

THERMALLY ENHANCED ELECTRICALLY INSULATIVE ADHESIVE PASTE

FIELD OF THE INVENTION

[0001] The present invention relates to thermal interface materials.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to thermally enhanced adhesive pastes particularly well suited for bonding high density, microcircuit electronic components to substrates.

[0003] The attachment of high density, microcircuit components onto substrates, such as silicon dies onto ceramic sheet, has been an important aspect of the electronics industry for many years. Generally, it is known to use a die attach paste which is deposited between the die and substrate. Typically, the die attach paste includes a filler, an adhesive and a carrier. The filler is selected to impart to the finished bonding layer desired conductive, resistive or dielectric properties. The adhesive is chosen to create a strong bond between the die and substrate. The carrier maintains all the components in a fluid, uniform mixture, which allows the paste to be applied easily to the die-substrate interface. It also has suitable volatility to migrate from between the die and substrate following heat treatment of the assembly. After the paste is deposited and the die and substrate are assembled, the assembly is typically heated to fuse the adhesive and drive off the carrier. Upon cooling, the die is firmly attached to the substrate.

[0004] The powder density of active components continues to rise, creating an increasing demand of higher thermally conductive adhesives to attach these components. These demands have previously been met by technologies described in the prior art, including U.S. Patent Nos. 6,111,005 and 6,140,402. These patents describe a technology involving the use of powdered organic polymer resins, suspended in a non-solvent along with highly thermally conductive filler. The type of powdered resin was varied depending on the application. For large area component attachments where the Coefficient of Thermal Expansion (CTE) mismatch to the substrate was also large, low modulus thermoplastic polymers were incorporated to handle the shear stress generated at the bondline of the adhesive. For smaller area components where the expansion mismatch to the substrate was lower, thermoset or combinations of thermoplastic and thermoset polymer powders

were employed in the adhesive composition with the filler. The use of the higher modulus polymers also increased the thermal conductivity.

[0005] U.S. Patent 6,265,471 describes an even higher thermal conductivity technology where the highly conductive filler is suspended in a liquid epoxy resin which is dissolved in a fugitive solvent. This technology increased the thermal conductivity over the prior technology described in U.S. Patent Nos. 6,111,005 and 6,140,402. Unfortunately, the elastic modulus of the thermosetting liquid resin system was relatively high when cured or cross-linked. Consequently, the application of this technology was limited to small area component attach and or substrates that were closely matched in CTE to the component, usually a semiconductor die. The prior art described in the technologies described above shows a linear relationship between the modulus and the thermal conductivity of the adhesive. Low modulus adhesives, described in U.S. Patent Nos. 6,111,005 and 6,140,402, were lower in thermal conductivity, whereas the higher modulus adhesives described in U.S. Patent 6,265,471 were higher in thermal conductivity. As higher function semiconductor devices grew in size and power, the need also grew for an adhesive with both high thermal conductivity and low modulus. Such adhesives were needed to absorb the bondline shear stresses caused by the thermal expansion mismatch between the die and the high expansion, high thermally conductive substrates. One large application in the marketplace is the attachment of large area, flip chip microprocessor devices to a high expansion, high thermally conductive heat spreader. Both high conductivity and low modulus properties are needed for this application. Heretofore, the adhesives described in U.S. Patents. Nos. 6,111,005, 6,140,402 and 6,265,471 were used in these applications. However, the microprocessor devices increased in power density and thus the demand increased for adhesives having even better thermal properties with low elastic modulus.

SUMMARY OF THE INVENTION

[0006] The present invention provides a thermal interface material that comprises (1) a first type of thermally conductive particle that is conformable wherein each of the first type of thermally conductive particle is itself a self-cohesive agglomeration of smaller platy particles (2) a second type of thermally conductive particle (3) a binder

[0007] According to certain embodiments the binder includes fine resin particles which are combined with the first type of ceramic particles and the second type of ceramic

particles in a fugitive liquid thereby forming a paste, where the thermoplastic particles are substantially insoluble in the fugitive liquid. The fugitive liquid can include a viscosity modifier.

[0008] According to alternative embodiments the binder is a liquid thermoset resin such as liquid epoxy.

[0009] According to certain embodiments the bulk thermal conductivity of the material of the first thermally conductive particles exceeds 200 W/mK.

[0010] According to certain embodiments the bulk thermal conductivity of the material of the second thermally conductive particles exceeds 10 W/mK.

[0011] According to certain embodiments the first type of ceramic particle comprises boron nitride.

[0012] According to certain embodiments the second type of thermally conductive particle is alumina.

[0013] Boron nitride and alumina are both ceramic particles.

[0014] According to certain embodiments the thermally conductive particles have a tap density of about from 0.5 to 2.5 gm/cc.

[0015] According to certain embodiments the shape of both types of particles is what is termed by those skilled in the art as spheroidal. As used in the present description the term spheroidal includes spherical as a special case. The usage of these terms does not imply that the shapes of the particles are precisely true to the mathematically defined ideal shapes.

[0016] According to certain embodiments the size distribution of the thermally conductive particles is bimodal. For example large particles of the first type can be used in combination with smaller particles of the second type. As a consequence the second type of thermally conductive particles will occupy interstices between the first type of thermally conductive particles.

[0017] According to certain embodiments the thermal interface material further comprises a sintering aid.

[0018] According to certain embodiments the thermal interface material is used as a die attach paste.

[0019] Embodiments that include mainly thermoplastic binder provide die attach pastes which are strong, yet sufficiently elastic to bond large area silicon dies to more expandable substrates without inducing excessive stress yet provide significantly higher thermal properties and electrical insulation than the prior art.

[0020] Embodiments that include a liquid epoxy binder provide enhanced thermal properties for the attachment of smaller components where the modulus of the cured adhesive is higher and where electrical insulation is required.

[0021] The invention further provides a die attach paste which can be applied by equipment and processes presently used in the industry without major modifications and produce a strong thermally conductive bond line when processed thereby. Embodiments of the invention provide sufficient adhesion between the component and substrate to pass industry standards for adhesion. Furthermore, because the thermoplastic resins can be repeatedly melted and solidified, those embodiments using thermoplastic resins are reworkable and suitable for multi-chip module technology or for High Brightness Light Emitting Diode(HBLED) arrays.

BRIEF DESCRIPTION OF THE FIGURES

[0022] FIG. 1 is a first electron micrograph of a cross sectional view of a thermal interface material according to an embodiment of the invention bonded to a substrate;

[0023] FIG. 2 is a second electron micrograph of a cross sectional view of a thermal interface material according to an embodiment of the invention between a substrate and a silicon die; and

[0024] FIG. 3 is a third electron micrograph showing a close up of boron nitride particles used in the thermal interface material.

DETAILED DESCRIPTION OF THE INVENTION

[0025] U.S. Patent No. 6,111,005 discloses thermoplastic binder compositions that can be used in the present invention. U.S. Patent No. 6,265,471 discloses a liquid epoxy binder that can be used in the present invention. U.S. Patent Nos. 6,111,005 and 6,265,471 are hereby incorporated by reference. Substituting the ceramic particles described hereinabove for the silver filler disclosed in the '471 and '005 patents yields a highly sintered, denser structure. This produces an unexpected increase in thermal

conductivity and decrease in thermal impedance. Furthermore, the pastes taught herein provide increased adhesion, which allows a decrease in the resin content (higher filler-to-resin ratio) which further increases the thermal conductivity.

[0026] The ceramic fillers used in the adhesive pastes of the present invention are present in particulate form. At least about 80% of the filler particles, and preferably substantially all of the filler particles, are characterized by round edges, and substantially free from flat surfaces. Spheroidal, as opposed to platy particles are especially preferred. As used herein the term "spheroidal" is not limited to mathematically precise shapes. As used herein, consistent with the usage in the art, the term "spheroidal" means a particle having length width and height dimensions that are comparable, as opposed to the case of a platy particle where the thickness is much smaller than the transverse (e.g., diameter) dimension.

[0027] Representative of ceramic filler particles which can be use in the present invention are those available from Saint-Gobain boron nitride (BN) under the par # of PCTH3MHF. Representative ceramic filler which can be used is spherical aluminum oxide (Al_2O_3) available from Denka Corp., Japan. As used herein, the term "conformable" refers to particles that compress under pressure or during curing.

[0028] According to some embodiments at least about 50% of the thermally conductive particles, i.e. the boron nitride is mono dispersed, and has a particle size of at least about 50 microns and the balance of the thermally conductive particles, i.e., the alumina has a particle size of less than about 10 microns. In such embodiments the alumina will occupy interstices between the BN particles.

[0029] The ceramic filler is preferably used in combination with at least one sintering aid, that is, any additive that enhances the sintering of the filler. Representative sintering aids include metal alkoxides, low melting point salts, organic inorganic hybrid composites. The sintering aid is generally present in a concentration of about from 0.1 to 0.5 weight percent of the cured materials.

[0030] The unexpected increase in thermal properties is not fully understood, but is believed to be due to the better packing and point contacts of the spheres as compared to the geometry of the flakes previously used in thermal interface materials of this type. Also believed to be significant is the presence of spherical conformable filler such as BN.

[0031] In embodiments that use a thermoplastic powder and a fugitive liquid, the two are preferably soluble in each other to an extent that does not exceed 20% and more preferably to an extent that does not extend beyond 10%. Furthermore the particles are preferably less than 40 microns in diameter.

[0032] Examples of thermoplastic powders that may be used include polyester, copolyester, polyamide, copolyamide, polyurethane, polybutylene terephthalate, polyolefin, acrylic, silicone, and liquid crystalline polymers.

[0033] Examples of the fugitive liquid include Terpenol, Norpar (normal paraffins), Linpar, hexane, alcohols.

[0034] In embodiments that use a fugitive liquid a viscosity modifier may be added to the fugitive liquid. The viscosity modifier is suitably present in an amount ranging from 0.05 to 5 volume % of the adhesive paste. Examples of viscosity modifiers include styrene-butadiene-styrene, styrene-isoprene-styrene, styrene ethylene/butylene-styrene, styrene-ethylene/propylene-styrene, styrene-butadiene, styrene-butadiene-styrene, styrenic block copolymers, and polyisobutylene.

[0035] Examples of thermoset binders that may be used include epoxies, silicones, reactive polyesters, polyurethanes and polyimides.

[0036] In the prior art thermal interface materials when a bonded assembly is heated, the resin powder melts and coalesces with other particles and migrates toward the bondline interfaces. This melting of the powders leaves a void in the bondline, hereafter referred to "bond drop out" (BDO). With the thermal interface material described herein, BDOs were not observed. It has been found that the combination of thermal interface materials described herein allow a very high loading of thermally conductive ceramic particles, without causing BDO. Percentages of thermally conductive ceramic particles (relative to the total solids weight in the cured product) higher than 75% e.g., 85 wt% have been achieved without BDO and while also attaining sufficient adhesive strength for die attach applications. The total solids weight includes the thermally conductive ceramic particles and the cured binder. Also in the case of a mixture of large and small fillers, the fine one(s) become the interstitial filler of the large ones.

[0037] Additives such as salts, low melting point glasses, mixed oxides and low melting point coatings on the ceramic particles can also be used in the present invention. These

components can further enhance thermal conductivity by allowing filler particles to “sinter” together in to a solid mass. These additives may serve as sintering aids for ceramic filler particles.

[0038] FIG. 1 and FIG. 2 are two electron micrograph of a thermal interface material 102 according to an embodiment of the invention bonding silicon die 204 to a substrate 104. Note that the silicon die is only visible in FIG. 2. FIGs. 1-2 are cross sections obtained by sectioning the bonded assembly of the silicon die 204 and substrate 104. Large boron nitride particles labeled BN and smaller spherical alumina particles labeled Al_2O_3 are immersed in a matrix of binder material, in this case polyester resin. According to certain embodiments the average size of the BN particles is at least 5 times larger than the average size of the Al_2O_3 particles that are used. It is believed that in the process of making the bond the BN particles may be conformed into different shapes when the silicon die is pressed onto a dispensed quantity of the thermal interface material.

[0039] FIG. 3 shows a close up of boron nitride particles used in the thermal interface material shown in FIGs. 1-2. Each of the boron nitride particles is a comfortable, cohesive agglomeration of smaller platy shaped boron nitride flakes.

[0040] In the following examples and comparative examples, combinations of filler, resin and fugitive liquid were combined to form a paste. The preparation of the adhesive from its principal components, and its methods of application and use, take advantage of the various methods and employ equipment well known in the art. The principal components can be mixed in equipment known in the art for paste preparation.

[0041] The thermal interface materials of the present invention can advantageously be used for attaching microcircuit electronic components (semiconductor dies) to substrates. In general, this comprises making an adhesive paste of the thermal interface material; applying the paste to a surface of a substrate to form a bond line and placing the electronic component on the bond line so that the paste is between the electronic component and the substrate; followed by heating the assembly to a sufficiently high temperature for a sufficient time that the organic thermoplastic resin softens and becomes fluid, but does not degrade, and the fugitive liquid devolatilizes from the paste; followed by cooling the heat-treated assembly to a temperature below which the thermoplastic polymer becomes solid, whereby the microcircuit electronic component is bonded to the substrate by a void-free

bond line. When thermoset resin is used, rather than as a particle, as part or all of the organic polymer, the processing temperature should be sufficiently high to crosslink the resin.

[0042] For purposes of demonstrating the invention, the wet adhesives are deposited on a ceramic substrate before the die is placed on the wet adhesive. All curing was done at 200° C. peak for 30 minutes. After curing, a force perpendicular to the side of the die was applied until the die was sheared off the substrate. This force was recorded in pounds per square inch (PSI) as the adhesion value for the particular composition being tested. The thermal conductivity measurements were done by the known laser flash method on pellets which were ½ inch in size and about 1/8 inch thick. This measuring technique is more fully described in ASTM E 1461, "Standard Test Method for Thermal Diffusivity by the Flash Method."

[0043] The present invention is now illustrated by examples of certain representative embodiments thereof, where all parts, proportions, and percentages are by weight unless otherwise indicated. The examples are intended to be illustrative only, and modifications and equivalents of the invention will be evident to those skilled in the art.

EXAMPLES 1-4 AND COMPARATIVE EXAMPLE A

Example A 1 2 3 4

	H987	MP8-109-3	MP8-118-1	MP8-114-2	MP8-123-1 w/Lipotin
Filler	AlN/BN non spherical	Al ₂ O ₃ /BN/ ZnO spherical	Al ₂ O ₃ /BN/ ZnO spherical	Al ₂ O ₃ /BN/ ZnO spherical	Al ₂ O ₃ /BN/ ZnO spherical
Filler ratio	50/50	35/55/10	35/55/10	35/55/10	35/55/10
Filler amount	50%	52%	75%	82%	82%
Resin	Liquid epoxy	Liquid epoxy	Liquid epoxy	Liquid epoxy	Liquid epoxy
BLT mils (microns)	1.6 (40.6)	1.7 (43.18)	1.9 (48.26)	2.7 (68.58)	2.0 (50.8)

Shear adhesion psi (bar)	4178(288)	5476 (378)	1061 (73)	511 (35)	737 (51)
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[0044] Spherical filler enhances adhesion; increase in filler loading lowers adhesion but Lipotin increases adhesion. Lipotin is a soya lecithin from Tego Chemie Service GmbH · Goldschmidtstrasse 100 · D-45127 Essen, Germany.

EXAMPLES 5-8 AND COMPARATIVE EXAMPLE B

Example	B	5	6	7	8
	DM4140k-2	PCz1-61-2	MP8-109-2	MP8-109-1	MP8-118-2 Lipotin
Filler	AlN/BN nonspherical	Al ₂ O ₃ /BN/ ZnO spherical	Al ₂ O ₃ /BN/ ZnO spherical	Al ₂ O ₃ /BN/ ZnO spherical	Al ₂ O ₃ /BN/ ZnO spherical
Filler ratio	50/50	35/55/10	35/55/10	35/55/10	35/55/10
Filler amount	76%	75%	75%	75%	75%
Resin	Copolyester resin/reactive polyester (6/4)	Copolyester resin	Copolyester resin (-635)/ reactive polyester (6/4)	Copolyester resin (-635)	Copolyester resin (-635)
BLT mils (microns)	1.6 (41)	4-7 (102-178)	2.7 (68.5)	2.5 (64)	2.3 (58)
Adhesion psi (bar)	811 (56)	930 (64)	811(56)	254 (18)	821 (57)
Rth k·cm ² /W	0.776	0.962	0.645		0.535
K (W/mk)	2	5.23			

[0045] Fine particle resin (-635mesh) in which most particles are less than 20 micron in diameter lowers bond line thickness (BLT). Addition of thermoset (0004) in the thermoplastic enhances adhesion. Lipotin enhances adhesion and lowers Rth

(interfacial thermal resistance). Copolyester resins from Bostik, Inc. Middleton, MA and reactive polyester made by Tomogawa of Tokyo, Japan were used.

Example 9 10 11 12

Filler	PCz1-69-1	PCz1-63-3	PCz1-45-1	PCz1-61-2
DAW3 (Al ₂ O ₃)	10.5	11	42.5	26
PCTH3MHF (BN)	52.5	56	42.5	41.5
Kadox 930 (ZnO)	7	8		7.5
Copolyester	30	25	25	25
% porosity	15	32.8	8.2	10.9
K (W/mK)	4.05	3.4	4.25	5.25
Adhesion psi (bar)	903 (62)	457 (32)	546 (38)	929 (64)

[0046] The above examples illustrate that reduction in porosity increases thermal conductivity even when % resin is increased. Also addition of ZnO increases thermal conductivity.

Example 13 14 15 16 17

Filler	PCz1-65-2	PCz1-60-2	PCz1-66-3	PCz1-61-1	PCz1-61-2
	75% filler	75%	75% filler	75%	75%
DAW 3	0.86	1.974		2.713	1.726
DAW 45	0.86				
DAW 10			1.726		

PCTH3MHF	2.713	1.974	2.713	1.726	2.713
Kadox 930	0.49	0.984	0.49	0.49	0.49
Copolyester	1.64	1.64	1.64	1.64	1.64
% porosity	13.2	0.2	11.3	21.0	10.9
k (W/mK)	5.06	4.49	5.13	3.09	5.25
Shear adhesion psi (bar)	796 (55)	1025 (71)	933 (64)	1008 (69)	929 (64)

DAW 3 – 3 micron alumina; DAW 10 – 10 micron alumina; DAW 45 – 45 micron alumina; PCTH3MHF – 3 mil BN. Kadox 930 is ZnO powder sold by Horshead Corp. Monaca, PA. . DAW are alumina powders from Denka, Japan.

[0047] The above examples show the importance of having BN at close to 50% of the total filler; also larger filler affords higher thermals.

COMPARATIVE EXAMPLES C-F

[0048] The following Comparative Examples illustrate that addition of interstitial filler with high conductivity such as AlN does not improve over all thermal conductivity of the composite.

Example C D E F

Filler	PCz1-48-3	PCz1-36-1	PCz1-38-3	PCz1-49-2
	85% filler	(85% filler)	(90% filler)	85% filler
DAW 3	5.04	3.9	4.12	
DAW 5				5.04
HC Starck A	0.58	1.7	1.77	0.58
Copolyester	0.98	0.98	0.65	0.98
% porosity	7.6	14.9	28.9	4.2
k (W/mK)	2.11	2.43	1.68	2.09

Shear adhesion psi (bar)	1393 (96)	1032 (71)	494 (34)	932 (64)
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HC Starck A is AlN powder provided by HC Starck; DAW 5 – 5 micron alumina;

Bulk thermal conductivity table

Material	Thermal conductivity (W/mK)
Al ₂ O ₃	20-30
BN	250-300
AlN	180-280
ZnO	40

EXAMPLE 18 AND COMPARATIVE EXAMPLE G

[0049] The general procedure of Examples 1-4 was repeated, except that a loading of the filler in the powdered resin was 75% by weight. In Example 18, a filler characterized by round edges was used. In Comparative Example G, a flake filler was used. The resulting pastes were tested as before, and the results summarized in the following table.

Example 18 G

	Al ₂ O ₃ /BN/ZnO 25/55/20	Al ₂ O ₃ /BN/AlN 25/55/20
% porosity	13.6	17.3
k (W/mK)	4.44	3.27

[0050] In the foregoing specification, specific embodiments of the present invention have been described. However, one of ordinary skill in the art appreciates that various modifications and changes can be made without departing from the scope of the present invention as set forth in the claims below. Accordingly, the specification and figures are to be regarded in an illustrative rather than a restrictive sense, and all such modifications are intended to be included within the scope of present invention. The benefits, advantages,

solutions to problems, and any element(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential features or elements of any or all the claims. The invention is defined solely by the appended claims including any amendments made during the pendency of this application and all equivalents of those claims as issued.

CLAIMS

We Claim

1. A thermal interface material comprising:
 - a first type of thermally conductive particle that is conformable wherein each of the first type of thermally conductive particle is itself a self-cohesive agglomeration of smaller platy particles;
 - a second type of thermally conductive particle;
 - resin particles; and
 - a fugitive liquid wherein the fugitive liquid and the resin particles are soluble in each other to an extent less than 20%.
2. The thermal interface material according to claim 1 wherein:
 - the resin particles comprise thermoplastic particles.
3. The thermal interface material according to claim 2 wherein the resin particles further comprise thermoset particles.
4. The thermal interface material according to claim 1 wherein the resin particles comprise thermoset particles.
5. The thermal interface material according to claim 1 wherein the first type of thermally conductive particle comprises boron nitride.
6. The thermal interface material according to claim 5 wherein the first type of thermally conductive particle is spheroidal.
7. The thermal interface material according to claim 5 wherein the second type of thermally conductive particle is aluminum nitride.

8. The thermal interface material according to claim 5 wherein the boron nitride particles have an average size that is at least five times an average size of the second type of thermally conductive particles.
9. The thermal interface material according to claim 8 wherein the mass of the thermally conductive particles as a percentage of a total mass of the thermally conductive particles and the resin particles is at least 75 %.
10. The thermal interface material according to claim 5 wherein the second type of thermally conductive particle is alumina.
11. The thermal interface material according to claim 10 wherein the boron nitride is monodispersed and comprises at least 50% by mass of a total mass of the boron nitride and alumina, and an average size of the boron nitride particles is larger than an average size of the alumina.
12. The thermal interface material according to claim 10 further comprising a third type of thermally conductive particle consisting essentially of zinc oxide.
13. The thermal interface material according to claim 10 wherein the second type of thermally conductive particle is spheroidal.
14. The thermal interface material according to claim 10 further comprising a sintering aid.
15. The thermal interface material according to claim 14 wherein the sintering aid comprises at least one material selected from the group consisting of: metal alkoxides, low melting point salts and organic inorganic hybrid composites.

16. The thermal interface material according to claim 11 wherein the resin particles comprise at least one material selected from the group consisting of: polyester, copolyester, polyamide, copolyamide, polyurethane, polybutylene terephthalate, polyolefin, acrylic, silicone, and liquid crystalline polymers.
17. A thermal interface material comprising:
a first type of thermally conductive particle that is conformable wherein each of the first type of thermally conductive particle is itself a self-cohesive agglomeration of smaller platy particles;
a second type of thermally conductive particle; and
a liquid epoxy binder.
18. The thermal interface material according to claim 17 wherein the first type of thermally conductive particle comprises boron nitride.
19. The thermal interface material according to claim 18 wherein the first type of thermally conductive particle is spheroidal.
20. The thermal interface material according to claim 18 wherein the second type of thermally conductive particle is aluminum nitride.
21. The thermal interface material according to claim 18 wherein the boron nitride particles have an average size that is at least five times an average size of the second type of thermally conductive particles.
22. The thermal interface material according to claim 18 wherein the second type of thermally conductive particle is alumina.
23. The thermal interface material according to claim 10 wherein the boron nitride is monodispersed and comprises at least 50% by mass of a total mass of the boron nitride

and alumina, and an average size of the boron nitride particles is larger than an average size of the alumina.

24. The thermal interface material according to claim 22 further comprising a third type of thermally conductive particle consisting essentially of zinc oxide.

25. The thermal interface material according to claim 22 wherein the second type of thermally conductive particle is spheroidal.

26. The thermal interface material according to claim 22 further comprising a sintering aid.

27. The thermal interface material according to claim 26 wherein the sintering aid comprises at least one material selected from the group consisting of: metal alkoxides, low melting point salts and organic inorganic hybrid composites.

28. The thermal interface material according to claim 23 wherein the resin particles comprise at least one material selected from the group consisting of: polyester, copolyester, polyamide, copolyamide, polyurethane, polybutylene teraphthalate, polyolefin, acrylic, silicone, and liquid crystalline polymers.