(54) Title: TRANSPARENT RUBBER MODIFIED STYRENEICS COMPOSITIONS

(57) Abstract: Transparent ABS compositions useful for extrusion of clear films of a rubbery nature with good adhesion to other polymers and useful for unique molding grade clear compositions with high elongations to failure are provided. The ABS compositions utilize a styrene-butadiene rubber grafted to styrene-acrylonitrile graft phase with a methyl methacrylate and styrene-acrylonitrile rigid matrix phase where the calculated refractive index of the graft phase approximately matches that of the matrix phase in order to achieve transparent blends with ductility.
TRANSPARENT RUBBER MODIFIED STYRENICS COMPOSITIONS

FIELD OF THE INVENTION

The present invention relates to transparent styrenics of a rubbery nature. More particularly, the invention relates to transparent acrylonitrile-butadiene-styrene polymers.

DESCRIPTION OF THE RELATED ART

Acrylonitrile-butadiene-styrene (ABS) plastics, which are rubber and thermoplastic composites, comprise a broad, versatile family of graft copolymers with an excellent balance of mechanical properties, processing latitude, recyclability and economics. Most ABS products consist of a two phase system of a grafted terpolymer, acrylonitrile-butadiene-styrene, dispersed in a glassy continuous matrix of styrene-acrylonitrile (SAN) copolymer. The graft terpolymer typically consists of a polybutadiene rubber core and grafted SAN shell, small amounts of styrene and acrylonitrile being grafted onto the rubber particles to compatibilize the two phases. The broad versatility of ABS results from the many compositional and structural variables that can be selected to achieve a desired property balance.

In the ABS manufacturing process, three distinct polymerization reactions or stages are involved. First the elastomeric (rubber) component, either butadiene homopolymer, a styrene-butadiene or an acrylonitrile-butadiene copolymer, is produced. This phase can be carried out either in a water-based emulsion or in a solution polymerization process. In the second stage, the styrene and acrylonitrile (50-90/10-50) are copolymerized optionally with other monomers and grafted onto the elastomeric phase to achieve the desired compatibility. The rubber content of an ABS graft may range from 10 to 90 weight percent. This stage can be performed either in emulsion, bulk/mass or via suspension and/or the emulsion-suspension
process route. In the third stage, styrene and acrylonitrile and, optionally, other olefin monomers are copolymerized either simultaneously with the second (grafting) stage or separately in an independent operation to form the rigid matrix. Again, this step may involve one or more of the following processes: emulsion, bulk or suspension polymerization. The SAN matrix may range from 10 to 90 weight percent of the ABS graft composition.

In addition, the ABS materials may be produced by various process techniques known as batch, semibatch or continuous polymerization for reasons of either manufacturing economics, product performance or both.

To alter specific properties of the resulting polymers, other monovinylidene aromatic, ethylenically unsaturated nitrile and acrylate monomers may be incorporated, either in addition to or in place of the various acrylonitrile-butadiene-styrene components. The physical properties of ABS plastics vary somewhat with their method of manufacture but more so with their composition. Specific performance requirements and extensive material differentiation are achieved by manipulation of monomer composition, microstructure, morphology or additives.

Transparent ABS grades have been made in various manners. Transparent ABS may be made by grafting styrene, acrylonitrile and optionally high levels of methyl methacrylate onto a special styrene-butadiene rubber (SBR) substrate. Here the refractive indices of the dispersed rubber phase and the rigid continuum must be closely matched. Another method is to use a polybutadiene rubber with particles sufficiently small that they do not reflect visible light and to graft upon it a methyl methacrylate-styrene-acrylonitrile copolymer with a refractive index matching that of the polybutadiene phase.
U.S. Patent No. 5,017,422 (1991) to Schuman et al. discloses transparent cast films of ABS plastics having a film thickness from 1 to 200 μm. A graft polymer of a diene rubber, preferably polybutadiene and graft monomers, preferably of styrene and acrylonitrile, were utilized to produce self supporting thin films by dissolving a solution of the ABS plastic with mold release agent in an inert organic solvent and casting on a support. This approach of using casting techniques points out the continuing need for transparent ABS polymers suitable for extrusion in thin films or layers.

While these approaches achieve transparency, there remains a number of unsolved and unmet needs in the field of transparent ABS resins with regard to particular properties and potentially advantageous properties. There is a need for more economical, lower cost transparent ABS resins, a need for transparent ABS resins extrudable in thin films, particularly thin films suitable for laminates, a need for transparent ABS films with good adhesion to other transparent polymers and a need for molding grade clear ABS compositions with rubbery charactership, ductility and high elongations to failure.

SUMMARY OF THE INVENTION

It is therefore seen that there is a particular need for low cost, transparent extruded ABS films of a rubbery nature with good adhesion to transparent polymers and a further need for molding grade clear ABS compositions with a rubbery nature. Such ABS resins would be particularly useful, for example, in the preparation of bulletproof laminates with other transparent polymers such as polycarbonates and acrylics and in the preparation of various molded objects where transparency and high elongation to failure as well as the other advantages of ABS plastics are desired.
To achieve these advantages, the present invention utilizes a modified vinyl aromatic-diene rubber substrate/vinyl aromatic-vinyl cyanide superstrate based high rubber graft phase with a vinyl aromatic-vinyl cyanide-vinyl carboxylic acid ester matrix rigid phase, optionally blended with other monomers or copolymers, to achieve transparent blends extrudable in thin films with ductility and good adhesion to other transparent polymers.

The present invention generally provides for an acrylonitrile-butadiene-styrene (ABS) type composition comprising: a) a matrix derived from a vinyl aromatic polymerizable species, a vinyl cyanide polymerizable species and a vinyl carboxylic acid ester polymerizable species wherein the matrix is present at a weight percent level of from about 30 to about 70 percent by weight based on the total weight of the composition and wherein the ratio of the combined weight of vinyl aromatic polymerizable species and vinyl cyanide polymerizable species to the weight of vinyl carboxylic acid ester polymerizable species is about 1.3 to about 1.7; b) a graft copolymer comprising a substrate copolymer and a superstrate copolymer, wherein the graft copolymer is present at a level of from about 30 to about 70 weight percent of total weight of the composition, wherein the substrate copolymer comprises a copolymer derived from about 0 to about 30 percent by weight of a vinyl aromatic polymerizable species and about 70 percent to about 100 percent by weight of a di-olefin based on the total weight of the substrate copolymer, and wherein the superstrate copolymer comprises a copolymer derived from a vinyl aromatic polymerizable species and a vinyl cyanide polymerizable species, wherein the substrate copolymer is present at a weight percent level of from about 40 to about 90 percent by weight of the graft copolymer and the superstrate copolymer is present at a weight percent level of from about 10 percent to about 50 percent based on the weight of the graft copolymer and wherein the substrate copolymer is present at a level of from
about 20 to about 45 weight percent of the total weight of the composition; and wherein the refractive index of the copolymer approximately matches the calculated refractive index of the graft copolymer so as to give a transparent composition. More particularly the present invention provides for an acrylonitrile-butadiene-styrene (ABS) type composition comprising: a) a matrix derived from a vinyl aromatic monomer, a vinyl cyanide monomer and a vinyl carboxylic acid ester monomer wherein the matrix is present at a weight percent level of from about 30 to about 70 percent by weight based on the total weight of the composition, wherein the ratio of the combined weight of matrix vinyl aromatic monomer and vinyl cyanide monomer to the weight of matrix vinyl carboxylic acid ester monomer is about 1.3 to about 1.7 and wherein the matrix vinyl aromatic monomer is present at a weight percent level from about 39.5 to about 53.5 percent by weight based on the total weight of the matrix, wherein the matrix vinyl cyanide monomer is present at a weight percent level from about 8.5 to about 19 percent by weight based on the total weight of the matrix and wherein the matrix vinyl carboxylic acid ester monomer is present at a weight percent level of from about 37 to about 43.5 percent by weight based on the total weight of the matrix; b) a graft copolymer comprising a substrate copolymer and a superstrate copolymer, wherein the graft copolymer comprises from about 30 percent to about 70 percent by weight based on the total weight of the composition, wherein the substrate copolymer comprises a copolymer derived from a vinyl aromatic monomer and a di-olefin monomer, wherein the substrate copolymer comprises a copolymer derived about 0 to about 30 percent by weight of a vinyl aromatic monomer and about 70 to about 100 percent by weight a di-olefin based on the total weight of the substrate copolymer, and wherein the superstrate copolymer comprises a copolymer derived from about 70 to about 85 weight percent of a vinyl aromatic monomer and about 15 to about 30 weight percent of a vinyl cyanide monomer based on the total weight of the superstrate copolymer, and wherein the substrate copolymer is present at a
level of from about 20 to about 45 weight percent of the total weight of the composition and present at a weight percent level of from about 40 to about 90 percent by weight of the graft copolymer and the superstrate copolymer is present at a weight percent level of from about 10 percent to about 50 percent based on the weight of the graft copolymer; c) wherein the substrate copolymer particle size is less than 2400 angstroms (0.24 microns); and d) wherein the refractive index of the copolymer approximately matches the calculated refractive index of the graft copolymer so as to give a transparent composition.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that by combining a styrene-butadiene rubber/styrene-acrylonitrile (SBR/SAN) high rubber graft phase with a rigid matrix phase derived from methyl methacrylate, styrene and acrylonitrile wherein the calculated refractive index of the graft phase approximately matches the refractive index of the matrix phase, low haze extrudable ABS transparent polymers with the ductility and performance advantages of ABS polymers may be prepared. Such SBR rubber based ABS polymers have been found to be particularly useful for extrusion into thin films for use in transparent polymer laminates as they exhibit good adhesion to other polymers as well as a low haze transparency and ductility.

The ABS polymers of this invention comprise a two-phase system. The first phase comprises a high rubber styrene-butadiene rubber (SBR) substrate with a copolymer of styrene-acrylonitrile (SAN) attached to it. This substrate is commonly referred to as the "graft phase" because the SAN is physically attached or grafted to the rubber through a chemical reaction. A second phase preferably comprises methyl methacrylate in the form of polymethylmethacrylate (PMMA) and SAN and is commonly referred to as the "free rigid phase." The SBR/SAN graft phase is dispersed throughout the
rigid phase PMMA/SAN that forms the a polymer continuum. The rubber 
interface is the surface forming the boundaries between the graft and rigid 
phases. The grafted SAN acts as a compatibilizer between the rubber and 
rigid phase at this interface and prevents the separation of these two 
otherwise immiscible phases.

The ABS type thermoplastic resins utilized by the present invention are 
graft copolymers of vinyl cyanide monomers, di-olefins, vinyl aromatic 
monomers and vinyl carboxylic acid ester monomers. Thus applicants define 
herein the phrase ABS type or acrylonitrile-butadiene-styrene type to include 
the group of polymers derived from vinyl cyanide monomers, di-olefins, 
viny 1 aromatic monomers and vinyl carboxylic acid ester monomers as 
hereinafter defined. Vinyl cyanide monomers are herein defined by the 
following structural formula:

\[ \text{H} \text{C}=\text{C}-\text{C}=\text{N} \text{, where } R \text{ is selected from the group consisting of} \]

hydrogen, alkyl groups of from 1 to 5 carbon atoms, bromine and chlorine. 
Examples of vinyl cyanide monomers include acrylonitrile, methacrylonitrile, 
ethacrylonitrile, \( \alpha \)-chloroacrylonitrile and \( \alpha \)-bromoacrylonitrile. The di-
olefins utilized in the present invention are herein defined by the following 
structural formula:

\[ \text{Q}\text{C}=\text{C}-\text{C}=\text{C}=\text{Q} \text{, where each } Q \text{ is independently selected from the} \]
group consisting of hydrogen, alkyl groups of from 1 to 5 carbon atoms, 
bromine and chlorine. Examples of di-olefins include butadiene, isoprene, 
1,3-heptadiene, methyl-1,3-pentadiene, 2,3-dimethylbutadiene, 2-ethyl-1,3-
pentadiene, 1,3-hexadiene, 2,4-hexadiene, chlorobutadiene, bromobutadiene, dichlorobutadiene, dibromobutadiene and mixtures thereof. Vinyl aromatic monomers are herein defined by the following structural formula:

![ structural formula for vinyl aromatic monomer ]

, where each X is independently selected from the group consisting of hydrogen, alkyl groups of from 1 to 5 carbon atoms, cycloalkyl, aryl, alkaryl, aralkyl, alkoxy, aryloxy and halogen and where R is selected from the group consisting of hydrogen, alkyl groups of from 1 to 5 carbon atoms, bromine and chlorine. Examples of substituted vinyl aromatic monomers include styrene, 4-methylstyrene, vinyl xylene, 3,5-diethylstyrene, p-tert-butyl-styrene, 4-n-propylstyrene, α-methyl-styrene, α-ethyl-styrene, α-methyl-p-methylstyrene, p-hydroxy-styrene, methoxy-styrenes, chlorostyrene, 2-methyl-4-chloro-styrene, bromo-styrene, α-chloro-styrene, α-bromo-styrene, dichloro-styrene, 2,6-dichloro-4-methyl-styrene, dibromostyrene, tetrachloro-styrene and mixtures thereof. Vinyl carboxylic acid ester monomers (esters of alpha-, beta- unsaturated carboxylic acids) are herein defined by the following structural formula:

![ structural formula for vinyl carboxylic acid ester monomer ]

, where J is selected from the group consisting of hydrogen and alkyl groups of from 1 to 8 carbon atoms and A is selected from the group consisting of alkyl groups of from 1 to 5 carbon atoms. Examples of vinyl carboxylic acid ester monomers include methyl methacrylate, methyl acrylate, ethyl methacrylate, ethyl acrylate, butyl methacrylate, butyl acrylate,
propyl methacrylate, propyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, methyl ethacrylate and mixtures thereof.

It will be understood that by the use of "monomers" are included all of the polymerizable species of monomers and copolymers typically utilized in polymerization reactions, including by way of example monomers, homopolymers of primarily a single monomer, copolymers of two or more monomers, terpolymers of three monomers and physical mixtures thereof. For example, a mixture of polymethylmethacrylate (PMMA) homopolymer and styrene-acrylonitrile (SAN) copolymer may be utilized to form the rigid matrix phase, or alternatively a methylmethacrylate-styrene-acrylonitrile (MMASAN) terpolymer may be utilized.

Various monomers may be further utilized in addition to or in place of those listed above to further modify various properties of the compositions disclosed herein. In general, the components of the present invention may be compounded with a copolymerizable monomer or monomers within a range not damaging the objectives and advantages of this invention. For example, the rubber phase may in addition to or in place of SBR may be comprised of polybutadiene, butadiene-acrylonitrile copolymers, polyisoprene, EPM and EPR rubbers (ethylene/proplylene rubbers), EPDM rubbers (ethylene/proplylene/non-conjugated diene rubbers) and crosslinked alkylacrylate rubbers based on C1-C8 alkylacrylates, in particular ethyl, butyl and ethylhexylacrylates, either alone or as a mixture of two or more kinds. Furthermore, the rubber may comprise either a block or random copolymer. In addition to or in place of styrene and acrylonitrile monomer used in the graft or matrix resins, monomers including vinyl carboxylic acids such as acrylic acid, methacrylic acid and itaconic acid, acrylamides such as acrylamide, methacrylamide and n-butyl acrylamide, alpha-, beta-unsaturated dicarboxylic anhydrides such as maleic anhydride and itaconic anhydride, imides of alpha-, beta-unsaturated dicarboxylic acids such as
maleimide, N-methylmaleimide, N-ethylmaleimide, N-Aryl maleimide and the halo substituted N-alkyl N-aryl maleimides, imidized polymethyl methacrylates (polyglutarimides), unsaturated ketones such as vinyl methyl ketone and methyl isopropenyl ketone, alpha-olefins such as ethylene and propylene, vinyl esters such as vinyl acetate and vinyl stearate, vinyl and vinyldiene halides such as the vinyl and vinyldiene chlorides and bromides, vinyl-substituted condensed aromatic ring structures such as vinyl naphthalene and vinyl anthracene and pyridine monomers may be used, either alone or as a mixture of two or more kinds.

The acrylonitrile-butadiene-styrene type (ABS) thermoplastic resin is preferably based on a SBR high rubber graft with a SAN/PMMA matrix phase. Rubber amounts between about 20 percent and about 45 percent are preferred. This ABS composition preferably comprises: a) a matrix derived from a vinyl aromatic monomer, a vinyl cyanide monomer and a vinyl carboxylic acid ester monomer, wherein the matrix is present at a weight percent level of from about 30 to about 70 percent by weight based on the total weight of the composition, more preferably from about 35 to about 50 percent by weight thereof, and most preferably from about 38 to about 47 percent by weight thereof; b) a graft copolymer (graft phase) comprising a substrate copolymer and a superstrate copolymer wherein the substrate copolymer comprises a copolymer derived from a vinyl aromatic monomer and a di-olefin and wherein the superstrate copolymer comprises a copolymer derived from both a vinyl aromatic monomer and a vinyl cyanide monomer wherein the graft copolymer is present at a level of from about 30 to about 70 weight percent of the total weight of the composition, more preferably from about 50 to about 65 percent by weight thereof, and most preferably from about 53 to about 62 percent by weight thereof; and c) wherein the refractive index of the matrix phase and the calculated refractive index of the graft phase are approximately the same (that is, matched to within about .005 or
less). The refractive index of the phases may be readily calculated based on the weight percentage of the components and their refractive indices, for example:

The refractive indices of butadiene, styrene, acrylonitrile and methyl methacrylate polymers are 1.515, 1.591, 1.515 and 1.491 respectively.

A butadiene/styrene ratio of 85:15 gives a calculated refractive index of \((.85 \times 1.515) + (.15 \times 1.591) = 1.526\).

The grafted SAN of S:AN of 80:20 gives a calculated refractive index of \((.80 \times 1.591) + (.20 \times 1.515) = 1.576\).

A graft copolymer of 65% styrene-butadiene rubber (B:S =85:15) and 35% grafted SAN (S:AN = 80:20) gives a calculated refractive index of \((.65 \times 1.526) + (.35 \times 1.576) = 1.544\).

In the example above, the matrix phase must have approximately the same (within ± 0.005) refractive index as the graft rubber phase. A matrix phase of 60% PMMA and 40 percent SAN of 75% styrene and 25% acrylonitrile has a refractive index ~1.539, thereby matching the graft phase refractive index to within 0.005.

The rigid matrix phase is preferably derived from a mixture of PMMA and SAN as this allows the PMMA/SAN ratio to be easily varied and allows economical preparation of the matrix phase. A MMASAN terpolymer may alternatively be utilized. The ratio of vinyl aromatic plus vinyl cyanide to vinyl carboxylic acid ester (for example, SAN copolymer to PMMA homopolymer) is preferably from about 1.3 to about 1.7 (that is, preferably from about 56.5 percent to about 63 percent vinyl aromatic-vinyl cyanide and from about 37 percent to about 43.5 percent vinyl carboxylic acid ester by weight based on the total weight of the matrix, with vinyl aromatic preferably
present at levels from about 39.5 percent to about 53.5 percent and vinyl cyanide preferably present at levels from about 8.5 percent to about 19 percent based on the total weight of the matrix), more preferably from about 1.4 to about 1.6 (from about 58.5 percent to about 61.5 percent vinyl aromatic-vinyl cyanide, from about 38.5 percent to about 61.5 percent vinyl carboxylic acid ester, with from about 41 percent to about 52.5 percent vinyl aromatic and from about 9 percent to about 18.5 percent vinyl cyanide based on the total weight of the matrix) and most preferably 1.5 (about 60 percent vinyl aromatic-vinyl cyanide and about 40 percent vinyl carboxylic acid ester based on the total weight of the matrix, with the vinyl aromatic present at a level of from about 42 percent to about 51 percent and the vinyl cyanide present at a level of about 9 percent to about 18 percent based on the total weight of the copolymer).

The graft copolymer is preferably derived from a vinyl aromatic-di-olefin rubber substrate copolymer. The graft copolymer preferably comprises from about 40 percent to about 90 percent of a substrate copolymer and from about 10 percent to about 60 percent of a superstrate copolymer based on the total weight of the graft copolymer, more preferably from about 55 percent to about 75 percent of a substrate copolymer and from about 25 percent to 45 percent of a superstrate copolymer by weight thereof, and most preferably about 65 percent by weight of a substrate copolymer and 35 percent by weight of a superstrate copolymer. The substrate copolymer preferably comprises a vinyl aromatic component level of from about 0 percent to about 30 percent by weight based on the total weight of the substrate copolymer, more preferably from 10 to 20 percent by weight thereof and most preferably 15 percent by weight thereof, and a di-olefin component level of from about 70 percent to about 100 percent of a di-olefin by weight based on the total weight of the substrate copolymer, more preferably from about 80 to about 90 percent by weight thereof, and most preferably about 85 percent by weight thereof.
The superstrate copolymer preferably comprises a vinyl aromatic component level of from about 70 percent to about 85 percent and a vinyl cyanide component level of from about 15 percent to about 30 percent by weight based on the total weight of the superstrate copolymer, more preferably a vinyl aromatic component level of about 75 percent to about 85 percent and a vinyl cyanide component level of about 15 percent to about 25 percent by weight thereof, and most preferably a vinyl aromatic component level of about 75 percent to about 80 percent and a vinyl cyanide component level of about 20 percent to about 25 percent based on the total weight of the superstrate copolymer. The superstrate may optionally contain a vinyl carboxylic acid ester component such as methyl methacrylate.

The graft phase preferably has a weight average particle size of less than 2400 angstroms (0.24 microns), more preferably less than 1600 angstroms (0.16 microns) and most preferably less than 1200 angstroms (0.12 microns). Generally, the particle size of the rubber has an effect upon the optimum grafting level for the graft copolymer. As a given weight percentage of smaller size rubber particles will provide greater surface area for grafting than the equivalent weight of a larger rubber particle size, the density of grafting may be varied accordingly. In general, smaller rubber particles preferably utilize a higher superstrate/substrate ratio than larger size particles to give generally comparable results.

A preferred vinyl carboxylic acid ester for use as one component of the matrix phase of the present invention comprises methyl methacrylate in the form of polymethyl methacrylate (PMMA). Use of commercially available, easily utilized PMMA in conjunction with SAN allows great flexibility in adjusting the percentage composition of methyl methacrylate in the matrix phase as well as allowing use of PMMA with varying molecular weights, PMMA with modifying monomers, etc. As is well known in the art, PMMA may be produced by the polymerization of methyl methacrylate monomer to
form a homopolymer. PMMA homopolymer exists in its pure form only theoretically and is generally available commercially as a mixture of the homopolymer and with one or more copolymers of methyl methacrylate with C₁-C₄ alkyl acrylates, such as ethyl acrylate. Such commercially available PMMA copolymers contain methyl methacrylate and from about 1 percent to about 30 percent by weight of one or more C₁-C₄ alkyl acrylates and are suitable for use in the present invention as the vinyl carboxylic acid ester matrix component. Copolymers of PMMA with minor amounts of one or more copolymerizable monomers are also intended to be encompassed, e.g., the copolymer of methyl methacrylate with styrene and/or acrylonitrile.

The graft phase may be coagulated, blended and colloidal with the matrix phase homopolymers, copolymers and/or terpolymers by the various blending processes that are well known in the art to form the ASA polymer polyblend.

A lubricant, metal release agent or mold release agent may optionally be utilized. Preferred lubricants and release agents are ethylene bis stearamide, ethylenediamine bis stearamide, butyl stearate, barium stearate, calcium stearate, calcium behenate, calcium laurate, zinc stearate, zinc laurate, aluminum stearate, magnesium stearate, glycerin, mineral oils, liquid paraffins, waxes, higher fatty amides, lower alcohol esters of higher fatty acids, polyvalent alcohol esters of fatty acids and silicone based mold release agents.

There may optionally be added to the resin phases, during or after formation, such additives as heat and ultraviolet light stabilizers, antioxidants, lubricants, flow aids, mold or metal release agents, antistatic agents, flame and fire retardants, plasticizers, fillers, pigments, dyes, special effect pigments, drip suppressants, mineral additives and fillers, reinforcing agents, and the like.
The thermoplastic ABS compositions of the present invention provide ductile transparent compositions of a rubbery nature, useful for extrusion into thin films with rubbery character ship and good adhesion to polycarbonates and acrylic, providing a lower cost approach to preparation of items such as bulletproof polymer laminates. The thermoplastic compositions are further useful in providing unique molding grade clear compositions with high elongations to failure due to the rubbery nature. The compositions are characterized by a haze of 10 or less and a notched Izod of 0.8 ft-lb/in (42.7 j/m) or more.

The following examples are presented as illustrations of the preparation and utility of the present ABS compositions. The examples are not intended in any way to limit the spirit and scope of the invention.

All United States patents referenced herein are hereby and herewith specifically incorporated by reference.

EXAMPLES

The examples illustrate the use of appropriate ABS compositions in parts by weight (Formulation 1 and Formulation 2) and the property advantages of the composition as compared to formulations utilizing only SAN (Formulation 3) or PMMA (Formulation 4).

The transparent ABS compositions were molded and extruded for property evaluations according to ASTM standards. Compounding was done on a twin screw extruder and on a Banbury, with and without commercial lubricant or metal release agent. Optical performance of the compositions was evaluated by measuring haze and light transmission of injection molded discs of 0.125 in. thick samples. The notched Izod impact performance of each of the compositions was tested according to ASTM D256. The tensile strength
and elongation was determined according to ASTM-D638. The capillary melt viscosity was determined according to ASTM-D3835.

HRG is a SBR/SAN graft (calculated refractive index of about 1.544) of 65% styrene-butadiene rubber (calculated refractive index of about 1.526) and 35% styrene-acrylonitrile (calculated refractive index of about 1.576), with the styrene-butadiene rubber being 85% butadiene and 15% styrene and the grafted styrene-acrylonitrile being 80% styrene and 20% acrylonitrile. The graft phase particle size averaged 800 angstroms (0.08 microns).

SAN is a copolymer of styrene-acrylonitrile of 75% styrene and 25% acrylonitrile with a weight molecular average of 100,000. PMMA is a polymethyl methacrylate commercially available as V920 from Rohm and Haas. The 60/40 SAN/PMMA mixture has a measured refractive index of ~1.539.

Commercially available zinc stearate metal release agent was utilized.

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No limitation with respect to the specific embodiments disclosed herein is intended or should be inferred. As those skilled in the art, upon attaining an understanding of the invention, may readily conceive of alterations to, modifications of, and equivalents to the preferred embodiments without departing from the principles of the invention, it is intended to cover all these alternatives, modifications and equivalents. By way of example, but not of limitation, it would be obvious to those skilled in the art that the invention may be modified with various other monomers including various vinyl aromatic, vinyl cyanide, di-olefin and vinyl carboxylic acid ester monomers.
WHAT IS CLAIMED IS:

1. An acrylonitrile-butadiene-styrene (ABS) type composition comprising:

   a) a matrix derived from a vinyl aromatic monomer, a vinyl cyanide monomer and a vinyl carboxylic acid ester monomer wherein the matrix is present at a weight percent level of from about 30 to about 70 percent by weight based on the total weight of the composition;

   b) wherein the ratio of the combined weight of matrix vinyl aromatic monomer and vinyl cyanide monomer to the weight of matrix vinyl carboxylic acid ester monomer is about 1.3 to about 1.7 and wherein the matrix vinyl aromatic monomer is present at a weight percent level from about 39.5 to about 53.5 percent by weight based on the total weight of the matrix, wherein the matrix vinyl cyanide monomer is present at a weight percent level from about 8.5 to about 19 percent by weight based on the total weight of the matrix and wherein the matrix vinyl carboxylic acid ester monomer is present at a weight percent level of from about 37 to about 43.5 percent by weight based on the total weight of the matrix;

   c) a graft copolymer comprising a substrate copolymer and a superstrate copolymer, wherein the graft copolymer comprises from about 30 percent to about 70 percent by weight based on the total weight of the composition;

   d) wherein the substrate copolymer comprises a copolymer derived from a vinyl aromatic monomer and a di-olefin.
monomer, wherein the substrate copolymer comprises a copolymer derived about 0 to about 30 percent by weight of a vinyl aromatic monomer and about 70 to about 100 percent by weight a di-olefin based on the total weight of the substrate copolymer, and wherein the superstrate copolymer comprises a copolymer derived from about 70 to about 85 weight percent of a vinyl aromatic monomer and about 15 to about 30 weight percent of a vinyl cyanide monomer based on the total weight of the superstrate copolymer;

e) wherein the substrate copolymer is present at a level of from about 20 to about 45 weight percent of the total weight of the composition and present at a weight percent level of from about 40 to about 90 percent by weight of the graft copolymer and the superstrate copolymer is present at a weight percent level of from about 10 percent to about 50 percent based on the weight of the graft copolymer;

f) wherein the substrate copolymer particle size is less than 2400 angstroms (0.24 microns); and

g) wherein the refractive index of the copolymer approximately matches the calculated refractive index of the graft copolymer so as to give a transparent composition.

2. An acrylonitrile-butadiene-styrene (ABS) type composition comprising:

   a) a matrix derived from a vinyl aromatic polymerizable species, a vinyl cyanide polymerizable species and a vinil carboxylic acid ester polymerizable species wherein the matrix is present at a weight percent level of from about 30
to about 70 percent by weight based on the total weight of
the composition and wherein the ratio of the combined
weight of vinyl aromatic polymerizable species and vinyl
cyanide polymerizable species to the weight of vinyl
carboxylic acid ester polymerizable species is about 1.3 to
about 1.7;

b) a graft copolymer comprising a substrate copolymer and a
superstrate copolymer, wherein the graft copolymer is
present at a level of from about 30 to about 70 weight percent
of total weight of the composition, wherein the substrate
copolymer comprises a copolymer derived from about 0 to
about 30 percent by weight of a vinyl aromatic
polymerizable species and about 70 percent to about 100
percent by weight of a di-olefin based on the total weight of
the substrate copolymer, and wherein the superstrate
copolymer comprises a copolymer derived from a vinyl
aromatic polymerizable species and a vinyl cyanide
polymerizable species;

c) wherein the substrate copolymer is present at a weight
percent level of from about 40 to about 90 percent by weight
of the graft copolymer and the superstrate copolymer is
present at a weight percent level of from about 10 percent to
about 50 percent based on the weight of the graft copolymer
and wherein the substrate copolymer is present at a level of
from about 20 to about 45 weight percent of the total weight
of the composition;
d) wherein the refractive index of the copolymer approximately matches the calculated refractive index of the graft copolymer so as to give a transparent composition; and

e) wherein the ABS resin is extruded into a thin film.

3. The ABS composition of claim 2 wherein the matrix vinyl aromatic polymerizable species is present at a weight percent level from about 39.5 to about 53.5 percent by weight based on the total weight of the matrix, wherein the matrix vinyl cyanide polymerizable species is present at a weight percent level from about 8.5 to about 19 percent by weight based on the total weight of the matrix and wherein the matrix vinyl carboxylic acid ester polymerizable species is present at a weight percent level of from about 37 to about 43.5 percent by weight based on the total weight of the matrix;

4. The ABS composition of claim 2 wherein the substrate copolymer comprises a copolymer derived about 0 to about 30 percent by weight of a vinyl aromatic polymerizable species and about 70 to about 100 percent by weight of a di-olefin based on the total weight of the substrate copolymer, and wherein the superstrate copolymer comprises a copolymer derived from about 70 to about 85 weight percent of a vinyl aromatic polymerizable species and about 15 to about 30 a vinyl cyanide polymerizable species based on the total weight of the superstrate copolymer;

5. The ABS composition of claim 2 wherein the substrate copolymer comprises particles of less than 2400 angstroms (0.24 microns).

6. The ABS composition of claim 2 wherein the vinyl aromatic polymerizable species comprises styrene, the vinyl cyanide polymerizable species comprises acrylonitrile, the di-olefin comprises butadiene and the vinyl carboxylic acid ester polymerizable species comprises methyl methacrylate.
7. The ABS composition of claim 2 wherein the matrix vinyl aromatic polymerizable species and the matrix vinyl cyanide polymerizable species comprise a SAN copolymer and the vinyl carboxylic acid ester polymerizable species comprises a PMMA homopolymer and the di-olefin comprises butadiene.

8. The ABS composition of claim 2 wherein the matrix vinyl aromatic polymerizable species, the vinyl cyanide polymerizable species and the vinyl carboxylic acid ester polymerizable species comprise a MMASAN terpolymer and the di-olefin comprises butadiene.

9. The ABS composition of claim 2 wherein the thin film is laminated with other polymers.

10. The ABS composition of claim 2 wherein the thin film is laminated with other polymers to form a bulletproof laminate.

11. The ABS composition of claim 6 wherein the thin film is laminated with polymers selected from the group consisting of polycarbonate polymers and acryllic polymers and physical mixtures and blends of these polymers.

12. The ABS composition of claim 2 wherein the ABS resin further comprises a metal release agent.

13. The ABS composition of claim 12 wherein the metal release agent is selected from the group consisting of ethylene bis stearamide, ethylenediamine bis stearamide, butyl stearate, barium stearate, calcium stearate, calcium behenate, calcium laurate, zinc stearate, zinc laurate, aluminum stearate, magnesium stearate, glycerin, mineral oils, liquid paraffins, waxes, higher fatty amides, lower alcohol esters of higher fatty
acids, polyvalent alcohol esters of fatty acids and silicone based mold release agents.

14. The ABS composition of claim 2 wherein the ABS resin is characterized by a haze of 10 or less and a notched Izod of 0.8 ft-lb/in or more.

15. The ABS composition of claim 2 wherein the superstrate copolymer further comprises a vinyl carboxylic acid ester polymerizable species.

16. An acrylonitrile-butadiene-acrylonitrile type (ABS) composition consisting essentially of:

a) a matrix derived from a vinyl aromatic polymerizable species, a vinyl cyanide polymerizable species and a vinyl carboxylic acid ester polymerizable species wherein the matrix is present at a weight percent level of from about 30 to about 70 percent by weight based on the total weight of the composition, wherein the ratio of the combined weight of vinyl aromatic polymerizable species and vinyl cyanide polymerizable species to the weight of vinyl carboxylic acid ester polymerizable species is about 1.3 to about 1.7, wherein the vinyl aromatic polymerizable species is present at a weight percent level from about 39.5 to about 53.5 percent by weight based on the total weight of the matrix, wherein the vinyl cyanide polymerizable species is present at a weight percent level from about 8.5 to about 19 percent by weight based on the total weight of the matrix and wherein the vinyl carboxylic acid ester polymerizable species is present at a
weight percent level of from about 37 to about 43.5 percent by weight based on the total weight of the matrix;

b) a graft copolymer derived from a substrate copolymer and a superstrate copolymer wherein the substrate copolymer is present at a weight percent level of from about 40 to about 90 percent by weight of the graft copolymer and the superstrate copolymer is present at a weight percent level of from about 10 percent to about 50 percent based on the weight of the graft copolymer;

c) wherein the substrate copolymer comprises a copolymer derived about 0 to about 30 percent by weight of a vinyl aromatic polymerizable species and about 70 to about 100 percent by weight a di-olefin based on the total weight of the substrate copolymer, and wherein the superstrate copolymer comprises a copolymer derived from about 70 to about 85 weight percent of a vinyl aromatic polymerizable species and about 15 to about 30 a vinyl cyanide polymerizable species based on the total weight of the superstrate copolymer;

d) wherein the substrate copolymer is present at a level of from about 20 to about 45 weight percent of the total weight of the composition; and

e) wherein the refractive index of the copolymer approximately matches the calculated refractive index of the graft copolymer so as to give a transparent composition; and

f) wherein the ABS resin is extruded into a thin film.
17. The ABS composition of claim 15 wherein the superstrate copolymer further comprises a vinyl carboxylic acid ester polymerizable species.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

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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)

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X Further documents are listed in the continuation of box C.  
X Patent family members are listed in annex.

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Date of the actual completion of the international search: 26 September 2001

Date of dispatch of the international search report: 05/10/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 940-2040, Tx. 31 651 apo nl,
Fax (+31-70) 340-3016

Authorized officer

Hammond, A
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| A        | US 5 017 422 A (SCHUMANN WERNER ET AL)  
cited in the application  
* column 2, line 7-13 ; the whole document* | 1-16                 |
| A        | EP 0 714 941 A (GEN ELECTRIC)  
5 June 1996 (1996-06-05)  
* claims 1-12 *  
page 4, line 53-55 | 1-16                 |
| A        | WO 99 23157 A (DOW CHEMICAL CO)  
14 May 1999 (1999-05-14)  
* claims 1-16 *  
page 3, line 34 -page 4, line 5 | 1-16                 |
# INTERNATIONAL SEARCH REPORT

**Information on patent family members**

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