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(54) COMPOSITIONS CONTAINING HYDROGENATED BLOCK COPOLYMERS AND ENGINEERING THERMOPLASTIC RESINS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The invention relates to a composition containing a partially hydrogenated block copolymer comprising at least two terminal polymer blocks A of a monoalkenyl arene having an average molecular weight of from 5,000 to 125,000 and at least one intermediate polymer block B of a conjugated diene having an average molecular weight of from 10,000 to 300,000, in which the terminal polymer blocks A constitute from 8 to 55% by weight of the block copolymer and no more than 25% of the arene double bonds of the polymer blocks A and at least 80% of the aliphatic double bonds of the polymer blocks B have been reduced by hydrogenation.

Engineering thermoplastic resins are a group of polymers that possess a balance of properties comprising strength, stiffness, impact resistance, and long term dimensional stability that make them useful as structural materials. Engineering thermoplastic resins are especially attractive as replacements for metals because of the reduction in weight that can often be achieved as, for example, in automotive applications.

For a particular application, a single thermoplastic resin may not offer the combination of properties desired and, therefore, means to correct this deficiency are of interest. One particularly appealing route is through blending together two or more polymers (which individually have the properties sought) to give a material with the desired combination of properties. This approach has been successful in limited cases, such as in the improvement of impact resistance for thermoplastic resins, e.g., polystyrene, polypropylene and poly(vinyl chloride), using special blending procedures or additives for this purpose. However, in general, blending of thermoplastic resins has not been a successful route to enable one to combine into a single material the desirable individual characteristics of two or more polymers. Instead, it has often been found that such blending results in combining the worst features of each with the result being a material of such poor properties as not to be of any practical or commercial value. The reasons for this failure are rather well understood and stem in part from the fact that thermodynamics teaches that most combinations of polymer pairs are not miscible, although a number of notable exceptions are known. More importantly, most polymers adhere poorly to one another. As a result, the interfaces between component domains (a result of their immiscibility) represent areas of severe weakness in blends and, therefore, provide natural flaws and cracks which result in facile mechanical failure. Because of this, most polymer pairs are said to be "incompatible". In some instances the term compatibility is used synonymously with miscibility, however, compatibility is used here in a more general way that describes the ability to combine two polymers together for beneficial results and may or may not connote miscibility.

One method which may be used to circumvent this problem in polymer blends is to "compatibilize" the two polymers by blending in a third component, often referred to as a "compatibilizing agent", that possesses a dual solubility nature for the two polymers to be blended. Examples of this third component are obtained in block or graft copolymers. As a result of this characteristic, this agent locates at the interface between components and greatly improves interphase adhesion and therefore increases stability to gross phase separation.

The invention covers a means to stabilize multipolymer blends that is independent of the prior art compatibilizing process and is not restricted to the necessity for restrictive dual solubility characteristics. The materials used for this purpose are special block copolymers capable of thermally reversible self-cross-linking. Their action in the present invention is not that visualized by the usual compatibilizing concept as evidenced by the general ability of these materials to perform similarly for a wide range of blend components which do not conform to the solubility requirements of the previous concept.

Now, the invention provides a composition containing a partially hydrogenated block copolymer comprising at least two terminal polymer blocks A of a monoalkenyl arene having an average molecular weight of from 5,000 to 125,000, and at least one intermediate polymer block B of a conjugated diene having an average molecular weight of from 10,000 to 300,000, in which the terminal polymer blocks A constitute from 8 to 55% by weight of the block copolymer and no more than 25% of the arene double bonds of the polymer blocks A and at least 80% of the aliphatic double bonds of the polymer blocks B have been reduced by hydrogenation, which composition is characterized in that the composition comprises:

(a) 4 to 40 parts by weight of the partially hydrogenated block copolymer;

(b) an acetal resin having a generally crystalline structure and a melting point over 120°C;

(c) 5 to 48 parts by weight of at least one dissimilar engineering thermoplastic resin being selected from the group consisting of polyamides, polyolefins, thermoplastic polyesters, poly(aryl ethers) as defined herein, poly-(aryl sulphones), polycarbonates, thermoplastic polyurethanes, halogenated thermoplastics, and nitrile resins,

in which the weight ratio of the acetal resin to the dissimilar engineering thermoplastic resin is greater than 1:1 so as to form a polyblend wherein at least two of the polymers form at least partial continuous interlocked networks with each other.

The block copolymer of the invention effectively acts as a mechanical or structural stabilizer which interlocks the various polymer structure networks and prevents the consequent separation of the polymers during processing and their subsequent use. As defined more fully hereinafter, the resulting structure of the polyblend (short for "polymer blend") is that of at least two partial continuous interlocking networks. This interlocked structure results in a dimensionally stable polyblend that will not delaminate upon extrusion and subsequent use.

To produce stable blends it is necessary that at least two of the polymers have at least partial continuous networks which interlock with each other. Preferably, the block copolymer and at least one other polymer have partial continuous interlocking network structures. In an ideal situation all of the polymers would have complete continuous networks which interlock with each other. A partial continuous network means that a portion of the polymer has a continuous network phase structure while the other portion has a disperse phase structure. Preferably, a major proportion (greater than 50% by weight) of the partial continuous network is continuous. As can be readily seen, a large variety of blend structures is possible since the structure of the polymer in the blend may be completely continuous, completely disperse, or partially continuous and partially disperse. Further yet, the disperse phase of one polymer may be dispersed in a second polymer and not in a third polymer. To illustrate some of the structures, the following lists the various combinations of polymer structures possible where all structures are complete as opposed to partial structures. Three polymers (A, B and C) are involved. The subscript "c" signifies a continuous structure while the subscript "d" signifies a disperse structure. Thus, the designation "A_cB" means that polymer A is continuous with polymer B, and the designation "B_dC" means that polymer B is disperse in polymer C, etc.

A_cB	A_cC	B_cC
A_dB	A_cC	B_cC
A_cB	A_cC	B_dC
B_dA	A_cC	B_cC
B_dC	A_cB	A_cC
C_dA	A_cB	A_cC
C_dB	A_cB	A_cC

Through practice of the invention, it is possible to improve one type of physical property of the composite blend while not causing a significant deterioration in another physical property. In the past this has not always been possible. For example, in the past it was expected that by adding an amorphous rubber such as an ethylene-propylene rubber to a thermoplastic polymer to improve impact strength, one would necessarily obtain a composite blend having a significantly reduced heat distortion temperature (HDT). This results from the fact that the amorphous rubber forms discrete particles in the composite and the rubber, almost by definition, has an exceedingly low HDT, around room temperature. However, in the present invention it is possible to significantly improve impact strength while not detracting from the heat distortion temperature. In fact, when the relative increase in Izod impact strength is measured against the relative decrease in HDT, the value of the ratio is much higher than one would expect. For example, in blends containing a polyacetal, block copolymer, and other engineering thermoplastics such as PBT and polycarbonates, this ratio is greater than 10, whereas one would typically expect positive values of less than 1.

It is particularly surprising that even just small amounts of the block copolymer are sufficient to stabilize the structure of the polymer blend over very wide relative concentrations. For example, as little as four parts by weight of the block copolymer is sufficient to stabilize a blend of 5 to 90 parts by weight polyacetal with 90 to 5 parts by weight of a dissimilar engineering thermoplastic.

In addition, it is also surprising that the block copolymers are useful in stabilizing polymers of such a wide variety and chemical make-up. As explained more fully hereinafter, the block copolymers have this ability to stabilize a wide variety of polymer over a wide range of concentrations since they are oxidatively stable, possess essentially an infinite viscosity at zero shear stress, and retain network or domain structure in the melt.

Another significant aspect of the invention is that the ease of processing and forming the various polyblends is greatly improved by employing the block copolymers as stabilizers.

The block copolymers employed in the composition according to the invention may have a variety of geometrical structure, since the invention does not depend on any specific geometrical structure, but rather upon the chemical constitution of each of the polymer blocks. Thus, the block copolymers may be linear, radial or branched. Methods for the preparation of such polymers are known in the art. The structure of the polymers is determined by their methods of polymerization. For example, linear polymers result by sequential introduction of the desired monomers into the reaction vessel when using such initiators as lithium-alkyls or dilithio-stilbene, or by coupling a two-segment block copolymer with a difunctional coupling agent. Branched structures, on the other hand, may be obtained by the use of suitable coupling agents having a functionality with respect to the precursor polymers of three or more. Coupling may be effected with multifunctional coupling agents, such as dihaloalkanes or -alkenes and divinyl benzene as well as certain polar compounds, such as silicon halides, siloxanes or esters of monohydric alcohols with carboxylic acids. The presence of any coupling residues in the polymer may be ignored for an adequate description of the polymers forming a part of the compositions of this invention. Likewise, in the generic sense, the specific structures also may be ignored. The invention applies especially to the use of selectively hydrogenated polymers having the configuration before hydrogenation of the following typical species:

polystyrene-polybutadiene-polystyrene (SBS)
polystyrene-polyisoprene-polystyrene (SIS)
poly(alpha-methylstyrene)polybutadiene-poly(alpha-methylstyrene) and
poly(alpha-methylstyrene)polyisoprene-poly(alpha-methylstyrene).

Both polymer blocks A and B may be either homopolymer or random copolymer blocks as long as each polymer block predominates in at least one class of the monomers characterizing the polymer blocks. The polymer block A may comprise homopolymers of a monoalkenyl arene and copolymers of a monoalkenyl arene with a conjugated diene as long as the polymer blocks A individually predominate in monoalkenyl arene units. The term "monoalkenyl arene" will be taken to include especially styrene and its analogues and homologues including alpha-methylstyrene and ring-substituted styrenes, particularly

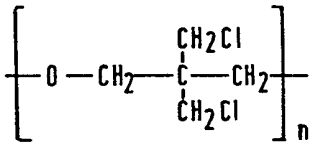
ring-methylated styrenes. The preferred monoalkenyl arenes are styrene and alpha-methylstyrene, and styrene is particularly preferred. The polymer blocks B may comprise homopolymers of a conjugated diene, such as butadiene or isoprene, and copolymers of a conjugated diene with a monoalkenyl arene as long as the polymer blocks B predominate in conjugated diene units. When the monomer employed is butadiene, it is preferred that between 35 and 55 mol. per cent of the condensed butadiene units in the butadiene polymer block have 1,2-configuration. Thus, when such a block is hydrogenated, the resulting product is, or resembles, a regular copolymer block of ethylene and butene-1 (EB). If the conjugated diene employed is isoprene, the resulting hydrogenated product is or resembles a regular copolymer block of ethylene and propylene (EP).

Hydrogenation of the precursor block copolymers is preferably effected by use of a catalyst comprising the reaction products of an aluminium alkyl compound with nickel or cobalt carboxylates or alkoxides under such conditions as to substantially completely hydrogenate at least 80% of the aliphatic double bonds, while hydrogenating no more than 25% of the alkenyl arene aromatic double bonds. Preferred block copolymers are those where at least 99% of the aliphatic double bonds are hydrogenated while less than 5% of the aromatic double bonds are hydrogenated.

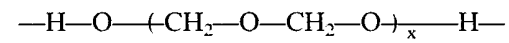
The average molecular weights of the individual blocks may vary within certain limits. The block copolymer present in the composition according to the invention has at least two terminal polymer blocks A of a monoalkenyl arene having a number average molecular weight of from 5,000 to 125,000, preferably from 7,000 to 60,000, and at least one intermediate polymer block B of a conjugated diene having a number average molecular weight of from 10,000 to 300,000, preferably from 30,000 to 150,000. These molecular weights are most accurately determined by tritium counting methods or osmotic pressure measurements.

The proportion of the polymer blocks A of the monoalkenyl arene should be between 8 and 55% by weight of the block copolymer, preferably between 10 and 30% by weight.

The acetal resins present in the compositions according to the invention include the high molecular weight polyacetal homopolymers made by polymerizing formaldehyde or trioxane. These polyacetal homopolymers are commercially available under the trade name DELRIN®. A related polyether-type resin is available under the trade name PENTON® and has the structure:



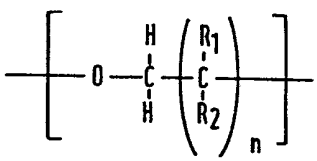
The acetal resin prepared from formaldehyde has a high molecular weight and a structure typified by the following:



where terminal groups are derived from controlled amounts of water and the x denotes a large (preferably 1500) number of formaldehyde units linked in head-to-tail fashion. To increase thermal and chemical resistance, terminal groups are typically converted to esters or ethers.

Also included in the term polyacetal resins are the polyacetal copolymers. These copolymers include block copolymers of formaldehyde with monomers or prepolymers of other materials capable of providing active hydrogens, such as alkylene glycols, polythiols, vinyl acetate-acrylic acid copolymers, or reduced butadiene/acrylonitrile polymers.

Celanese has commercially available a copolymer of formaldehyde and ethylene oxide under the trade name CELCON® that is useful in the blends of the present invention. These copolymers typically have a structure comprising recurring units having the formula:



wherein each R_1 and R_2 is selected from the group consisting of hydrogen, lower alkyl and lower halogen substituted alkyl radicals and wherein n is an integer from zero to three and wherein n is zero in from 85% to 99.9% of the recurring units.

Formaldehyde and trioxane can be copolymerized with other aldehydes, cyclic ethers, vinyl compounds, ketenes, cyclic carbonates, epoxides, isocyanates and ethers. These compounds include ethylene oxide, 1,3-dioxolane, 1,3-dioxane, 1,3-dioxepene, epichlorohydrin, propylene oxide, isobutylene oxide, and styrene oxide.

The term "dissimilar engineering thermoplastic resin" refers to engineering thermoplastic resins different from those encompassed by the polyacetals present in the compositions according to the invention.

The term "engineering thermoplastic resin" encompasses the various polymers found in the classes listed in Table A below and thereafter defined in the specification.

TABLE A

1. Polyolefins
2. Thermoplastic polyesters
3. Poly(aryl ethers) and poly(aryl sulphones)
4. Polycarbonates
5. Polyamides
6. Thermoplastic polyurethanes
7. Halogenated thermoplastics
8. Nitrile resins

Preferably these engineering thermoplastic resins have glass transition temperatures or apparent crystalline melting points (defined as that temperature at which the modulus, at low stress, shows a catastrophic drop) of over 120°C, preferably between 150°C and 350°C, and are capable of forming a continuous network structure through a thermally reversible cross-linking mechanism. Such thermally reversible cross-linking mechanisms include crystallites, polar aggregations, ionic aggregations, lamellae, or hydrogen bonding. In a specific embodiment, where the viscosity of the block copolymer or blended block copolymer composition at processing temperature Tp and a shear rate of 100 s^{-1} is η, the ratio of the viscosity of the engineering thermoplastic resins, or blend of engineering thermoplastic resin with viscosity modifiers to η may be between 0.2 and 4.0, preferably 0.8 and 1.2. As used in the specification and claims, the viscosity of the block copolymer, polyacetal and the thermoplastic engineering resin is the "melt viscosity" obtained by employing a piston-driven capillary melt rheometer at constant shear rate and at some consistent temperature above melting, say 260°C. The upper limit (350°C) on apparent crystalline melting point or glass transition temperature is set so that the resin may be processed in low to medium shear rate equipment at commercial temperature levels of 350°C or less.

The engineering thermoplastic resin includes also blends of various engineering thermoplastic resins and blends with additional viscosity modifying resins.

These various classes of engineering thermoplastics are defined below.

The polyolefins, if present in the compositions according to the invention are crystalline or crystallizable. They may be homopolymers or copolymers and may be derived from an alpha-olefin or 1-olefin having 2 to 5 carbon atoms. Examples of particular useful polyolefins include low-density polyethylene, high-density polyethylene, isotactic polypropylene, poly(1-butene), poly(4-methyl-1-pentene), and copolymers of 4-methyl-1-pentene with linear or branched alpha-olefins. A crystalline or crystallizable structure is important in order for the polymer to be capable of forming a continuous structure with the other polymers in the polymer blend according to the invention. The number average molecular weight of the polyolefins may be above 10,000, preferably above 50,000. In addition, the apparent crystalline melting point may be above 100°C, preferably between 100°C and 250°C, and more preferably between 140°C and 250°C. The preparations of these various polyolefins are well known. See generally "Olefin Polymers", Volume 14, Kirk-Othmer Encyclopedia of Chemical Technology, pages 217-335 (1967).

When a high-density polyethylene is employed, it has an approximate crystallinity of over 75% and a density in kilograms per litre (kg/l) of between 0.94 and 1.0 while when a low density polyethylene is employed, it has an approximate crystallinity of over 35% and a density of between 0.90 kg/l and 0.94 kg/l. The composition according to the invention may contain a polyethylene having a number average molecular weight of 50,000 to 500,000.

When a polypropylene is employed, it is the so-called isotactic polypropylene as opposed to atactic polypropylene. The number average molecular weight of the polypropylene employed may be in excess of 100,000. The polypropylene may be prepared using methods of the prior art. Depending on the specific catalyst and polymerization conditions employed, the polymer produced may contain atactic as well as isotactic, syndiotactic or so-called stereo-block molecules. These may be separated by selective solvent extraction to yield products of low atactic content that crystallize more completely. The preferred commercial polypropylenes are generally prepared using a solid, crystalline, hydrocarbon-in-soluble catalyst made from a titanium trichloride composition and an aluminium alkyl compound, e.g., triethyl aluminium or diethyl aluminium chloride. If desired, the polypropylene employed is a copolymer containing minor (1 to 20 per cent by weight) amounts of ethylene or another alpha-olefin as comonomer.

The poly(1-butene) preferably has an isotactic structure. The catalysts used in preparing the poly(1-butene) are preferably organo-metallic compounds commonly referred to as Ziegler-Natta catalysts. A typical catalyst is the interacted product resulting from mixing equimolar quantities of titanium tetrachloride and triethylaluminium. The manufacturing process is normally carried out in an inert diluent such as hexane. Manufacturing operations, in all phases of polymer formation, are conducted in such a manner as to guarantee rigorous exclusion of water even in trace amounts.

One very suitable polyolefin is poly(4-methyl-1-pentene). Poly(4-methyl-1-pentene) has an apparent crystalline melting point of between 240 and 250°C and a relative density of between 0.80 and 0.85. Monomeric 4-methyl-1-pentene is commercially manufactured by the alkali-metal catalyzed dimerization of propylene. The homopolymerization of 4-methyl-1-pentene with Ziegler-Natta catalysts is described in the Kirk-Othmer Enclopedia of Chemical Technology, Supplement volume, pages 789-792 (second edition, 1971). However, the isotactic homopolymer of 4-methyl-1-pentene has certain technical defects, such as brittleness and inadequate transparency. Therefore, commercially available poly(4-methyl-1-pentene) is actually a copolymer with minor proportions of other alpha-olefins, together with the addition of suitable oxidation and melt stabilizer systems. These copolymers are described in the Kirk-Othmer Encyclopedia of Chemical Technology, Supplement volume, pages 792-907 (second edition, 1971), and are available under the trade name TPX® resin. Typical alpha-olefins are linear alpha-olefins having from 4 to 18 carbon atoms. Suitable resins are copolymers of 4-methyl-1-pentene with from 0.5 to 30% by weight of a linear alpha-olefin.

If desired, the polyolefin is a mixture of various polyolefins. However, the much preferred polyolefin is isotactic polypropylene.

The thermoplastic polyesters, if present in the compositions according to the invention, have a generally crystalline structure, a melting point over 120°C, and are thermoplastic as opposed to thermosetting.

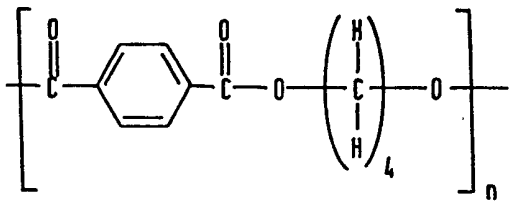
The term "thermoplastic polyester" is used herein in its widest possible sense, referring to any thermoplastic material comprising a plurality of ester groups. Thus, polyesters of cellulose, referred to hereinafter as "cellulosic esters" are included as well within the scope of this invention. One particularly useful group of polyesters are those thermoplastic polyesters prepared by condensing a dicarboxylic acid or the lower alkyl ester, acid halide, or anhydride derivatives thereof with a glycol, according to methods well known in the art.

Among the aromatic and aliphatic dicarboxylic acids suitable for preparing polyesters are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, terephthalic acid, isophthalic acid, p-carboxyphenoacetic acid, p,p'-dicarboxydiphenyl, p,p'-dicarboxydiphenylsulphone, p-carboxyphenoxyacetic acid, p-carboxyphenoxypropionic acid, p-carboxyphenoxybutyric acid, p-carboxyphenoxyvaleric acid, p-carboxyphenoxyhexanoic acid, p,p'-dicarboxydiphenylmethane, p,p-dicarboxydiphenylpropane, p-p'-dicarboxydiphenyloctane, 3-alkyl-4-(β-carboxyethoxy)-benzoic acid, 2,6-naphthalene dicarboxylic acid, and 2,7-naphthalene dicarboxylic acid. Mixtures of dicarboxylic acids can also be employed. Terephthalic acid is particularly preferred.

The glycols suitable for preparing the polyesters include straight-chain alkylene glycols of 2 to 12 carbon atoms, such as ethylene glycol, 1,3-propylene glycol, 1,6-hexylene glycol, 1,10-decamethylene glycol, and 1,12-dodecamethylene glycol. Aromatic glycols can be substituted in whole or in part. Suitable aromatic dihydroxy compounds include p-xylylene glycol, pyrocatechol, resorcinol, hydroquinone, or alkyl-substituted derivatives of these compounds. Another suitable glycol is 1,4-cyclohexane dimethanol. Much preferred glycols are the straight-chain alkylene glycols having 2 to 4 carbon atoms.

A preferred group of polyesters are poly(ethylene terephthalate), poly(propylene terephthalate), and poly(butylene terephthalate). A much preferred polyester is poly(butylene terephthalate). Poly(butylene terephthalate), a crystalline copolymer, may be formed

by the polycondensation of 1,4-butanediol and dimethyl terephthalate or terephthalic acid, and has the generalized formula:

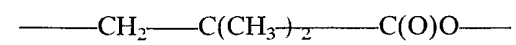


where n varies from 70 to 140. The average molecular weight of the poly(butylene terephthalate) preferably varies from 20,000 to 25,000.

Commercially available poly(butylene terephthalate) is available under the trade name VALOX® thermoplastic polyester. Other commercial polymers include CELANEX®, TENITE® and VITUF®.

Other useful polyesters include the cellulosic esters. The thermoplastic cellulosic esters employed herein are widely used as moulding, coating and film-forming materials and are well known. These materials include the solid thermoplastic forms of cellulose nitrate, cellulose acetate (e.g., cellulose diacetate, cellulose triacetate), cellulose butyrate, cellulose acetate butyrate, cellulose propionate, cellulose tridecanoate, and acetylated hydroxyethyl cellulose as described on pages 25-28 of Modern Plastics Encyclopedia, 1971-72, and references listed therein.

Another useful polyester is a polypivalolactone. Polypivalolactone is a linear polymer having recurring ester structural units mainly of the formula:

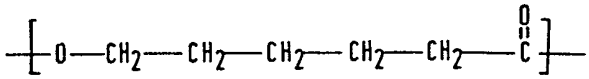


i.e., units derived from pivalolactone. Preferably, the polyester is a pivalolactone homopolymer. Also included, however, are the copolymers of pivalolactone with no more than 50 mol.%, preferably not more than 10 mol.% of another beta-propiolactone, such as beta-propiolactone, alpha,alpha-diethyl-beta-propiolactone and alpha-methyl-alpha-ethyl-beta-propiolactone. The term "beta-propiolactones" refers to beta-propiolactone (2-oxetanone) and to derivatives thereof which carry no substituents at the beta-carbon atom of the lactone ring. Preferred beta-propiolactones are those containing a tertiary or quaternary carbon atom in the alpha-position relative to the carbonyl group. Especially preferred are the alpha,alpha-dialkyl-beta-propiolactones wherein each of the alkyl groups independently has from one to four carbon atoms. Examples of useful monomers are:

alpha-ethyl-alpha-methyl-beta-propiolactone,
alpha-methyl-alpha-isopropyl-beta-propiolactone,
alpha-ethyl-alpha-n-butyl-beta-propiolactone,
alpha-chloromethyl-alpha-methyl-beta-propiolactone,
alpha,alpha-bis(chloromethyl)-beta-propiolactone, and
alpha,alpha-dimethyl-beta-propiolactone (pivalolactone).

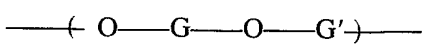
These polypivalolactones have an average molecular weight in excess of 20,000 and a melting point in excess of 120°C.

Another useful polyester is a polycaprolactone. Preferred poly(ε-caprolactones) are substantially linear polymers in which the repeating unit is:



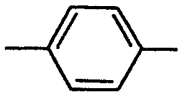
These polymers have similar properties to the polypivalolactones and may be prepared by a similar polymerization mechanism.

Various polyaryl polyethers are also useful as engineering thermoplastic resins. The defined poly(aryl polyethers) which are employed in the composition according to the invention comprise the linear thermoplastic polymers composed of recurring units having the formula:



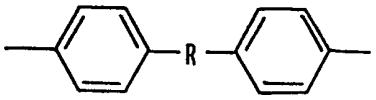
I

wherein G is the residuum of a dihydric phenol selected from the group consisting of:



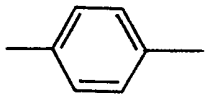
II

and



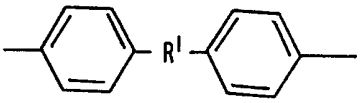
III

wherein R represents a bond between aromatic carbon atoms, ——O——, ——S——, ——S—S——, or a divalent hydrocarbon radical having from 1 to 18 carbon atoms inclusive, and G′ is the residuum of a dibromo or di-iodobenzenoid compound selected from the group consisting of:



IV

and



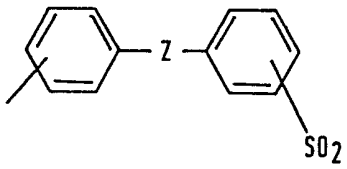
V

wherein R′ represents a bonds between aromatic carbon atoms, ——O——, ——S——, ——S—S——, or a divalent hydrocarbon radical having from 1 to 18 carbon atoms inclusive, with the provisions that when R is ——O——, R′ is other than ——O——; when R′ is ——O——, R is other than ——O——; when G is II, G′ is V, and when G′ is IV, G is III. Polyarylene polyethers of this type exhibit excellent physical properties as well as excellent thermal oxidative and chemical stability. Commercial poly(aryl polyethers) of this type are available under the trade name ARYLON T® Polyaryl ethers, having a melt temperature of between 280°C and 310°C.

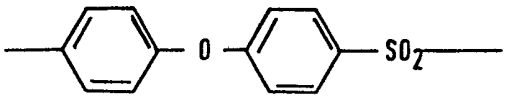
Another group of useful engineering thermoplastic resins include aromatic poly(sulphones) comprising repeating units of the formula:

——Ar——SO_2——

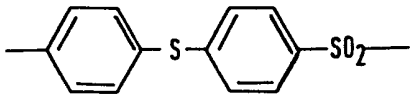
in which Ar is a bivalent aromatic radical and may vary from unit to unit in the polymer chain (so as to form copolymers of various kinds). Thermoplastic poly(sulphones) generally have at least some units of the structure:



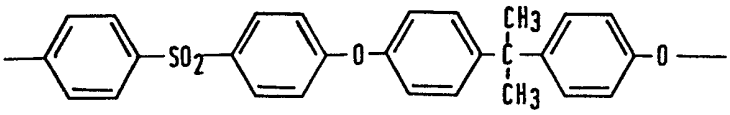
in which Z is oxygen or sulphur or the residue of an aromatic diol, such as a 4,4'-bisphenol. One example of such a poly(sulphone) has repeating units of the formula:



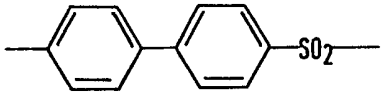
another has repeating units of the formula:



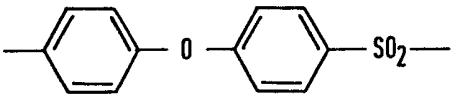
and others have repeating units of the formula:



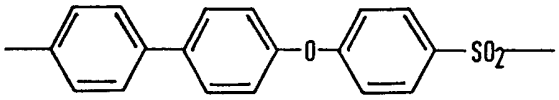
or copolymerized units in various proportions of the formula:



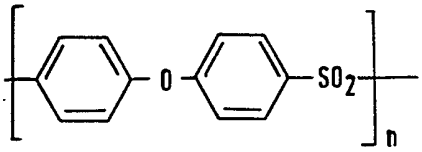
and



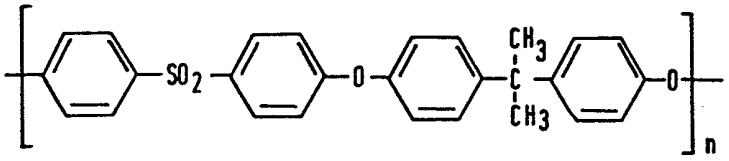
The thermoplastic poly(sulphones) may also have repeating units having the formula:



Poly(ether sulphones) having repeating units of the following structure:

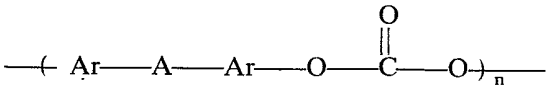


and poly(ether sulphones) having repeating units of the following structure:



are also useful as engineering thermoplastic resins.

The polycarbonates which may be present in the compositions according to the invention are of the general formulae:



I

and

II

wherein Ar represents a phenylene or an alkyl, alkoxy, halogen or nitro-substituted phenylene group; A represents a carbon-to-carbon bond or an alkylidene, cycloalkylidene, alkylene, cycloalkylene, azo, imino, sulphur, oxygen, sulphoxide or sulphone group, and n is at least two.

The preparation of the polycarbonates is well known. A preferred method of preparation is based on the reaction carried out by dissolving the dihydroxy component in a base, such as pyridine and bubbling phosgene into the stirred solution at the desired rate. Tertiary amines may be used to catalyze the reaction as well as to act as acid acceptors throughout the reaction. Since the reaction is normally exothermic, the rate of phosgene addition can be used to control the reaction temperature. The reactions generally utilize equimolar amounts of phosgene and dihydroxy reactants, however, the molar ratios can be varied dependent upon the reaction conditions.

In the formulae I and II mentioned, Ar and A are, preferably, p-phenylene and isopropylidene, respectively. This polycarbonate is prepared by reacting para, para'-isopropylidenediphenol with phosgene and is sold under the trade mark LEXAN® and under the trade mark MERLON®. This commercial polycarbonate has a molecular weight of around 18,000, and a melt temperature of over 230°C. Other polycarbonates may be prepared by reacting other dihydroxy compounds, or mixtures of dihydroxy compounds, with phosgene. The dihydroxy compounds may include aliphatic dihydroxy compounds although for best high temperature properties aromatic rings are essential. The dihydroxy compounds may include within the structure diurethane linkages. Also, part of the structure may be replaced by siloxane linkage.

By polyamide is meant a condensation product which contains recurring aromatic and/or aliphatic amide groups as integral parts of the main polymer chain, such products being known generically as "nylons". A polyamide may be obtained by polymerizing a mono-aminomonocarboxylic acid or an internal lactam thereof having at least two carbon atoms between the amino and carboxylic acids groups; or by polymerizing substantially equimolar proportions of a diamine which contains at least two carbon atoms between the amino groups and a dicarboxylic acid; or by polymerizing a mono-aminocarboxylic acid or an internal lactam thereof as defined above together with substantially equimolar proportions of a diamine and a dicarboxylic acid. The dicarboxylic acid may be used in the form of a functional derivative thereof, for example an ester.

The term "substantially equimolecular proportions" (of the diamine and of the dicarboxylic acid) is used to cover both strict equimolecular proportions and the slight departures therefrom which are involved in conventional techniques for stabilizing the viscosity of the resultant polyamides.

As examples of the said mono-aminomonocarboxylic acids or lactams thereof may be mentioned those compounds containing from 2 to 16 carbon atoms between the amino and carboxylic acid groups, said carbon atoms forming a ring with the ——CO.NH—— group in the case of a lactam. As particular examples of aminocarboxylic acids and lactams there may be mentioned ε-aminocaproic acid, butyrolactam, pivalolactam, caprolactam, capryl-

lactam, enantholactam, undecanolactam, dodecanolactam and 3- and 4-amino benzoic acids.

Examples of the said diamines are diamines of the general formula $H_2N(CH_2)_nNH_2$, wherein n is an integer of from 2 to 16, such as trimethylenediamine, tetramethylenediamine, pentamethylenediamine, octamethylenediamine, decamethylenediamine, dodecamethylenediamine, hexadecamethylenediamine, and especially hexamethylenediamine.

C-alkylated diamines, e.g, 2,2-dimethylpentamethylenediamine and 2,2,4-and 2,4,4-trimethylhexamethylenediamine are further examples. Other diamines which may be mentioned as examples are aromatic diamines, e.g., p-phenylenediamine, 4,4'-diaminodiphenyl sulphone, 4,4'-diaminodiphenyl ether and 4,4'-diaminodiphenyl sulphone, 4,4'-diaminodiphenyl ether and 4,4'-diaminodiphenylmethane; and cycloaliphatic diamines, for example diaminodicyclohexylmethane.

The said dicarboxylic acids may be aromatic, for example isophthalic and terephthalic acids. Preferred dicarboxylic acids are of the formula HOOC.Y.COOH, wherein Y represents a divalent aliphatic radical containing at least 2 carbon atoms, and examples of such acids are sebacic acid, octadecanedioic acid, suberic acid, azelaic acid, undecanedioic acid, glutaric acid, pimelic acid, and especially adipic acid. Oxalic acid is also a preferred acid.

Specifically the following polyamides may be incorporated in the thermoplastic polymer blends of the invention:

polyhexamethylene adipamide (nylon 6:6)
polypyrrolidone (nylon 4)
polycaprolactam (nylon 6)
polyheptolactam (nylon 7)
polycapryllactam (nylon 8)
polynonanolactam (nylon 9)
polyundecanolactam (nylon 11)
polydodecanolactam (nylon 12)
polyhexamethylene azelaiamide (nylon 6:9)
polyhexamethylene sebacamide (nylon 6:10)
polyhexamethylene isophthalamide (nylon 6:iP)
polymetaxylyleneadipamide (nylon MXD:6)
polyamide of hexamethylene diamine and n-dodecanedioic acid (nylon 6.12)
polyamide of dodecamethylenediamine and
n-dodecanedioic acid (nylon 12:12).

Nylon copolymers may also be used, for example copolymers of the following:
hexamethylene adipamide/caprolactam (nylon 6:6/6)
hexamethylene adipamide/hexamethylene-isophthalamade (nylon 6:6/6ip)
hexamethylene adipamide/hexamethylene-terephthalamide (nylon 6:6/6T)
trimethylhexamethylene oxamide/hexamethylene oxamide (nylon trimethyl-6:2/6:2)
hexamethylene adipamide/hexamethylene-azelaiamide (nylon 6:6/6:9)
hexamethylene adipamide/hexamethylene-azelaiamide/caprolactam (nylon 6:6/6:9/6).

Also useful is nylon 6:3. This polyamide is the product of the dimethyl ester of terephthalic acid and a mixture of isomeric trimethyl hexamethylenediamine.

Preferred nylons include nylon 6,6/6, 11, 12, 6/3 and 6/12.

The number average molecular weights of the polyamides may be above 10,000.

Polyurethanes, otherwise known as isocyanate resins, also can be employed as engineering thermoplastic resin as long as they are thermoplastic as opposed to thermosetting. For example, polyurethanes formed from toluene di-iso-cyanate (TDI) or diphenyl methane 4,4-di-isocyanate (MDI) and a wide range of polyols, such as, polyoxyethylene glycol, polyoxypropylene glycol, hydroxy-terminated polyesters, polyoxyethylene-oxypropylene glycols are suitable.

These thermoplastic polyurethanes are available under the trade name Q-THANE ® and under the trade name PELLETHANE® CPR.

Another group of useful engineering thermoplastics include those halogenated thermoplastics having an essentially crystalline structure and a melt point in excess of 120°C. These halogenated thermoplastics include homopolymers and copolymers derived from tetrafluoroethylene, chlorotrifluoro-ethylene, bromotrifluoroethylene, vinylidene fluoride, and vinylidene chloride.

Polytetrafluoroethylene (PTFE) is the name given to fully fluorinated polymers of the basic chemical formula $+CF_2—CF_2+_n$ which contain 76% by weight fluorine. These polymers are highly crystalline and have a crystalline melting point of over 300°C. Commercial PTFE is available under the trade name TEFLON® and under the trade name FLUON®. Polychlorotrifluoroethylene (PCTFE) and poly bromotrifluoroethylene (PBTFE) are also available in high molecular weights and can be employed in the present

invention.

Especially preferred halogenated polymers are hompolymers and copolymers of vinylidene fluoride. Poly(vinylidene fluoride) homopolymers are the partially fluorinated polymers of the chemical formula $\{ CH_2—CH_2 \}_n$. These polymers are tough linear polymers with a crystalline meltingpoint at 170°C. Commercial homopolymer is available under the trade name KYNAR®. The term "poly(vinylidene fluoride)" as used herein refers not only to the normally solid hompolymers of vinylidene fluoride, but also to the normally solid copolymers of vinylidene fluoride containing at least 50 mol.% of polymerized vinylidene fluoride units, preferably at least 70 mol. % vinylidene fluoride and more preferably at least 90 mol.%. Suitable comonomers are halogenated olefins containing up to 4 carbon atoms, for example, sym. dichlorodifluoroethylene, vinyl fluoride vinyl chloride, vinylidene chloride, perfluoropropene, perfluorobutadiene, chlorotrifluoroethylene, trichloroethylene and tetrafluoroethylene.

Another useful group of halogenated thermoplastics include homopolymers and copolymers derived from vinylidene chloride. Crystalline vinylidene chloride copolymers are especially preferred. The normally crystalline vinylidene chloride copolymers that are useful in the present invention are those containing at least 70% by weight of vinylidene chloride together with 30% or less of a co-polymerizable monoethylenic monomer. Exemplary of such monomers are vinyl chloride, vinyl acetate, vinyl propionate, acrylonitrile, alkyl and aralkyl acrylates having alkyl and aralkyl groups of up to about 8 carbon atoms, acrylic acid, acrylamide, vinyl alkyl ethers, vinyl alkyl ketones, acrolein, allyl ethers and others, butadiene and chloropropene. Known ternary compositions also may be employed advantageously. Representative of such polymers are those composed of at least 70% by weight of vinylidene chloride with the remainder made up of, for example, acrolein and vinyl chloride, acrylic acid and acrylonitrile, alkyl acrylates and alkyl methacrylates, acrylonitrile and butadiene, acrylonitrile and itaconic acid, acrylonitrile and vinyl acetate, vinyl propionate or vinyl chloride, allyl esters or ethers and vinyl chloride, butadiene and vinyl acetate, vinyl propionate, or vinyl chloride and vinyl ethers and vinyl chloride. Quaternary polymers of similar monomeric composition will also be known. Particularly useful for the purposes of the present invention are copolymers of from 70 to 95% by weight vinylidene chloride with the balance being vinyl chloride. Such copolymers may contain conventional amounts and types of plasticizers, stabilizers, nucleators and extrusion aids. Further, blends of two or more of such normally crystalline vinylidene chloride polymers may be used as well as blends comprising such normally crystalline polymers in combination with other polymeric modifiers, e.g., the copolymers of ethylene-vinyl acetate, styrene-maleic anhydride, styrene-acrylonitrile and polyethylene.

The nitrile resins useful as engineering thermoplastic resin are those thermoplastic materials having an alpha, beta-olefinically unsaturated mononitrile content of 50% by weight or greater. These nitrile resins may be homopolymers, copolymers, grafts of copolymers onto a rubbery substrate, or blends of homopolymers and/or copolymers.

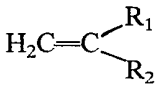
The alpha, beta-olefinically unsaturated mononitriles encompassed herein have the structure

$$CH_2=\underset{\displaystyle R}{\overset{|}{C}}—CN$$

where R is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a halogen. Such compounds include acrylonitrile, alpha-bromoacrylonitrile, alpha-fluoroacrylonitrile, methacrylonitrile and ethacrylonitrile. The most preferred olefinically unsaturated nitriles are acrylonitrile and methacrylonitrile and mixtures thereof.

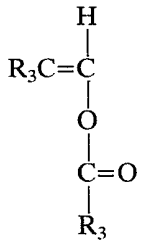
These nitrile resins may be divided into several classes on the basis of complexity. The simplest molecular structure is a random copolymer, predominantly acrylonitrile or methacrylonitrile. The most common example is a styrene-acrylonitrile copolymer. Block copolymers of acrylonitrile, in which long segments of polyacrylonitrile alternate with segments of polystyrene, or of polymethyl methacrylate, are also known.

Simultaneous polymerization of more than two comonomers produces an interpolymer, or in the case of three components, a terpolymer. A large number of comonomers are known. These include alpha-olefins of from 2 to 8 carbon atoms. e.g., ethylene, propylene, iso-butylene, butene-1, pentene-1, and their halogen and aliphatic substituted derivatives as represented by vinyl chloride and vinylidene chloride; monovinylidene aromatic hydrocarbon monomers of the general formula:



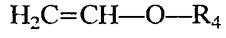
wherein R_1 is hydrogen, chlorine or methyl and R_2 is an aromatic radical of 6 to 10 carbon atoms which may also contain substituents, such as halogen and alkyl groups attached to the aromatic nucleus, e.g., styrene, alpha-methyl styrene, vinyl toluene, alpha-chlorostyrene, ortho-chlorostyrene, para-chlorostyrene, meta-chlorostyrene, ortho-methyl styrene, para-methyl styrene, ethyl styrene, isopropyl styrene, dichlorostyrene and vinyl naphthalene. Especially preferred comonomers are isobutylene and styrene.

Another group of comonomers are vinyl esters monomers of the general formula:



wherein R_3 is selected from the group comprising hydrogen, alkyl groups of from 1 to 10 carbon atoms, aryl groups of from 6 to 10 carbon atoms including the carbon atoms in ring-substituted alkyl substituted; e.g., vinyl formate, vinyl acetate, vinyl propionate and vinyl benzoate.

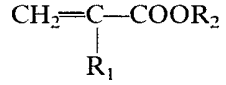
Similar to the foregoing and also useful are the vinyl ether monomers of the general formula:



wherein R_4 is an alkyl group of from 1 to 8 carbon atoms, an aryl group of from 6 to 10 carbons, or a monovalent aliphatic radical of from 2 to 10 carbon atoms, which aliphatic radical may be hydrocarbon or oxygen-containing, e.g., an aliphatic radical with ether linkages, and may also contain other substituents, such as halogen and carbonyl. Examples of these monomeric vinyl ethers include vinyl methyl ether, vinyl ethyl ether, vinyl n-butyl ether, vinyl 2-chloroethyl ether, vinyl phenyl ether, vinyl iso-butyl ether, vinyl cyclohexyl ether, p-butyl cyclohexyl ether, vinyl ether or p-chlorophenyl glycol.

Other comonomers are those comonomers which contain a mono- or dinitrile function. Examples of these include methylene glutaronitrile, (2,4-dicyanobutene-1), vinyl-idene cyanide, crotonitrile, fumarodinitrile, maleodinitrile.

Other comonomers include the esters of olefinically unsaturated carboxylic acids, preferably the lower alkyl esters of alpha, beta-olefinically unsaturated carboxylic acids and more preferred the esters having the structure:



wherein R_1 is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or a halogen and R_2 is an alkyl group having from 1 to 2 carbon atoms. Compounds of this type include methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate and methyl alpha-chloro acrylate. Most preferred are methyl acrylate, ethyl acrylate, methyl methacrylate and ethyl methacrylate.

Another class of nitrile resins are the graft copolymers which have a polymeric backbone on which branches of another polymeric chain are attached or grafted. Generally the backbone is preformed in a separate reaction. Polyacrylonitrile may be grafted with chains of styrene, vinyl acetate, or methyl methacrylate, for example. The backbone may consist of one, two, three, or more components, and the grafted branches may be composed of

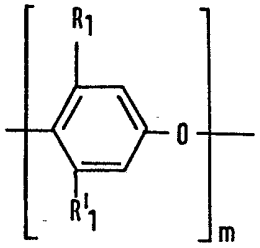
one, two, three or more comonomers.

The most promising products are the nitrile copolymers that are partially grafted on a preformed rubbery substrate. This substrate contemplates the use of a synthetic or natural rubber component such as poly-butadiene, isoprene, neoprene, nitrile rubbers, natural rubbers, acrylonitrile-butadiene copolymers, ethylene-propylene copolymers, and chlorinated rubbers which are used to strengthen or toughen the polymer. This rubbery component may be incorporated into the nitrile containing polymer by any of the methods which are well known to those skilled in the art, e.g., direct polymerization of monomers, grafting the acrylonitrile monomer mixture onto the rubber backbone or physical admixtures of the rubbery component. Especially preferred are polymer blends derived by mixing a graft copolymer of the acrylonitrile and comonomer on the rubber backbone with another copolymer of acrylonitrile and the same comonomers. The acrylonitrile-based thermoplastics are frequently polymer blends of a grafted polymer and an ungrafted homopolymer.

Commercial examples of nitrile resins include BAREX® 210 resin, an acrylonitrile-based high nitrile resin containing over 65% nitrile, and LOPAC® resin containing over 70% nitrile, three-fourths of it derived from methacrylonitrile.

In order to better match the viscosity characteristics of the thermoplastic engineering resin, the polyacetal and the block copolymer, it is sometimes useful to first blend the dissimilar thermoplastic engineering resin with a viscosity modifier before blending the resulting mixture with the polyacetal and block copolymer. Suitable viscosity modifers have a relatively high viscosity, a melt temperature of over 230°C, and possess a viscosity that is not very sensitive to changes in temperature. Examples of suitable viscosity modifiers include poly(2,6-dimethyl-1,4-phenylene)oxide and blends of poly(2,6-dimethyl-1,4-phenylene)oxide with polystyrene.

The poly (phenylene oxides) included as possible viscosity modifiers may be presented by the following formula:



wherein R_1 is a monovalent substituent selected from the group consisting of hydrogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and phenol nucleus and being free of a tertiary alpha-carbon atoms, hydrocarbonoxy radicals free of aliphatic, tertiary alpha-carbon atoms, and halohydro-carbonoxy radicals having at least two carbon atoms, between the halogen atom and phenol nucleus and being free of an aliphatic, tertiary alpha-carbon atom; R'_1 is the same as R_1 and may additionally be a halogen; m is an integer equal to at least 50, e.g., from 50 to 800 and preferably 150 to 300. Included among these preferred polymers are polymers having a molecular weight in the range of between 6,000 and 100,000, preferably 40,000. Preferably, the poly(phenylene oxide) is poly (2,6-dimethyl-1,4-phenylene) oxide.

Commercially, the poly(phenylene oxide) is available as a blend with styrene resin. These blends typically comprise between 25 and 50% by weight polystyrene units, and are available under the trade name NORYL® thermoplastic resin. The preferred molecular weight when employing a poly (phenylene oxide)/polystyrene blend is between 10,000 and 50,000, preferably around 30,000.

The amount of viscosity modifier employed depends primarily upon the difference between the viscosities of the block copolymer and the engineering thermoplastic resin at the temperature Tp. The amounts may range from 0 to 100 parts by weight viscosity modifier per 100 parts by weight engineering thermoplastic resin, preferably from 10 to 50 parts by weight per 100 parts of engineering thermoplastic resin.

There are at least two methods (other than the absence of delamination) by which the presence of an interlocking network can be shown. In one method, an interlocking network is shown when moulded or extruded objects made from the blends of this invention are placed in a refluxing solvent that quantitatively dissolves away the block copolymer and other soluble components, and the remaining polymer structure (comprising the thermo-

plastic engineering resin and polyacetal) still has the shape and continuity of the moulded or extruded object and is intact structurally without any crumbling or delamination, and the refluxing solvent carries no insoluble particulate matter. If these criteria are fulfilled, then both the unexacted and extracted phases are interlocking and continuous. The unextracted phase must be continuous because it is geometrically and mechanically intact. The extracted phase must have been continuous before extraction, since quantiative extraction of a dispersed phase from an insoluble matrix is highly unlikely. Finally, interlocking networks must be present in order to have simultaneous continuous phases. Also, confirmation of the continuity of the extracted phase may be confirmed by microscopic examination. In the present blends containing more than two components, the interlocking nature and continuity of each separate phase may be established by selective extraction.

In the second method, a mechanical property such as tensile modulus is measured and compared with that expected from an assumed system where each continuous isotropically distributed phase contributes a fraction of the mechanical response, proportional to its compositional fraction by volume. Correspondence of the two values indicates presence of the interlocking network, whereas, if the interlocking network is not present, the measured value is different than that of the predicted value.

An important aspect of the present invention is that the relative proportions of the various polymers in the blend can be varied over a wide range. The relative proportions of the polymers are presented below in parts by weight (the total blend comprising 100 parts):

	Parts by weight	Preferred parts by weight
Dissimilar engineering thermoplastic resin	5 to 48	10 to 35
Block copolymer	4 to 40	8 to 20

The polyacetal is present in an amount greater than the amount of the dissimilar engineering thermoplastics, i.e., the weight ratio of polyacetal to dissimilar engineering thermoplastic is greater than 1:1. Accordingly, the amount of polyacetal may vary from 30 parts by weight to 91 parts by weight, preferably from 48 to 70 parts by weight. Note that the minimum amount of block copolymer necessary to achieve these blends may vary with the particular engineering thermoplastic.

The dissimilar engineering thermoplastic resin, polyacetal and the block copolymer may be blended in any manner that produces the interlock network. For example, the resin, polyacetal and block copolymer may be dissolved in a solvent common for all and coagulated by admixing in a solvent in which none of the polymers are soluble. But, a particular useful procedure is to intimately mix the polymers in the form of granules and/or powder in a high shear mixer. "Intimately mixing" means to mix the polymers with sufficient mechanical shear and thermal energy to ensure that interlocking of the various networks is achieved. Intimate mixing is typically achieved by employing high shear extrusion compounding machines, such as twin screw compounding extruders and thermoplastic extruders having at least a 20:1 L/D ratio and a compression ratio of 3 or 4:1.

The mixing or processing temperature (Tp) is selected in accordance with the particular polymers to be blended. For example, when melt blending the polymers instead of solution blending, it will be necessary to select a processing temperature above the melting point of the highest melting point polymer. In addition, as explained more fully hereinafter, the processing temperature may also be chosen so as to permit the isoviscous mixing of the polymers. The mixing or processing temperature may be between 150°C and 400°C, preferably between 230°C and 300°C.

Another parameter that is important in melt blending to ensure the formation of interlocking networks is matching the viscosities of the block copolymer, polyacetal and the dissimilar engineering thermoplastic resin (isoviscous mixing) at the temperature and shear stress of the mixing process. The better the interdispersion of the engineering resin and polyacetal in the block copolymer network, the better the change for formation of co-continuous inter-locking networks on subsequent cooling. Therefore, it has been found that when the block copolymer has a viscosity η poise at temperature Tp and shear rate of 100 s^{-1}, it is preferred that the engineering thermoplastic resin and/or the polyacetal have such a viscosity at the temperature Tp and a shear rate of 100 s^{-1} that the ratio of the viscosity of the block copolymer divided by the viscosity of the engineering thermoplastic and/or polyacetal be between 0.2 to 4.0, preferably between 0.8 and 1.2. Accordingly, as

used herein, isoviscous mixing means that the viscosity of the block copolymer divided by the viscosity of the other polymer or polymer blend at the temperature Tp and a shear rate of 100 s^{-1} is between 0.2 and 4.0. It should also be noted that within an extruder, there is a wide distribution of shear rates. Therefore, isoviscous mixing can occur even through the viscosity curves of two polymers differ at some of the shear rates.

In some cases, the order of mixing the polymers is critical. Accordingly, one may choose to mix the block copolymer with the polyacetal or other polymer first, and then mix the resulting blend with the dissimilar engineering thermoplastic, or one may simply mix all the polymers at the same time. There are many variants on the order of mixing that can be employed, resulting in the multi-component blends of the present invention. It is also clear that the order of mixing can be employed in order to better match the relative viscosities of the various polymers.

The block copolymer or block copolymer blend may be selected to essentially match the viscosity of the engineering thermoplastic resin and/or polyacetal. Optionally, the block copolymer may be mixed with a rubber compounding oil or supplemental resin as described hereinafter to change the viscosity characteristics of the block copolymer.

The particular physical properties of the block copolymers are important in forming co-continuous interlocking networks. Specifically, the most preferred block copolymers when unblended do not melt in the ordinary sense with increasing temperature, since the viscosity of these polymers is high non-Newtonian and tends to increase without limit as zero shear stress is approached. Further, the viscosity of these block copolymers is also relatively insensitive to temperature. This rheological behaviour and inherent thermal stability of the block copolymer enhances its ability to retain its network (domain) structure in the melt so that when the various blends are made, interlocking and continuous networks are formed.

The viscosity behaviour of the engineering thermoplastic resins, and polyacetals on the other hand, is more sensitive to temperature than that of the block copolymers. Accordingly, it is often possible to select a processing temperature Tp at which the viscosities of the block copolymer and dissimilar engineering resin and/or polyacetal fall within the required range necessary to form interlocking networks. Optionally, a viscosity modifier, as hereinabove described, may first be blended with the engineering thermoplastic resin or polyacetal to achieve the necessary viscosity matching.

The blend of partially hydrogenated block copolymer, polyacetal and dissimilar engineering thermoplastic resin may be compounded with an extending oil ordinarily used in the processing of rubber and plastics. Especially preferred are the types of oil that are compatible with the elastomeric polymer blocks of the block copolymer. While oils of higher aromatic content are satisfactory, those petroleum-based white oils having low volatility and less than 50% aromatics content as determined by the clay gel method (tentative ASTM method D 2007) are particularly preferred. The oils preferably have an initial boiling point above 260°C.

The amount of oil employed may vary from 0 to 100 phr (phr = parts by weight per hundred parts by weight of block copolymer), preferable from 5 to 30 phr.

The blend of partially hydrogenated block copolymer, polyacetal and dissimilar engineering thermoplastic resin may be further compounded with a resin. The additional resin may be a flow promoting resin such as an alpha-methylstyrene resin and an end-block plasticizing resin. Suitable end-block plasticizing resins include coumaroneindene resins, vinyl toluene-alpha-methylstyrene copolymers, polyindene resins and low molecular weight polystyrene resins.

The amount of additional resin may vary from 0 to 100 phr, preferably from 5 to 25 phr.

Further the composition may contain other polymers, fillers, reinforcements, anti-oxidants, stabilizers, fire retardants, anti-blocking agents and other rubber and plastic compounding ingredients.

Examples of fillers that can be employed are mentioned in the 1971-1972 Modern Plastics Encyclopedia, pages 240-247.

Reinforcements are also useful in the present polymer blends. A reinforcement may be defined as the material that is added to a resinous matrix to improve the strength of the polymer. Most of these reinforcing materials are inorganic or organic products of high molecular weight. Examples of reinforcements are glass fibres, asbestos, boron fibres, carbon and graphite fibres, whiskers, quartz and silica fibres, ceramic fibres, metal fibres, natural organic fibres, and synthetic organic fibres. Especially preferred are reinforced polymer blends containing 2 to 80 per cent by weight of glass fibres, based on the total weight of the resulting reinforced blend.

The polymer blends of the invention can be employed as metal replacements and in those areas where high performance is necessary.

In the illustrative Examples given below, various polymer blends were prepared by

mixing the polymers in a 3.125 cm Sterling Extruder having a Kenics Nozzle. The extruder has a 24:1 L/D ratio and a 3.8:1 compression ratio screw.

The various materials employed in the blends are listed below:

1) Block copolymer - a selectively hydrogenated block copolymer according to the invention having a structure S-EB-S.
2) Oil - TUFFLO 6056 rubber extending oil.
3) Nylon 6 - PLASKON® 8207 polyamide.
4) Nylon 6-12 - ZYTEL® 158 polyamide.
5) Polypropylene - an essentially isotactic poly-propylene having a melt flow index of 5 (230°C/2.16 kg).
6) Poly(butylene terephthalate) ("PBT") - VALOX® 310 resin.
7) Polycarbonate - MERLON ® M-40 polycarbonate.
8) Poly(ether sulphone) - 200 P.
9) Polyurethane - PELLETHANE® CPR.
10) Polyacetal - DELRIN® 500.
11) Poly(acrylonitrile-co-styrene) - BAREX® 210.
12) Fluoropolymer - TEFZEL® 200 poly(vinylidene fluoride) copolymer.

In all blends containing an oil component, the block copolymer and oil were premixed prior to the addition of the other polymers.

Illustrative Example I

Various polymer blends were prepared according to the invention. A blend of two block copolymers of a higher and lower molecular weight was employed in some polymer blends in order to better match the viscosity with the polyacetal and/or other dissimilar engineering thermoplastic resin. In some blends, an oil was mixed with the block copolymer in order to better match viscosities. Comparative blends not containing a block copolymer were also prepared. However, these blends were not easily mixed. For example, blend 115 containing just the polyacetal and Nylon 6 suffered from die swell, surging, and melt fracture. In contrast, in each blend containing a block polymer, the polymer blend was easily mixed, and the extrudate was homogeneous in appearance. Further, in each blend containing a block copolymer, the resulting polyblend had the desired continuous, interlocking networks as established by the criteria hereinabove described.

The compositions and test results are presented below in Tables 1 and 2. The compositions are listed in percent by weight.

TABLE 1

Blend No.	47	78	77	78	93	94	112
Blend of block copolymers					15.0	30.0	
Oiled block copolymers	15.0	30.0	15.0	30.0			15.0
Polyacetal	42.5	35.0	21.3	17.5	21.3	17.5	21.3
Poly(butylene terephthalate)	4.25	35.0	63.7	52.5			
Polycarbonate					63.7	52.5	
Nylon 6							63.7
Poly(acrylonitrile-co-styrene)							

TABLE 1 (cont'd)

Blend No.	113	174	175	89	108	115	171
Blend of block copolymers		15.0	30.0				
Oiled block copolymers	30.0						
Polyacetal	17.5	21.3	17.5	25.0	25.0	25.0	25.0
Poly(butylene terephthalate)				75.0			
Polycarbonate					75.0		
Nylon 6	52.5					75.0	
Poly(acrylonitrile-co-styrene)		63.8	52.5				75.0

TABLE 2

Blend No.	Polymer type	% Block copolymers	1*	2	3	4	5	6	7	8	9
112	Nylon 6	15	5,500	3.28	3.10	5,800	6	6,800	2.1	1,700	0.38
113		30	3,500	2.15	2.06	3,700	4	3,800	1.1	900	0.22
89	PBT	0	6,920	4.17	3.98	-	3	11,800	3.30	2,600	0.60
77		15	4,500	3.04	2.93	5,020	3	8,000	2.51	1,700	0.31
78		30	3,400	2.12	2.06	2,500	5	7,000	1.70	1,000	0.22
108	Polycarbonate	0	9,150	4.11	3.88	-	4	14,300	3.97	6,900	2.37
93		15	6,500	2.97	2.86	6,600	5	10,100	2.94	4,810	1.79
94		30	4,800	2.20	2.07	4,800	6	6,800	2.13	3,030	1.25

TABLE 2 (cont'd)

Blend No.	Polymer type	% Block copolymer	10	11	12	13	14	15	16	17
112	Nylon 6	15	313	5.67	0.896	86	1.61	1.64	0.68	0.85
113		30	212	4.87	0.734	44	2.36	2.00	1.18	0.95
89		0	318	4.69	0.127	116	0.28	0.25	0.56	0.52
77	PBT	15	301	5.80	0.113	94	0.51	0.56	0.55	0.52
78		30	202	5.52	0.111	61	0.78	0.81	0.70	0.68
108		0	286	4.74	0.14	120	1.45	1.81	1.26	1.41
93	Polycarbonate	15	278	5.09	0.13	100	3.23	4.34	1.33	1.98
94		30	277	4.90	0.09	77	4.82	5.31	2.51	1.84

**Data Column Headings*

1. Tensile at break, psi
2. Young's modulus, psi $\times 10^5$
3. Secant modulus, psi $\times 10^5$
4. Yield, psi
5. Percent elongation
6. Maximum, psi
7. Modulus, psi $\times 10^5$
8. Maximum, psi
9. Modulus, psi $\times 10^5$
10. Heat distortion temperature, °F
11. Linear expansion, $\times 10^5$, inches per inch per degree Centigrade
12. Water absorption, %
13. Rockwell hardness, R#
14. Gate end, ft-lbs/inch
15. Dead end, ft-lbs/inch
16. Gate end, ft-lbs/inch
17. Dead end, ft-lbs/inch

The results of the above blends indicate the presence of unobvious properties for the blends. For example, by examining the ratio of the relative increase in Izod impact strength (at 23°C) over the relative decrease in heat distortion temperature for polymer blends as the percentage of block copolymers is increased from 0% to 15% at a fixed 1:3 ratio of polyacetal to dissimilar engineering thermoplastic, it can be seen that much larger than expacted values are obtained. One skilled in the art would typically expect this value to be positive and less than 1. However, for blends containing PBT and polycarbonate the ratios are 13 and 28 respectively.

WHAT WE CLAIM IS:-

1. A composition containing a partially hydrogenated block copolymer comprising at least two terminal polymer blocks A of a monoalkenyl arene having an average molecular weight of from 5,000 to 125,000, and at least one intermediate polymer block B of a conjugated diene having an average molecular weight of from 10,000 to 300,000, in which the terminal polymer blocks A constitute from 8 to 55% by weight of the block copolymer and no more than 25% of the arena double bonds of the polymer blocks A and at least 80% of the aliphatic double bonds of the polymer blocks B have been reduced by hydrogenation, characterized in that the composition comprises:

(a) 4 to 40 parts by weight of the partially hydrogenated block copolymer,

(b) an acetal resin having a generally crystalline structure and a melting point over 120°C,

(c) 5 to 48 parts by weight of at least one dissimilar engineering thermoplastic resin being selected from the group consisting of polyamides, polyolefins, thermoplastic polyesters, poly(aryl ethers) as defined herein, poly(aryl sulphones), polycarbonates, thermoplastic polyurethanes, halogenated thermoplastics, and nitrile resins,

in which the weight ratio of the acetal resin to the dissimilar engineering thermoplastic resin is greater than 1:1 so as to form a polyblend wherein at least two of the polymers form at least partial continuous interlocked networks with each other.

2. A composition as claimed in claim 1, in which the polymer blocks A have a number average molecular weight of from 7,000 to 60,000 and the polymer blocks B have a number average molecular weight of from 30,000 to 150,000.

3. A composition as claimed in claim 1 or 2, in which the terminal polymer blocks A constitute from 10 to 30% by weight of the block copolymer.

4. A composition as claimed in any one of the preceding claims, in which less than 5% of the arene double bonds of the polymer blocks A and at least 99% of the aliphatic double bonds of the polymer blocks B have been reduced by hydrogenation.

5. A composition as claimed in any one of claims 1-4, in which the acetal resin is a polyacetal copolymer.

6. A composition as claimed in any one of claims 1-5, in which the dissimilar engineering thermoplastic resin has an apparent crystalline melting point in excess of 120°C.

7. A composition as claimed in claim 6, in which the dissimilar engineering thermoplastic resin has an apparent crystalline melting point of between 150°C and 350°C.

8. A composition as claimed in any one of claims 1-7, in which the dissimilar engineering thermoplastic resin is a polyolefin having a number average molecular weight in excess of 10,000 and an apparent crystalline melting point of above 100°C.

9. A composition as claimed in claim 8, in which the polyolefin is a homopolymer or copolymer derived from an alpha-olefin or 1-olefin having 2 to 5 carbon atoms.

10. A composition as claimed in any one of claims 8-9, in which the number average molecular weight of the polyolefin is in excess of 50,000.

11. A composition as claimed in any one of claims 8-10, in which the apparent crystalline melting point of the polyolefin is between 140°C and 250°C.

12. A composition as claimed in any one of claims 8-11, in which the composition contains a high density polyethylene having an approximately crystallinity of over 75% and a density of between 0.94 and 1.0 kg/l.

13. A composition as claimed in any one of claims 8-11, in which the composition contains a low density polyethylene having an approximate crystallinity of over 35% and a density of between 0.90 and 0.94 kg/l.

14. A composition as claimed in any one of claims 8-13, in which the composition contains a polyethylene having a number average molecular weight of 50,000 to 500,000.

15. A composition as claimed in any one of claims 8-11, in which the composition contains an isotactic polypropylene.

16. A composition as claimed in claim 15, in which the propylene has a number average molecular weight in excess of 100,000.

17. A composition as claimed in any one of claims 8-11, in which the composition contains a polypropylene being a copolymer which contains ethylene or another alpha-olefin as comonomer in an amount in the range of from 1 to 20% by weight.

18. A composition as claimed in any one of claims 8-11, in which the composition contains poly(1-butene) as polyolefin.

19. A composition as claimed in any one of claims 8-11, in which the composition contains as polyolefin a homopolymer of 4-methyl-1-pentene having an apparent crystalline melting point of between 240 and 250°C and a relative density of between 0.80 and 0.85.

20. A composition as claimed in any one of claims 8-11, in which the composition contains as polyolefin a copolymer of 4-methyl-1-pentene and an alpha-olefin.

21. A composition as claimed in claim 20, in which the composition contains as polyolefin a copolymer of 4-methyl-1-pentene and a linear alpha-olefin having from 4 to 18 carbon atoms, the linear alpha-olefin being present in an amount in the range of from 0.5 to 30% by weight.

22. A composition as claimed in any one of claims 1-7, in which the dissimilar engineering thermoplastic resin is poly(ethylene terephthalate), poly(propylene terephthalate) or poly (butylene terephthalate).

23. A composition as claimed in any one of claims 1-7, and 22, in which the dissimilar engineering thermoplastic resin is poly(ethylene terephthalate), (propylene terephthalate) or poly (butylene terephthalate).

24. A composition as claimed in claim 23, in which the dissimilar engineering thermoplastic resin is poly(butylene terephthalate) having an average molecular weight in the range of from 20,000 to 25,000.

25. A composition as claimed in any one of claims 1-7 and 22, in which the engineering thermoplastic resin is a cellulosic ester.

26. A composition as claimed in any one of claims 1-7 and 22, in which the engineering thermoplastic resin is a homopolymer of pivalolactone.

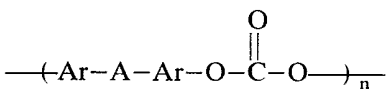
27. A composition as claimed in any one of claims 1-7 and 22, in which the engineering the thermoplastic resin is a copolymer of pivalolactone with no more than 50 mol.% of another beta-propiolactone.

28. A composition as claimed in claim 27, in which the engineering thermoplastic resin is a copolymer of pivalolactone with no more than 10 mol.% of another beta-propiolactone.

29. A composition as claimed in any one of claims 26-28, in which the engineering thermoplastic resin is a polypivalolactone having an average molecular weight in excess of 20,000 and a melting point in excess of 120°C.

30. A composition as claimed in any one of claims 1-7 and 22, in which the engineering thermoplastic resin is a polycaprolactone.

31. A composition as claimed in any one of claims 1-7, in which the engineering thermoplastic resin is a polycarbonate having the general formula:



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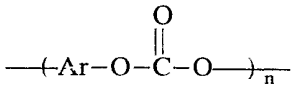


II

wherein Ar represents a phenylene or an alkyl, akoxy, halogen or nitro-substituted phenylene group, A represents a carbon-to-carbon bond or an alkylidene, cycloalkylidene, alkylene, cycloalkylene, azo, imino, sulphur, oxygen, sulphoxide or sulphone group, and n is at least two.

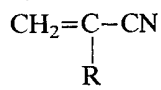
32. A composition as claimed in any one of claims 1-7, in which the engineering thermoplastic resin is a polycarbonate that has been prepared by reacting para, para, -isopropylidenediphenol with phosgene.

33. A composition as claimed in any one of claims 1-7, in which the dissimilar engineering thermoplastic resin is a polyamide having a number average molecular weight in excess of 10,000.

34. A composition as claimed in any one of claims 1-7, in which the engineering thermoplastic resin is a homopolymer of copolymer derived from tetrafluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene, vinylidene fluoride and vinylidene chloride.

35. A composition as claimed in any one of claims 1-7, in which the engineering thermoplastic resin is a nitrile resin having an alpha, beta-olefinically unsaturated mononitrile content of greater than 50% by weight.

36. A composition as claimed in claim 35, in which the alpha, beta-olefinically unsaturated mononitrile has the general formula:



wherein R represents hydrogen, an alkyl group having from 1 to 4 carbon atoms or a halogen.

37. A composition as claimed in claim 35 to 36, in which the nitrile resin is a homopolymer, a copolymer, a graft of a copolymer onto a rubbery substrate or a blend of homopolymers and/or copolymers.

38. A composition as claimed in any one of claims 1-37, in which the composition contains the block copolymer and the dissimilar thermoplastic resin in an amount of from 8 to 20 parts by weight and from 10 to 35 parts by weight, respectively.

39. A composition as claimed in any one of the preceding claims, in which the composition contains an extending oil in an amount of from 0 to 100 phr.

40. A composition as claimed in claim 39, in which the composition contains an extending oil in an amount of from 5 to 30 phr.

41. A composition as claimed in any one of the preceding claims, in which the composition contains a flow-promoting resin as additional resin in an amount from from 0 to 100 phr.

42. A composition as claimed in claim 41, in which the composition contains a flow-promoting resin as additional resin in an amount of from 5 to 25 phr.

43. A composition as claimed in claim 41 or 42, in which the composition contains an additional resin selected from the group consisting of an alpha-methylstyrene resin, coumarone-indene resins, vinyl toluene-alpha-methylstryene copolymers, polyindene resins and low molecular weight polystyrene resins.

44. A composition as claimed in any one of the preceding claims, substantially as hereinbefore described, with particular reference to the Examples.

45. A process for the preparation of a composition as claimed in claims 1-44, characterized in that

(a) 4 to 40 parts by weight of a partially hydrogenated block copolymer comprising at least two terminal polymer blocks A of a monoalkenyl arene having an average molecular weight of from 5,000 to 125,000 and at least one intermediate polymer block B of a conjugated diene having an average molecular weight of from 10,000 to 300,000, in which the terminal polymer blocks A constitute from 8 to 55% by weight of the block copolymer and no more than 25% of the arene double bonds of the polymer blocks A and at least 80% of the aliphatic double bonds of the polymer blocks B have been reduced by hydrogenation, are mixed at a processing temperature Tp of between 150°C and 400°C with

(b) an acetal resin having a generally crystalline structure and a melting point over 120°C, and

(c) 5 to 48 parts by weight of at least on dissimilar engineering thermoplastic resin being selected from the group consisting of polyamides, polyolefins, thermoplastic polyesters, poly(aryl ethers) as defined herein, poly(aryl sulphones), polycarbonates, thermoplastic polyurethanes, halogenated thermoplastics and nitrile resins, in which the weight ratio of the acetal resin to the dissimilar engineering thermoplastic resin is greater than 1:1, so as to form a polyblend wherein at least two of the polymers form at least partial continuous interlocked networks with each other.

46. A process as claimed in claim 45, characterized in that the polymers are mixed at a processing temperature Tp of between 230°C and 300°C.

47. A process as claimed in claim 45 or 46, characterized in that the polymers are dissolved in a solvent common for all and coagulated by admixing in a solvent in which none of the polymers are soluble.

48. A process as claimed in claim 45 or 46, characterized in that the polymers are mixed as granules and/or powder in a device which provides shear.

49. A process as claimed in any one of claims 45-48, characterized in that the ratio of the viscosity of the block copolymer divided by the viscosity of the polyacetal, the dissimilar engineering thermoplastic resin or the mixture of the polyacetal and the dissimilar engineering thermoplastic resin is between 0.2 to 4.0 at the processing temperature Tp and a shear rate of 100 s^{-1}.

50. A process as claimed in claim 49, characterized in that the viscosity ratio of the viscosity of the block copolymer divided by the viscosity of the polyacetal, the dissimilar

engineering thermoplastic resin or the mixture of the polyacetal and the dissimilar engineering thermoplastic resin is between 0.8 and 1.2 at the processing temperature Tp and a shear rate of 100 s^{-1}.

51. A process as claimed in any one of claims 45-50, characterized in that the dissimilar thermoplastic resin is first blended wth a viscosity modifier before blending with the polyacetal and the block copolymer.

52. A process as claimed in any one of claims 45-51, characterized in that as viscosity modifier poly(2,6-di-methyl-1,4-phenylene)oxide, or a blend of poly(2,6-dimethyl-1,4-phenylene) oxide with polystyrene is used.

53. A process as claimed in claim 51 or 52, characterized in that the viscosity modifier is used in an amount of from 0 to 100 parts by weight per 100 parts by weight of engineering thermoplastic resin.

54. A process as claimed in claim 53, characterized in that the viscosity modifier is used in an amount of from 10 to 50 parts by weight per 100 parts by weight of engineering thermoplastic resin.

55. A process as claimed in any one of claims 45-54, characterized in that the block copolymer and the dissimilar engineering thermoplastic resin are used in an amount of from 8 to 20 parts by weight and from 10 to 35 parts by weight, respectively.

56. A process as claimed in any one of claims 45-55, substantially as hereinbefore described.

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