of an Instron machine, soak the specimen in the water for 30 minutes and then pat the specimen dry using paper towels.

Place each dried test specimen on the Instron machine's two lower loading noses with a support span of 16 millimeters (mm). Quickly (no more than six (6) seconds between zero strain and 5% strain deformation) apply a 5% strain deformation to the test specimen, then allow it to relax over time and record stress relaxation over time. As between two materials, one with a faster stress decay also has a poorer creep resistance. A slower decaying rate of stress relaxation is desirable for the application.

Analyze the stress relaxation data to obtain both initial stress decay rate (τ_1) and long term stress decay rate (τ_2). As a first step, normalize stress versus time data based upon measured maximum stress value applied to a test specimen. The stress value typically reaches a maximum some three to six seconds after starting the stress relaxation test. Fit the
 5 normalized stress (σ) versus time (t) (in seconds) data in a second order exponential decay function:

$$\sigma = A_0 + A_1 \exp\left(-\frac{t}{T_1}\right) + A_2 \exp\left(-\frac{t}{T_2}\right)$$

Where, σ is the normalized stress value from 0 to 1, A_0 , A_1 , A_2 , T_1 and T_2 are data fitting parameters,

10
$$\tau_1 = \frac{T_1}{60},$$

$$\tau_2 = \frac{T_2}{3600}$$

Increasing values for τ_1 and τ_2 indicate slowing rates of applied stress decay.

Ex 1

Compression mold CBC-1 at a temperature of 250°C into plaques measuring 5 in
 15 (12.7 cm) x 5 in (12.7 cm) and having a thickness of 0.030 in 0.08 cm). Die cut test specimens from the plaques. Measure tensile properties of this material with and without the water immersion described above for determining resistance to stress cracking. Measure elongation strain at break and stress relaxation in accord with procedures detailed above and summarize measurements in Table 2 below.

20 Ex 2

Replicate Ex 1 but use CBC-2 rather than CBC-1. Summarize measurements in Table 2 below

CEx A

Replicate Ex 1 but use TPU rather than CBC-1. Summarize measurements in Table
 25 2 below

CEx B

Replicate Ex 1 but use CBC-3 rather than CBC-1. Summarize measurements in Table 2 below

Table 2

Ex/CEx	Strain at Break (no immersion/treatment) (%)	Strain at Break (with immersion/treatment) (%)	Initial Stress Decay rate (minutes)	Long term Stress Decay Rate (hours)
1	240	213	6.7	2.2
2	300	300	nm	nm
A	160	187	4.2	1.5
B	20	10	1.7	1.5

“nm” means not measured

The results in Table 2 show that both initial and long term stress decay rates are more than 50% slower for CBC-1 than for CEx A (TPU). The results also show that not all CBC's perform equally well in that CEx B (CBC-3, 70 wt% styrene content) with a much lower elongation strain at break than either CBC-1 (Ex 1) or CBC-2 (Ex 2) at 20% versus, respectively, 240% and 300%, has a very low strain at break (10%) relative to Ex 1 (240 %) and a much more rapid initial stress decay rate at 1.7 minutes than either TPU (4.2 minutes) or CBC-1 (6.7 minutes). The long term stress decay rate of CBC-3 is also more rapid than CBC-1 at 1.5 hours versus 2.2 hours. CBC-1 shows an improvement over TPU in terms of strain at break (before and after immersion) and both initial and long term stress decay rates while CBC-3 performs worse than TPU in the same properties. On that basis, CBC-1 represents a viable candidate for use in orthodontic applications, but CBC-3 does not. CBC-2 should also be a viable candidate based on its higher, relative to CBC-1, strain at break.

Based on information and belief, human saliva exposure, especially over extended periods of time, increases magnitude of performance differences between TPU and CBC.

Ex 3. Silane modified CBC material

In a container, mix three (3) parts by weight (pbw) of liquid vinyltrimethoxysilane (VTMS) (Dow Corning Z-3600, CAS number 2768-02-7) and 0.08 pbw of liquid 2,5-Di-tert-butylperoxy-2,5-dimethylhexane (LUPEROX™ 101, Aldrich, CAS number 78-63-7) to 100 pbw CBC-2 resin. Allow the liquids to diffuse and imbibe into the CBC-2 resin at room temperature (nominally 25 degrees centigrade (°C) overnight (at least 12 hours).

Feed the container contents into an 18 millimeter (mm) Leistritz ZSE-18 twin screw extruder (Leistritz Corporation, Somerville, NJ) equipped with a pelletizer to effect reactive extrusion compounding of the container contents. The extruder operates at a set point temperature of 220°C with an extruder output of 5 pounds per hour (lbs/hr) (11 kilograms per hour (kg/hr)).

Place the pellets in a vacuum oven operating at a set point temperature of 90°C overnight (at least 12 hours) to remove ungrafted silane (VTMS).

Compression mold the compounded, pelletized container contents (also known as “silane-grafted CBC material” into plaques as in Ex 1, but use a mold temperature of 220°C rather than 250°C.

Prepare the plaques for physical property testing by immersing them in an aqueous dodecylbenzenesulfonic acid solution (10 wt% dodecylbenzenesulfonic acid, based on total solution weight) heated to a set point temperature of 80°C for 72 hours in an effort to promote siloxanes crosslinking.

The plaques have a tensile modulus of 168,000 pounds per square inch (psi) (1158 kilopascals (kPa)) and an average elongation strain at break (with immersion) of 92%. The plaques have an initial stress decay rate (also known as “short term decay rate”) of 6.5 minutes and a long term stress decay rate of 2.1 hours.

Ex 3 demonstrates that functionalized CBC polymers are also suitable for the use in orthodontic applications.

WHAT IS CLAIMED IS:

1. A cyclic block copolymer composition, the composition comprising a cyclic block copolymer that is a substantially fully hydrogenated vinyl aromatic-conjugated diene block copolymer, said substantially fully hydrogenated block copolymer having an
5 elongation strain at break of more than 30% and a modulus that is within a range of from greater than or equal to 150,000 psi (1034 MPa) to less than 270,000 psi (1862 MPa), both elongation strain at break and modulus being determined in accord with American Society for Testing and Materials (ASTM) Test D638-02a.
2. The cyclic block copolymer composition of Claim 1, wherein the
10 elongation strain at break is at least 50%.
3. The cyclic block copolymer composition of Claim 1 or Claim 2, wherein the block copolymer is selected from a group consisting of a sequentially-polymerized pentablock copolymer, a sequentially-polymerized triblock copolymer, a multi-armed block copolymer, or a coupled block copolymer.
- 15 4. The cyclic block copolymer composition of any of Claims 1 through 3, wherein the composition further comprises an amount of at least one other polymer or copolymer selected from a group consisting of a) hydrogenated vinyl aromatic-conjugated diene block copolymers; b) hydrogenated random vinyl aromatic-conjugated diene
20 copolymers; c) hydrogenated vinyl aromatic homopolymers; d) cyclic olefin polymers; e) and cyclic olefin copolymers.; f) non-hydrogenated vinyl aromatic-conjugated diene block copolymers; and g) non-hydrogenated random vinyl aromatic-conjugated diene copolymers.
5. The cyclic block copolymer composition of any of Claims 1 through 4, wherein the cyclic block copolymer is a functionalized cyclic block copolymer selected from silane-grafted cyclic block copolymers, maleic anhydride grafted cyclic block
25 copolymers, acrylate-grafted cyclic block copolymers, methacrylate-grafted cyclic block copolymers, and siloxane grafted cyclic block copolymers.
6. A multi-layer, thermoformable, polymeric sheet, the sheet comprising at least one hard layer and at least one soft layer, the hard layer comprising the cyclic block copolymer composition of any of Claims 1 through 5, and the soft layer comprising an
30 elastomeric, substantially fully hydrogenated cyclic block copolymer composition, the elastomeric cyclic block copolymer composition comprising a substantially fully hydrogenated vinyl aromatic-conjugated diene block copolymer composition, said

composition having a prehydrogenated vinyl aromatic content of less than 50 percent by weight based upon total vinyl aromatic-conjugated diene block copolymer weight prior to hydrogenation, and a number average molecular weight within a range of from 30,000 grams per mole to 250,000 grams per mole.

5 7. A multi-layer, thermoformable, polymeric sheet, the sheet comprising at least one hard layer and at least one soft layer, the hard layer comprising the cyclic block copolymer composition of any of Claims 1 through 5, and the soft layer comprising at least one of a cyclic vinyl aromatic-conjugated diene block copolymer in which only the diene block is substantially fully hydrogenated and the vinyl aromatic block is substantially free of
10 hydrogenation, an olefin elastomer, and a thermoplastic polyurethane.

8. A mono-layer sheet, the mono-layer sheet comprising the cyclic block copolymer composition of any of Claims 1 through 5, the mono-layer sheet having a thickness of at least 20 mils (0.51 millimeters (mm)).

9. A process for preparing a thermoformed sheet, the process
15 comprising subjecting a sheet selected from the multi-layer sheet of Claim 6 or Claim 7 and the mono-layer sheet of Claim 8 to thermoforming conditions, the thermoforming conditions including use of a thermoforming device, a thermoforming temperature within a range of from the cyclic block copolymer composition's glass transition temperature (T_g) to a temperature 100 degrees centigrade (°C) in excess of the T_g, and a pressure sufficient to
20 effect, in conjunction with the thermoforming device and the thermoforming temperature, a change in shape from sheet form to a desired shape.

10. The process of Claim 9, wherein the desired shape is an orthodontic appliance.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/059537

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08L51/00 C08L53/00 C08L53/02 C08F8/04 B32B7/02
B32B25/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L C08F B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 632 890 B1 (BATES FRANK S [US] ET AL) 14 October 2003 (2003-10-14)	1-3
Y	column 2, line 38 - column 4, line 47 column 7, line 62 - column 8, line 35; example 2; table II	5
X	WO 01/44315 A1 (DOW CHEMICAL CO [US]) 21 June 2001 (2001-06-21) page 4, line 9 - line 29 page 5, line 30 - page 6, line 13 page 8, line 1 - line 25 page 9, line 12 - page 10, line 6 page 12, line 20	1-4,6-7
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

26 January 2010

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	page 2, line 7 - line 35 page 4, line 14 - page 6, line 16 page 11, line 1 - line 15 page 30, line 21 - line 26 page 31, line 14 - line 16 page 34, line 3 - line 16 page 35, line 1 - line 3 -----	10
Y	US 4 578 429 A (GERGEN WILLIAM P [US] ET AL) 25 March 1986 (1986-03-25) column 5, line 14 - column 6, line 9 -----	5
Y	US 2006/078841 A1 (DESIMONE JOSEPH M [US] ET AL) 13 April 2006 (2006-04-13) cited in the application paragraph [0021] -----	10

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Information on patent family members

International application No

PCT/US2009/059537

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