



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 267/06, 269/00 C08L 9/04, 33/02, 33/04 C08L 33/08, 35/06, 37/00 C08L 45/00, 47/00, 51/04 C08L 53/02	A1	(11) International Publication Number: WO 92/13015 (43) International Publication Date: 6 August 1992 (06.08.92)
(21) International Application Number: PCT/US91/00474 (22) International Filing Date: 23 January 1991 (23.01.91) (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventor; and (75) Inventor/Applicant (for US only) : HENTON, David, E. [US/US]; 5409 Woodview Pass, Midland, MI 48640 (US). (74) Agent: BIEBER, James, B.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i>
(54) Title: PREPARATION AND USE OF FUNCTIONALIZED POLYMERIC COMPOSITIONS (57) Abstract Preparation and use of a functionalized polymeric composition comprising a first phase and a second phase. The first phase comprises a first copolymer of a monovinylidene monomer and a comonomer selected to have at least one reactive epoxide functionality. The second phase is dispersed with the first phase. The second phase comprises a copolymer of an olefin monomer and one or more ethylenically unsaturated monomers copolymerizable with the olefin monomer wherein at least one of the ethylenically unsaturated monomers copolymerisable with the olefin monomer comprises a reactive functionality capable of reacting with one or more of the reactive epoxide functionalities of the first copolymer.		

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PREPARATION AND USE OF FUNCTIONALIZED POLYMERIC COMPOSITIONS

5 This invention relates to preparation and use
of a functionalized polymeric composition comprising two
normally incompatible polymers. Specifically, it
relates to a polymeric composition having functional
groups, said polymeric composition comprising a first
phase which comprises a copolymer having a reactive
functional group, and a second phase comprising a
10 copolymer having a reactive functionality capable of
reacting with the functional groups of the first
copolymer, the second phase being dispersed with the
first phase.

15 In the preparation of polymeric compositions
formed by the blending of a preformed polymer with
another preformed polymer, the compatibility of the
resulting copolymers is dependent upon the amount of
copolymerizable comonomer incorporated into the
20 copolymer matrix. For example, a copolymer of styrene
and glycidyl methacrylate (GMA) may be compatible with a
preformed polymer, whereas a different copolymer
containing a greater amount or different type of
25 comonomer may be incompatible with the same preformed

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polymer. In the latter event, blending of the preformed polymer and the comonomer does not result in an improved polymeric composition.

As a consequence of the above described
5 problem, manufacturers who desire to blend two normally incompatible polymers generally polymerize the monomers of one polymer in the presence of the preformed second polymer. During this process, chain transfer, or
10 reaction, with the preformed polymer occurs and some of the first polymer is polymerized from a site on the preformed polymer. The prior art technique is limited to preformed polymers which have active hydrogens capable of being extracted by radicals or reactive
15 groups that can copolymerize with the growing polymer. Most polymers can not be used in this process because of the lack of reactivity. This technique also requires that the preformed polymer be soluble or dispersible in a solvent or monomer system suitable for polymerization
20 of the first monomer.

In view of the deficiencies of the prior art, it would be highly desirable to provide functionalized copolymers capable of reacting with a variety of
25 normally incompatible copolymers.

It would be desirable to provide an improved, economical method for preparing the above polymeric composition, particularly for use in blending the
30 copolymers.

Finally, it would be particularly desirable to provide a functionalized polymeric composition having an elastomeric component for use in preparation of impact resistant blends.

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A first broad aspect of the invention is a method for making a polymeric composition that is capable of being formed into an article having good impact and/or ductility properties, which method includes the step of melt blending a first polymeric
5 phase with at least a second polymeric phase, in a weight ratio within the range of 1:9 to 9:1, characterized by the steps of:

(a) providing a first phase in an amount of 90
10 to 10 weight percent and a second phase in an amount of 10 to 90 weight percent, said weight percents being based on the total weight of the polymeric composition,

the first phase comprising a first copolymer
15 being formed from a first monomer mixture which comprises at least 70 weight percent of a monovinylidene monomer, and up to 30 weight percent of an ethylenically unsaturated comonomer copolymerizable with the
20 monovinylidene monomer and additionally comprising at least one reactive epoxide functionality capable of reacting after the first copolymer is formed, said weight percents being based on the total weight of the first monomer mixture, wherein the first copolymer has a
25 melt index, as determined by ASTM D-1238 Condition G, of between 0.1 g/10 minutes to 40 g/10 minutes, and a number average molecular weight, as determined by gel permeation, of between 20,000 to 150,000;

30 the second phase comprising a second copolymer being formed from a second monomer mixture which comprises at least 20 weight percent of an olefin monomer, and up to 80 weight percent of one or more ethylenically unsaturated monomers copolymerizable with the olefin monomer, wherein at least one of the

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ethylenically unsaturated monomers copolymerizable with the olefin monomer comprises a reactive functionality after the second copolymer is formed which is capable of reacting with one or more of the reactive epoxide functionalities of the first copolymer, said weight percents being based on the total weight of the second monomer mixture, wherein the second copolymer has a melt index, as determined by ASTM-1238 Condition I, of between 0.1 grams/10 minutes and 100 grams/10 minutes and a number average molecular weight, as determined by standard gel permeation, of between 20,000 and 150,000;

(b) dispersing the second phase with the first phase to form an intimate mixture under conditions sufficient to form enough interface between the first and second copolymers to cause a reaction between one or more of the reactive epoxide functionalities of the first copolymer and one or more of the reactive acid functionalities of the second copolymer.

A second broad aspect of the invention is use of the polymeric composition formed by the first broad aspect of the invention in fabricating an article, wherein the article is fabricated using a method selected from the group consisting of casting, blowing, extrusion, molding, injection molding, blow molding, coextrusion, laminating, or calendering.

The first phase of the polymeric composition of the present invention comprises a first copolymer derived from (a) a monovinylidene monomer and optionally, an ethylenically unsaturated monomer copolymerizable therewith, and (b) a comonomer selected to have at least one reactive epoxide functionality,

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which epoxide functionality is available for reacting after the first copolymer is formed.

Monovinylidene monomers suitable for use in forming the first copolymer of the present invention are the acrylates and methacrylates of aliphatic alcohols selected from those alcohols having from 1 to 12 carbon atoms, (e.g., methylacrylate, ethylacrylate, methyl methacrylate, butylacrylate and nonylacrylate); monovinylidene aromatic monomers including those polymers based on styrene; α -alkyl monovinylidene monoaromatic compounds (such as α -methylstyrene, α -ethylstyrene, α -methylvinyltoluene and α -methyldialkyl styrene); ring-substituted alkyl styrenes, (such as ortho-, meta-, and para-vinyltoluene, ortho-ethylstyrene, para-ethylstyrene, 2,4-dimethylstyrene, and para-tertiary butylstyrene); ring-substituted halostyrenes (such as ortho-chlorostyrene, para-chlorostyrene, ortho-bromo-styrene and 2,4-dichlorostyrene,); ring-alkyl-, ring-halo-substituted styrenes (such as 2-chloro-4-methylstyrene and 2,6-dichloro-4-methylstyrene); vinylanthracene and vinylanthracene. The alkyl substituents are generally selected to have 1 to 4 carbon atoms and may include isopropyl and isobutyl groups. If desired, mixtures of one or more of such monovinylidene monomers may be used.

The first phase comprises one or more ethylenically unsaturated comonomers selected to have at least one reactive epoxide functionality, said ethylenically unsaturated comonomers being copolymerizable with the monovinylidene monomers. The epoxide functionality is available for reacting after the first copolymer is formed. Suitable epoxy-containing comonomers include the glycidyl acrylates,

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glycidyl methacrylates and allyl glycidyl ether.
Preferably, the ethylenically unsaturated comonomers
copolymerizable with the monovinylidene monomer are
selected to have one or more of the reactive epoxide
functionalities of the first phase and are selected from
5 the group consisting of glycidyl methacrylate, glycidyl
acrylate, allyl glycidyl ether, and mixtures thereof.

In addition to the monovinylidene monomers and
the epoxy-containing ethylenically unsaturated
10 comonomers, the balance of the monomer mixture used to
form the first phase may additionally comprise minor
amounts of suitably copolymerizable monomers which do
not adversely affect the properties of the composition.
15 As is known to the skilled artisan, exemplary monomers
include the unsaturated nitriles (e.g., acrylonitrile,
methacrylonitrile, ethacrylonitrile); the anhydrides
(e.g., maleic anhydride, citraconic anhydride, itaconic
anhydride); vinyl halides (e.g., vinyl chloride, vinyl
20 bromide etc.; vinylidene halides (e.g., vinylidene
chloride and vinylidene bromide); vinyl esters (e.g.,
vinyl acetate and vinyl propionate); dialkyl maleate or
fumurates (e.g., dimethyl maleate, diethyl maleate,
dibutyl maleate and the corresponding fumurates); and
25 α -olefin monomers having from 1 to 10 carbon atoms
(e.g., ethylene, propylene, 1-butene, 1-pentene,
4-methyl-1-pentene, 1-hexene, and 1-octene. A
particularly preferred monomer is acrylonitrile. These
monomers may be present in an amount of up to 20 weight
30 percent, preferably from up to 10 weight percent, most
preferably from up to about 5 weight percent, based on
total weight of the monomer mixture used to form the
first phase.

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The first copolymer which can be employed generally has a melt index as determined by ASTM D-1238 Condition G of between 0.1 g/10 minutes and 40 g/10 minutes, preferably between 0.5 g/10 minutes to 20 g/10 minutes. The number average molecular weight of the first copolymer as determined by standard gel permeation is generally between 20,000 and 150,000, and preferably between 35,000 to 90,000. Ordinarily, the first copolymer is selected to have an intrinsic viscosity of between 0.2 and 1 dl/gram at 25°C in toluene.

Techniques for polymerizing the first copolymer are well known in the art. The Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition, (1980), sets forth general polymerization methods.

To improve the impact resistance of the polymeric composition, the first copolymer may advantageously be grafted to rubber substrates, it being understood that such grafting does not bind the reactive epoxide functionality. Suitable rubbery substrate polymers include any polymer or copolymer which are selected to have a glass transition temperature (T_g) of less than about 0°C, preferably not higher than -20°C as determined by American Society of Testing and Materials (ASTM) test Method D 746-52T.

Graftable rubber substrates suitable for use in the first phase of the present invention may be formed from various elastomeric materials. The elastomeric materials preferred for use in the present invention are diene rubbers, acrylate rubbers, ethylene propylene rubbers, hydrogenated diene rubbers, and EPDM rubbers, or mixtures thereof. A diene rubber is any rubbery polymer of one or more conjugated 1,3-diene, e.g.,

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butadiene, isoprene, piperylene, chloroprene. An acrylate rubber is any rubbery polymer of one or more acrylate monomers, e.g., 2-ethylhexyl acrylate, butylacrylate. An EPDM rubber is an interpolymer formed from ethylene, propylene and one or more dienes.

5

Such rubbery polymers include homopolymers, interpolymers, and block copolymers of conjugated 1,3-dienes and/or acrylate monomers with up to an equal amount by weight of one or more copolymerizable monoethylenically unsaturated monomers, such as monovinylidene aromatic hydrocarbons (e.g., styrene; a ring-substituted alkylstyrene, such as o-, m-, and p-vinyl toluene, 2,4-diethylstyrene, the ring-substituted ethylstyrenes, p-tert-butylstyrene; an alpha-alkylstyrene, such as alpha-methylstyrene, alpha-ethylstyrene, alpha-methyl-p-methylstyrene; vinyl naphthalene); ring-substituted halo monovinylidene aromatic hydrocarbons (e.g., the o-, m-, and p-chlorostyrenes, 2,4-dibromostyrene, 2-methyl-4-chlorostyrene); acrylonitrile; methacrylamide, N-butyl acrylamide); unsaturated ketones (e.g., methyl vinyl ketone, methyl isopropenyl ketone, etc.); alphaolefins (e.g., ethylene, propylene); pyridines; vinyl esters (e.g., vinyl acetate, vinyl stearate, etc); vinyl and vinylidene halides (e.g., the vinyl and vinylidene chlorides and bromides).

A most preferred group of elastomeric polymers for use in the first phase of the present invention includes those polymers derived from 75 to 100 percent by weight of butadiene and/or isoprene and the balance substantially being one or more of the monomers selected from the group consisting of monovinylidene aromatic hydrocarbons (e.g., styrene) and unsaturated nitriles

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(e.g., acrylonitrile). Particularly advantageous elastomeric materials for the preparation of the graftable rubber substrates of the present invention are butadiene homopolymers or an interpolymer of 80 to 96 percent by weight butadiene and the balance
5 substantially being acrylonitrile and/or styrene and/or methyl methacrylate.

The graftable rubber substrate suitably is selected to have a volume average particle diameter
10 within the range of from 300 Angstroms to 25,000 Angstroms. Preferably, the particles have a diameter within the range of from 800 Angstroms to 20,000 Angstroms.

15 The graftable rubber substrates of the present invention may contain up to about 2 percent of a cross-linking agent based on the weight of the elastomeric polymer-forming monomer or monomers. The cross-linking
20 agent can be any of the agents conventionally used for cross-linking acrylate rubbers. Suitable examples include divinylbenzene, diallyl maleate, diallyl fumurate, diallyl adipate, allyl acrylate, allyl methacrylate, diacrylates, and dimethylacrylates of
25 polyhydric alcohols (e.g., ethylene glycol dimethacrylate).

Methods of producing the graftable rubber substrates of the present invention are well-known in
30 the prior art. Typically, the graftable rubber substrates are formed through an emulsion polymerization process, anionic polymerization process, or Ziegler-Nata polymerization process. Exemplary processes are described in The Kirk-Othmer Encyclopedia of Chemical

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Technology at Vol 8, Pages 549-559 and Vol 18, Pages 740-744.

5 In some applications, it may be desirable to select the graftable rubber substrates to have a broad particle diameter range or which comprise two or more distinct groups having different average particle diameters. For example, it is sometimes desirable to select the graftable rubber substrates to have an average particle diameter within the range of from 800
10 Angstroms to 2000 Angstroms and a second group of graftable rubber substrates having an average particle diameter within the range of from 4000 Angstroms to 20,000 Angstroms. The first copolymer is free-radically
15 grafted to the graftable rubber substrate, by processes well-known in the prior art. Examples of known polymerization processes suitable for use in the present invention include mass, mass-solution, mass-suspension, suspension, and emulsion polymerization processes as
20 well as other modifications and/or combinations of such processes. See, for example, U.S. Patent Nos. 4,430,478 which teach such processes.

25 Typically, the graft polymerization process involves combining the graftable rubber substrate with the monomers from which the first copolymer is to be formed. The monomers are then polymerized to chemically combine or graft at least a portion of the graft-forming polymer on the graftable rubber substrate.
30

Those skilled in the art will appreciate the possibility of using a multi-stage graft polymerization process. In such a process, a portion of the first copolymer is formed from a particular monomer mixture and the remainder of the first copolymer is formed from

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a different monomer mixture. For example, the graftable rubber substrates may have a first layer of a first copolymer grafted thereto. Then, a second layer of first copolymer may be formed wherein the second layer comprises reactive epoxide functionalities capable of reacting with the one or more of the reactive functionalities of the second phase. Through the use of a multi-stage graft polymerization process it is possible to achieve the desirable physical properties of the compositions of the present invention with a relatively small amount of the ethylenically unsaturated monomer having reactive epoxide functionalities.

In many instances the process used to graft the first copolymer onto the graftable rubber substrate inherently produces an amount of free first copolymer, that is, an amount of free first copolymer which is not grafted to the graftable rubber substrate. Generally, the amount of free first copolymer present in the polymeric compositions of the present invention will be within the range of from 1.0 to 80 weight percent based on total polymeric composition weight. It is to be understood that free first copolymer may be incorporated into the polymeric compositions of the present invention through the above process or by blending the graftable rubber substrate with a separately prepared first polymer.

The graftable rubber substrate has grafted thereto an amount of first copolymer such that the weight ratio of the chemically attached graft to the graftable rubber is within the range of from 0.05:1 to 1.5:1 (graft to rubber ratio), beneficially from 0:1 to

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1.0:1. Preferably, the graft to rubber ratio is from 0.2:1 to 0.7:1.

The second phase of the present invention comprises an olefin monomer and one or more ethylenically unsaturated comonomers copolymerizable with the olefin monomer, wherein at least one of the ethylenically unsaturated monomers copolymerizable with the olefin monomer comprises a reactive functionality capable of reacting with one or more of the reactive epoxide functionalities of the first copolymer. The reactive functionality of the second copolymer is available for reacting with one or more of the reactive epoxide functionalities of the first copolymer after the second copolymer is formed.

By "olefin monomer" is meant an aliphatic hydrocarbon having one or more double bonds or mixtures thereof. Preferred monomers include the α -olefin monomers having from 1 to 10 carbon atoms such as ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, and 1-octene. Ethylene is particularly preferred.

Exemplary ethylenically unsaturated comonomers copolymerizable with the olefin monomers include monobasic carboxylic acids or polybasic carboxylic acids and partial esters and amides thereof (e.g., acrylic acid, methacrylic acid, crotonic acid, fumaric acid, maleic acid and itaconic acid; the corresponding partial esters, e.g., monomethyl fumarate and the corresponding partial amides, e.g., fumaric acid). After polymerization of the olefin monomers and the ethylenically unsaturated comonomers, the reactive functionality of the ethylenically unsaturated comonomer

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will be available for reacting with the epoxide functionality of the first copolymer.

In addition to the olefin monomer and one or more ethylenically unsaturated comonomers
5 copolymerizable with the olefin monomer, the balance of the monomer mixture used to form the second phase may additionally comprise an amount of suitably copolymerizable monomers which do not adversely affect
10 the properties of the composition. As is known to the skilled artisan, exemplary monomers include carbon monoxide and vinyl acetate. These non-hydrocarbon monomers may be present in an amount of up to 80 weight percent, beneficially up to 50 weight percent,
15 preferably up to about 30 weight percent, based on total weight of the monomer mixture used to form the second phase.

The second copolymer which can be employed
20 generally has a melt index as determined by ASTM-1238 Condition I of between 0.1 grams/10 minutes and 100 grams/10 minutes, preferably between 0.5 to 75. The number average molecular weight of the second copolymer as determined by standard gel permeation is generally
25 between 20,000 and 150,000, and preferably between 35,000 and 90,000.

Techniques for polymerizing the second copolymer are well known in the art. The Kirk-Othmer
30 Encyclopedia of Chemical Technology, 3rd edition, (1980), sets forth general polymerization methods.

The second phase of the present invention can be dispersed with the first phase of the present invention through methods well-known in the prior art.

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Typically, the second phase will be melt blended with the first phase under conditions sufficient to cause the reaction between one or more of the reactive epoxide functionalities of the first copolymer with the one or more reactive functionalities of the second copolymer.

5 The temperature at which the copolymerization occurs should be effective to melt and mix the polymers, and to induce a reaction. The upper temperature is determined by the thermal stability of the polymers, and the point

10 at which the mixture becomes infusible. The lower temperature is determined by the viscosity of the polymer mixture and the point prior to which the mixture components can react. Preferably, the temperature should be in a range from 177°C to 316°C, most preferably

15 from 204°C to 274°C.

The shear mixing should be sufficient to provide enough interface between the polymers so that the reaction can occur to form a graft polymer.

20 Exemplary melt processing equipment includes heated two-roll compounding mills, Brabender mixers, Banbury mixers, single screw extruders and twin screw extruders. The melt processing equipment is preferably a twin screw compounder operating between 50 RPM and 500 RPM.

25

An amount of the second phase is dispersed with the first phase such that the first phase comprises from 10 to 90 weight percent, and the second phase comprises from 10 to 90 weight percent, said weight percents being

30 based on the total weight of the functionalized polymeric composition. Preferably, an amount of the second phase is dispersed with the first phase so that the resultant polymeric composition comprises from 50 to 90 weight percent of the first phase and 10 to 50 weight percent of the second phase. When approximately equal

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volume levels of first phase and second phase are present, it is possible to have interpenetrating substantially cocontinuous phases.

Applicant has found that the polymeric compositions produced according to the method of the present invention possess improved physical properties when compared to compositions obtained by polymerizing the monomers of either the first or second phases alone, or polymerizing monomers of both the first or second phases where said monomers of either phase do not possess a functionality capable of reacting with a functionality of the other phase. Specifically, the polymeric compositions of the present invention possess an improved combination of impact strength and ductility.

The compositions of the present invention may be blended with thermoplastic resins to achieve modified physical properties. Exemplary thermoplastic resins include polyolefins e.g., ultra-low density polyethylene, medium density polyethylene, high density polyethylene, polypropylene, poly 1-butene; and monovinylidene aromatic polymers e.g., styrene, α -methylstyrene, m-ethylstyrene, p-methoxy- α -methylstyrene, p-ethyl- α -methylstyrene, p-ethyl- α -ethylstyrene, 2,4-diethylstyrene and m-isopropylstyrene. When the thermoplastic resin is a polyolefin, the polyolefin employed will preferably be present in an amount of from 1 to 80 percent by weight of polyblend. When the thermoplastic resin is a monovinylidene aromatic polymer, the monovinylidene aromatic polymer employed will preferably be present in an amount of from 1 to 30 percent by weight of polyblend.

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The compositions of the present invention have a good balance of properties, rendering them suitable for formation into tool housings, automotive parts, sheets, films and containers. The articles formed from the polymeric composition of the present invention
5 possess a good balance of toughness and ductility, which render them suitable for use in applications previously unavailable to conventional articles.

The following examples are presented to further
10 illustrate but not limit the scope of this invention. All parts and percentages are by weight unless otherwise indicated. Due to rounding and experimental error, the given percentages may not always equal exactly 100
15 percent.

Examples and Comparative Examples

Functionalized polymeric compositions are
20 prepared with various components set forth in Table I.

Each of the polymeric components used in the examples and comparative examples is coded and described hereinafter at Table I.

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TABLE I
Polymer Components

<u>Code</u>	<u>Polymer</u>
5	S/GMA-1 A styrene/glycidal methacrylate copolymer having polymerized therein 90 weight percent styrene and 10 weight percent glycidyl methacrylate, said weight percentages being based upon the total weight of the copolymer.
10	The polymerization is carried out as follows: Into a one gallon glass reactor is loaded 1000g of water, 1.94g of sodium bicarbonate; 0.48g of ethylenediaminetetraacetic acid (EDTA $2Na^+$); and 45.2g of a polystyrene seed latex, having 13.6g of polystyrene latex particle of 264 Angstroms (A). The reactor is purged with nitrogen and heated to 75°C while being agitated at 150 revolutions per minute (rpm). When the temperature reaches 75°C, the addition of continuous aqueous and monomer streams into the reactor is initiated. The aqueous stream contains 0.32% sodium dodecyl benzene sulfonate (NDBS) soap and 0.21% sodium persulfate and is added at a rate of 153.8g/hr for 5 hours; the monomer stream consists of 90% styrene, 10% glycidyl methacrylate, and 0.20 parts n-octyl mercaptan and is added at a rate of 246.2g/hour for 5 hours. After completion of the aqueous and monomer addition, the latex is heated for one hour at 75°C, is steam stripped to remove residuals, and is freeze coagulated to isolate the epoxy-containing thermoplastic. The conversion of monomers to polymer is 97.7%.
15	
20	
25	
30	S/GMA-2 A styrene/glycidyl methacrylate copolymer made similar to S/GMA-1, except that it contains S/GMA in a 90/10 weight ratio.
	AMS/AN/ GMA A terpolymer of α -methylstyrene/acrylonitrile/glycidyl methacrylate (65/25/10 weight ratio) made similar to S/GMA-1.
	EAA-1 An ethylene/acrylic acid copolymer having polymerized therein 93.5 percent ethylene and 6.5 percent acrylic acid, both percentages

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being based upon copolymers weight. The copolymer has a density (ASTM Test D-792) of 0.932 grams per cubic centimeter and a melt index (ASTM Test D-1238) of 5.5 grams per ten minutes. The copolymer is commercially available from The Dow Chemical Company under the trade designation EAA Resin 459.

5 EAA-2 An ethylene/acrylic acid copolymer having polymerized therein 90.0 percent ethylene and 10.0 percent acrylic acid, both percentages being based upon copolymers weight. The copolymer has a density (ASTM Test D-792) of 0.932 grams per cubic centimeter and a melt index (ASTM Test D-1238) of 5.5 grams per ten minutes. The copolymer is commercially available from The Dow Chemical Company under the trade designation EAA Resin 455.

15 S/GMA-
GRC-1 The polymerization of the grafted copolymer (GRC) is carried out as follows: A relatively small (1400 Angstroms), monodisperse rubber particle is grafted with styrene/glycidyl methacrylate (95/5) in an emulsion process as follows: Into a one gallon glass reactor is placed 1645g of rubber latex (1400 Angstroms), styrene/butadiene/acrylonitrile (ABS), 5/93/2, 569g of rubber solids). The reactor is flushed with nitrogen and heated to 90°C while being agitated at 150 rpm. When the temperature reaches 85°C, two continuous addition (conadd) streams are started. An aqueous stream containing 0.94% sodium dodecyl benzene sulfonate NDBS soap and 0.24% sodium persulfate is added at a rate of 108g/hour for six hours. A monomer stream containing 95.0% styrene, 5.0% glycidyl methacrylate and 0.05 parts (BOM) n-octyl mercaptan is added at a rate of 51.0g/hour for six hours. After stopping the conadd streams, the latex is heated an additional 0.25 hours at 90°C, steam stripped to remove residual monomers and stabilized with (1/3) mixture of TOPANOL® CA, commercially available from Canadian Industries, and dilauryl thiodipropionate (0.2%, based on rubber). The GRC is isolated by freeze coagulation.

A grafted rubber concentrate (GRC) of 66.8% styrene/butadiene/acrylonitrile rubber and

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5 33.2% styrene/glycidylmethacrylate S/GMA (95/5) is obtained. The GRC has grafted thereto 43% (weight of grafted phase divided by the weight of rubber X 100) of a styrene/glycidyl methacrylate copolymer having polymerized therein 95 percent styrene and 5 percent glycidyl methacrylate, both percentages being based upon the rigid phase graft copolymer weight.

GRC-1 A grafted rubber concentrate prepared similar to S/GMA-GRC-1, except that it does not contain the epoxy functional monomer.

10 GRC-2 A grafted rubber concentrate prepared similar to S/GMA-GRC-1, except that in place of styrene/glycidyl methacrylate copolymer (95/5) a styrene/acrylonitrile/glycidyl methacrylate copolymer (66/25.5/8.5 weight ratio) is used.

15 HDPE A high density polyethylene resin having a density (ASTM Test D-1505) of 0.965 grams per cubic centimeter and a melt index, (ASTM Test D-1238) of 0.8 decigrams per minute. The resin is commercially available from The Dow Chemical Company under the trade designation HDPE 12065.

20 HIPS A rubber-modified high impact polystyrene, commercially available from The Dow Chemical Company under the trade designation Styron 484.

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Preparation of Molded Samples

Molded samples to test the physical properties of the compositions of this invention are prepared as follows. Various components from Table I are added to a plastic bag and tumble mixed. More sophisticated equipment could have been used but was not necessary. When the substituents have been thoroughly mixed, they are single passed through an 0.8 inch counter-rotating nonintermeshing twin screw extruder at a feed rate of about 10 lbs/hour while the screws rotate at 200 rpm. The extruder is heated (from back to front) with a temperature profile of 164°C to 204°C (from back to front).

The pellets are air dried at 80°C for several hours before being injection molded. A two-ounce Negri-Bossi reciprocating screw injection molding machine is preheated to 191°C (375°F) in zone 1 and 204°C (400°F) in zone 2 and the hydraulic injection pressure is 800/600 pounds per square inch with a 45 second cycle time.

Polymeric compositions are converted into samples for testing purposes. The test samples are subjected to physical property tests which are described below and footnoted in the respective tables.

¹ Notched Izod Impact Strength measures the toughness of the samples which contain a notch, in foot pounds per inch notch. Notched Izod Impact Strength is determined according to American Society of Testing and Materials Test Method D-256, Method A.

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2 Dart impact measures the toughness of the sample in inch pounds. Dart impact is determined using 3.63 kg drop weight and an opening of 3.2 cm on a test specimen having a thickness of 3.175 mm and a Dart of
5 1.59 cm with a radius of curvature of 0.795 cm.

3 Tensile yield (T_y) measures the yield strength of the sample in pounds per square inch. T_y is determined according to American Society of Testing and
10 Materials Test Method D-638 at 0.2 inches/min.

4 Tensile rupture (T_r) measures the tensile strength upon failure of the sample in pounds per square inch. T_r is determined according to American Society of
15 Testing and Materials Test Method D-638 at 0.2 inches/min.

5 Modulus ($T_m \times 10^5$) measures the modulus of the sample in pounds per square inch. $T_m \times 10^5$ is determined
20 according to American Society of Testing and Materials Test Method D-638 at 0.2 inches/min.

6 Percent Elongation ($\%E$) measures the elongation to failure of the sample in percent. $\%E$ is determined
25 according to American Society of Testing and Materials Test Method D-638 at 0.2 inches/min.

7 Vicat measures the heat distortion temperature of the sample in degrees Fahrenheit. Vicat is
30 determined according to American Society of Testing and Materials Test Method D-1525-82.

Results of the physical property tests, where available, are set forth in Table II together with

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identity and amount of polymer components of each of the respective combinations.

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TABLE II
 PROPERTIES OF VARIOUS GRAFTS
 WITH OLEFIN-CARBOXYLIC ACID COPOLYMERS
 AND STYRENE/GLYCIDAL METHACRYLATE COPOLYMERS

Example/ Compar- ative Example	Polymer Code	Component Amount**	Izod Impact ¹	Dart ²	Ty ³	T _m ⁴	(T _m x 10 ⁵) ⁵	%E ⁶
1*	(1) HIPS	(1) 50						
	(2) E/AA-459	(2) 40	0.3	<10	1220	1170	0.83	3
	(3) GRC 1	(3) 10						
2	(1) S/GmA-1	(1) 50						
	(2) E/AA-459	(2) 40	7.2	150	2540	2430	0.81	44
	(3) S/GmA GRC-1	(3) 10						

* Not an example of the invention.

** Amounts are in percentages based upon weight of blend

*** Not measured.

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Blends of these components previously described show an excellent combination of physical properties as seen in Table II. Specifically, the control samples, lacking functional groups in the first phase, have
5 significantly poorer physical properties than the alloys of the present invention.

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TABLE III
PROPERTIES OF VARIOUS GRAFTS
WITH OLEFIN-CARBOXYLIC ACID COPOLYMERS
AND STYRENE/GLYCIDAL METHACRYLATE COPOLYMERS

<u>Example/ Compar- ative Example</u>	<u>Polymer Code</u>	<u>Component Amount**</u>	<u>Izod Impact¹</u>	<u>Dart²</u>	<u>Ty³</u>	<u>Tr⁴</u>	<u>(T_m x 10⁵)⁵</u>	<u>gE⁶</u>	<u>Vicat(°F)⁷</u>
3	(1) S/GmA-1	(1) 50	7.2	150	2541	2432	0.81	44	***
	(2) EAA-1	(2) 40							
	(3) S/GmA- GRC 1	(3) 10							
4	(1) S/GmA-1	(1) 60	5.1	90	3330	3260	1.0	24	***
	(2) EAA-2	(2) 40							
5	(1) AMS/AN/- GMA	(1) 50	1.5	160	2660	2490	0.88	38	192
	(2) EAA-2	(2) 40							
	(3) GRC-2	(3) 10							

* Not an example of the invention.

** Amounts are in percentages based upon weight of blend

*** Not measured.

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Blends of these components previously described show an excellent combination of physical properties as seen in Table III. As can be seen from the above table, compositions according to the present invention having
5 various comonomers in the first phase and grafted rubber modifiers possess very desirable physical properties. Specifically, the control samples, lacking functional groups in the first phase, have significantly poorer
10 physical properties than the alloys of the present invention.

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TABLE IV
PROPERTIES OF BLENDS OF
FUNCTIONAL POLYMERS
WITH NONFUNCTIONAL POLYMERS

<u>Example/</u> <u>Compar-</u> <u>ative</u> <u>Example</u>	<u>Polymer</u> <u>Code</u>	<u>Component</u> <u>Amount**</u>	<u>Izod</u> <u>Impact¹</u>	<u>Dart²</u>	<u>Ty³</u>	<u>Tr⁴</u>	<u>(T_m x 10⁵)⁵</u>	<u>gE⁶</u>
6*	HIPS 484	(1) 70	0.3	<20	2000	1675	1.51	11
	EAA-2	(2) 20						
	S/GMA GRC-1	(3) 10						
7*	HIPS 484	(1) 50	0.3	<20	1060	980	0.78	14
	EAA-1	(2) 40						
	S/GMA GRC-1	(3) 10						
8	HIPS 484	(1) 10	10.4	320+	2490	2440	0.72	100+
	S/GMA--2	(2) 30						
	EAA-2	(3) 40						
	S/GMA GRC-1	(4) 20						
9	HDPE	(1) 65	0.8	80	2710	No Break	1.50	250+
	EAA-2	(2) 10						
	S/GMA-2	(3) 18						
	S/GMA GRC-1	(4) 7						

* Not an example of the invention.

** Amounts are in percentages based upon weight of blend.

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Blends of these components previously described, and mixtures of polyolefins or low levels of additional nonfunctional first phase polymers show an excellent combination of physical properties as seen in Table IV.

5 As can be seen from the above table, compositions according to the present invention possess very desirable physical properties. Specifically, the control samples, having high levels of first phase
10 polymer, have significantly poorer physical properties than the alloys of the present invention.

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1. A method for making a polymeric composition that is capable of being formed into an article having good impact and/or ductility properties, which method includes the step of melt blending a first polymeric phase with at least a second polymeric phase, in a weight ratio within the range of 1:9 to 9:1, characterized by the steps of:

(a) providing a first phase in an amount of 90 to 10 weight percent and a second phase in an amount of 10 to 90 weight percent, said weight percents being based on the total weight of the polymeric composition,

the first phase comprising a first copolymer being formed from a first monomer mixture which comprises at least 70 weight percent of a monovinylidene monomer, and up to 30 weight percent of an ethylenically unsaturated comonomer copolymerizable with the monovinylidene monomer and additionally comprising at least one reactive epoxide functionality capable of reacting after the first copolymer is formed, said weight percents being based on the total weight of the first monomer mixture, wherein the first copolymer has a melt index, as determined by ASTM D-1238 Condition G, of between 0.1 g/10 minutes to 40 g/10 minutes, and a

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number average molecular weight, as determined by gel permeation, of between 20,000 to 150,000;

5 the second phase comprising a second copolymer
being formed from a second monomer mixture which
comprises at least 20 weight percent of an olefin
monomer, and up to 80 weight percent of one or more
ethylenically unsaturated monomers copolymerizable with
the olefin monomer, wherein at least one of the
10 ethylenically unsaturated monomers copolymerizable with
the olefin monomer comprises a reactive functionality
after the second copolymer is formed which is capable of
reacting with one or more of the reactive epoxide
functionalities of the first copolymer, said weight
15 percents being based on the total weight of the second
monomer mixture, wherein the second copolymer has a melt
index, as determined by ASTM-1238 Condition I, of
between 0.1 grams/10 minutes and 100 grams/10 minutes
and a number average molecular weight, as determined by
20 standard gel permeation, of between 20,000 and 150,000;

(b) dispersing the second phase with the first
phase to form an intimate mixture under conditions
25 sufficient to form enough interface between the first
and second copolymers to cause a reaction between one or
more of the reactive epoxide functionalities of the
first copolymer and one or more of the reactive acid
functionalities of the second copolymer.

30 2. The method of Claim 1 wherein step (b) is
performed at a temperature in the range of 177°C to
316°C.

35 3. The method of Claim 1 wherein the
monovinylidene monomer of the first phase is selected

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from the group consisting of acrylates and methacrylates of aliphatic alcohols having from 1 to 12 carbon atoms, monovinylidene aromatic monomers, α -alkyl monovinylidene monoaromatic compounds, ring-substituted alkyl styrenes, 5 ring-substituted halostyrenes, ring-alkyl, ring-halo-substituted styrenes, vinyl naphthalene and vinylanthracene.

4. The method of Claim 1 wherein the 10 ethylenically unsaturated comonomer of the first phase selected to have at least one reactive epoxide functionality capable of reacting after forming the first copolymer, is selected from the group consisting of glycidyl acrylates, glycidyl methacrylates, and allyl 15 glycidyl ether.

5. The method of Claim 1 wherein the monomer mixture used to form the first copolymer further comprises up to 20 weight percent, based on the total 20 weight of the monomer mixture, of at least one monomer selected from the group consisting of unsaturated nitriles, the anhydrides, vinyl halides, vinylidene halides, vinyl esters, dialkyl maleates, dialkyl 25 fumurates, and α -olefins having from 1 to 10 carbon atoms.

6. The method of Claim 1 wherein the first phase further comprises a rubbery polymer.

30 7. The method of Claim 6 wherein the rubbery polymer is selected from the group consisting of diene rubbers, acrylate rubbers, ethylene-propylene-diene rubbers, hydrogenated diene rubber, ethylene propylene 35 rubbers and mixtures thereof.

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8. The method of Claim 1 wherein the first phase is formed from a first monomer mixture comprising from 0.1 to 40 weight percent of the ethylenically unsaturated monomer comprising at least one epoxide functionality, said weight percents being based on the total weight of the first monomer mixture.

9. The method of Claim 1 wherein the olefin in the second phase is selected from the group consisting of α -olefin monomers having from 1 to 10 carbon atoms.

10. The method of Claim 1 wherein the ethylenically unsaturated monomers being copolymerizable with the olefin monomers and additionally having a reactive functionality capable of reacting with one or more of the reactive epoxide functionalities of the first copolymer is selected from the group consisting of ethylenically unsaturated monobasic carboxylic acids; and polybasic carboxylic acids, and C₁₋₄ esters and amides thereof.

11. The method of Claim 1 wherein the first phase is present in an amount from 50 to 90 weight percent, and the second phase is present in an amount of from 10 to 50 weight percent, said weight percent being based on the total weight of the polymeric composition.

12. The method of Claim 1 wherein:

the first phase comprises a first copolymer being formed from a monomer mixture which comprises styrene in an amount of from 80 to 99.5 weight percent, and glycidyl methacrylate in an amount of from 0.5 to 20 weight percent, based on total monomer mixture weight;

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the second phase comprises a second copolymer of ethylene and a carboxylic acid selected from the group of acrylic acid and methacrylic acid, wherein the carboxylic acid is present in the monomer mixture in an amount of from 1.0 to 20 weight percent, based on total monomer mixture weight.

13. Use of the polymeric composition formed by Claim 1 in fabricating an article, wherein the article is fabricated using a method selected from the group consisting of casting, blowing, extrusion, molding, injection molding, blow molding, coextrusion, laminating, and calendering.

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/00474

I. CLASSIFICATION		SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶	
According to International Patent Classification (IPC) or to both National Classification and IPC			
IPC (5): C08F 267/06, 269/00; C08L 9/04, 33/02, 33/04, 33/08, 35/06, 37/00, 45/00, 47/00, 51/04, 53/02 <i>con't</i>			
II. FIELDS SEARCHED			
Minimum Documentation Searched ⁷			
Classification System	Classification Symbols		
U.S.	525/74, 75, 85, 86, 88, 197, 207, 208, 210, 211 221, 222, 285, 286		
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸			
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹			
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²		Relevant to Claim No. ¹³
Y	US, A, 3,658,741 (KNUTSON ET AL) 25 APRIL 1972; See columns 1-4.		1-5 & 8-12
Y	US, A, 3,770,848 (LABANA ET AL) 06 NOVEMBER 1973; See columns 1-3.		1-5 & 8-12
Y	US, A, 3,852,236 (HEILMAN) 03 DECEMBER 1974 See columns 1-6.		1-5 & 8-12
Y	US, A, 4,528,329 (INOUE ET AL) 09 JULY 1985 See columns 1-4.		6-7
¹⁴ Special categories of cited documents: ¹⁵ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family			
IV. CERTIFICATION			
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report	
16 APRIL 1991		13 MAY 1991	
International Searching Authority		Signature of Authorized Officer	
ISA/US		<i>Jacob Ziegler</i> Jacob Ziegler	

FURTHER INFORMATION

CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☒ Claim numbers 13, because they relate to subject matter^{1,2} not required to be searched by this Authority, namely:

Use claim is non-statutory.

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out^{1,3}, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

PCT/US91/00474

CONTINUATION FORM PCT/ISA/210 SECOND SHEET
CLASSIFICATION OF SUBJECT MATTER

U.S. CL.

525/74, 75, 95, 86, 88, 197, 207, 208, 210, 211,
221, 222, 285, 286