PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C08L 77/06 // (C08L 77/06
C08L 51/06)

A1

(11) International Publication Number: **WO 91/07467**

(43) International Publication Date: 30 May 1991 (30.05.91)

(21) International Application Number: PCT/US90/06744

(22) International Filing Date: 16 November 1990 (16.11.90)

(30) Priority data:
8926094.7 17 November 1989 (17.11.89) GB

(71) Applicant *(for all designated States except US):* EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : JONES, Brenton, Georges [AU/BE]; Kasteelstraat 87, B-3090 Overijse (BE). CARTASEGNA, Silvestro [IT/BE]; Avenue Gén.-de-Longueville 14, B-1150 Bruxelles (BE). STUYVER, Johan [BE/BE]; Brusselbaan 190A, B-9320 Erembodegem (BE). KAUFMAN, Lawrence, George [US/US]; 498 Auten Road 3D, Somerville, NJ 08876 (US). DOYLE, Michael, John [GB/US]; Box 317B RD #1, Upper Black Eddy, PA 18972 (US). WHITE, Donald, Andrew [GB/US]; 3 Greenfield Gardens, Edison, NJ 08837 (US).

(74) Agents: MULLER, William, G.; Exxon Chemical Company, 1900 East Linden Avenue, Linden, NJ 07036-0710 (US) et al.

(81) Designated States: AT (European patent), AU, 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, KR, LU (European patent), NL (European patent), SE (European patent), US.

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: TOUGHENED POLYAMIDE AND COMPOSITIONS, PROCESS FOR THEIR PREPARATION AND MOULDED ARTICLES MADE THEREFROM

(57) Abstract

The notched impact strength, particularly at room temperature, and the ductile/brittle transition temperature of a polyamide 6 may be increased by including a modifier which is an amorphous or semi-crystalline polyolefin containing sites which adhere to polyamide 6, such as maleic anhydride, the modifier being dispersed in the polyamide in the form of particles which have a number average diameter of at least 0.2 µm and in which the volume fraction of particles having a diameter greater than 1 µm is 15 to 60 %. Part of the polyolefin modifier can be replaced by ethylene based homo- and copolymers.

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Toughened polyamide and compositions, process for their preparation and moulded articles made therefrom.

The present invention relates to blends of polyamide 6 which have a good notched Izod impact strength, a process for their production and moulded particles made from such polyamide 6 compositions.

Unmodified thermoplastic polyamides such as polyamide 6 (nylon 6) are considered to be "tough" materials since they have a high resistance to crack initiation. This can be measured in terms of the high energy needed to initiate a crack or break, demonstrated by the tensile test, unnotched impact test (Izod and/or Charpy) or the dart drop impact test.

However, such unmodified polyamides have a low resistance to crack propagation and high sensitivity to strain rate. Thus although a large amount of energy is required to initiate a crack, once a crack or other such strain or flaw has occurred, the polyamide breaks easily. Such notch sensitivity and brittle breakage leads to catastrophic failure of moulded and extruded particles because the finished particles frequently have sharp corners and/or edges which are more prone to strains, cracks and notches.

Much research has been carried out into ways of improving the impact strength of polyamides, and it is now common to add an impact modifier. Typically the modifier is a "rubbery" polymer such as an amorphous or semi-crystalline polyolefin onto which has been grafted sites which adhere to the polyamide matrix. However, blends of polyamides and an impact modifier which have previously been proposed tend not to have sufficiently high notched impact strength at room temperature. More specifically, it is desirable that the polyamide blends have a notched impact strength which is greater at room temperature than at a lower temperature such as 0°C. A low ductile/brittle transition temperature (DBTT) is also desirable. Previous blends of polyamide and impact modifier have had notched impact strengths showing a maximum in impact strength below room temperature (hence an "impact reversion effect" at room temperature and too high a DBTT).

A correlation has previously been observed between the DBTT and the size of the particles of impact modifier dispersed in the polyamide. In particular, it has been reported (see eg. US Patent 4174358) that to obtain the optimum impact strength it is necessary for the particles of modifier to have a size less than one micrometre. The present inventors have surprisingly found that if a certain proportion of the particles have a size greater than one micrometre then blends can be obtained which have improved toughness, and in particular an improved DBTT and a reduction in the notched impact strength reversion effect.

The present invention provides a polymer blend comprising from 5 to 40% by weight and preferably 15 to 25% by weight of an amorphous or semi-crystalline polyolefin modifier which contains sites which adhere to polyamide 6, dispersed as particles in 95 to 60% by weight and preferably 85 to 75% by weight of polyamide 6, in which blend the dispersed particles have a number average diameter (dn) of at least 0.2 micrometre (μm), and the volume fraction of particles having a diameter greater than one micrometer (μm) is from 15 to 60%.

Below the minimum value of number average particle diameter (dn) the blend tends to have insufficient toughness. This shows itself in a high DBTT, low notched impact strength over the entire temperature range of 0°C to room temperature and a decrease in notched impact strength as temperature increases (i.e., an impact strength reversion).

However, blends with similar dn provide quite different room temperature notched impact strengths depending upon the volume fraction of particles greater than one micrometre in diameter. It is therefore necessary for the particles of modifier to meet both requirements of the particle distribution defined above i.e. to have a minimum number average diameter of at least 0.2 µm and to have a volume fraction of 15 to 60% of modifier being in the form of particles whose diameter is greater than 1 µm.

When the volume fraction of particles of diameter 1 µm or more is below 15%, the room temperature notched Izod impact strength is too low to be useful in practice. However, when the volume fraction is above 60% the notched Izod impact strength decreases with increasing temperature from 0°C to room temperature.

Preferably the volume fraction of particles having a diameter greater than 1 µm is 25 to 50%. The number average diameter is preferably 0.2 to 1 µm.

Polyamides which may be used in the blends are those denoted polyamide 6 (i.e. polycaprolactam). The number average molecular weight may be from, for example 13,000 to 50,000. The melt viscosity may be, for example, from 110 to 600 Pa. Sec. Suitable commercially available polyamides 6 include ULTRAMID B3 of BASF; ORGAMIDE of Atochem; SNIAMID of SNIA Technopolimeri; DURETHAN of Bayer; TECHNYL of Rhone-Poulenc; and MARANYL of ICI.

The modifier may be a "rubbery" polyolefin which may contain (e.g., be grafted with) sites which adhere to polyamide 6. The "rubbery" polyolefin is an amorphous or semi-crystalline homo- or copolymer of olefins, particularly olefins having 2 to 6, preferably 2 to 4 carbon atoms, e.g. ethylene, propylene, n-butylene. Copolymers of ethylene and propylene are particularly preferred.

Adhering sites contained within, e.g., grafted to, the polyolefin may be e.g., monocarboxylic acid groups, unsaturated dicarboxylic acid groups or their anhydrides. Suitable acids/anhydrides include maleic acid/anhydride, itaconic acid/anhydride, nadic acid/anhydride and methyl nadic acid/anhydride. Maleic anhydride is particularly preferred.

It is possible to replace part of the amorphous or semi-crystalline polyolefin modifier by ethylene based homo- and copolymers, etc., both crystalline and amorphous. In other words the modifier may also be a blend of the rubbery polyolefins containing adhering sites with ethylene based homo- and copolymers, etc., which do not contain adhering sites. Examples of ethylene based polymers include the rubbery polyolefin defined above, but unmodified with adherent groups, as well as typically crystalline polymers exemplified by polyethylene and polyethylene co- and terpolymers having at least 85 mol% ethylene. High density polyethylene (HDPE) and very low density polyethylene (VLDPE) in addition to ethylene-propylene rubbery copolymers are particularly preferred. In such blends the most effective compositions have been achieved by using a minor fraction (10 to 20 wt% and preferrably 12 to 15 wt% of the modifier blend) of a highly grafted rubbery polyolefin. Highly grafted means from 1.5 to 3.5% functionality by weight of the rubbery polyolefin.

The proportion of adhering sites in the impact modifier depends on the particular adhering groups chosen, and henceforth will be described in terms of groups which are grafted. For example, if the grafted group is maleic anhydride then it will typically be from 0.1 to 2.0, more preferably 0.3 to 1.5% by weight of the impact modifier.

The melt flow rate (MFR), measured at 10 kg/230°C by ASTM D 1238-85, of the impact modifier is generally from 1 to 100, more preferably 3 to 50.

The blends may contain one or more conventional additives such as stabilizers, inhibitors of degradation, lubricants, mould release agents, colourants, fibres and particulate fillers and reinforcements and nucleating agents.

Stabilizers include materials which stabilize the blend against oxidation or thermal degradation such as cuprous halides and halides of alkali metals such as sodium, potassium and lithium; hindered phenols, hydroquinones and derivatives thereof. A stabilizer against degradation caused by ultra violet light may also be included, e.g. a resorcinol, salicylate, benzotriazole or benzophenone.

Suitable lubricants and mould release agents include stearic acid, stearic alcohol and stearamides. Suitable colouring agents include dyes such as nigrosine and pigments such as titanium dioxide, cadmium sulphide, ultra marine blue and carbon black. Particulate fillers and reinforcements which may be used include e.g. carbon fibres, glass fibres, amorphous silica, calcium silicate, aluminium silicate, magnesium carbonate, kaolin and chalk. Nucleating agents which may be used include. e.g. talc, calcium fluoride, sodium phenyl phosphinate, alumina and PTFE. The blends may be prepared by mixing the polyamide 6 and the impact modifier (and any other components) in a mixer such as a Banbury mixer or extruder, particulary a twin screw extruder.

To control the particle size distribution of the impact modifier in the blend several parameters may be altered; for example, the viscosity of the impact modifier or the proportion of adhering sites in the impact modifier. Structural changes to the polyamide e.g. its viscosity and reactive end groups may also be used to obtain the necessary distribution. Additives such as nucleating agents and the conditions under which the blend is produced also affect the particle size distribution.

If the viscosity of the impact modifier is low such that the modifier/polyamide matrix viscosity ratio is approaching unity then the particle size of the modifier in the blend will be low, i.e. the volume fraction of particles having a diameter greater than 1 µm will be less than 15%. Increasing the viscosity of the modifier or decreasing the viscosity of the polyamide increases this volume fraction and hence improves the impact strength.

The conditions under which the blend is produced, and in particular the specific energy consumption (SEC), i.e. energy given to the blend during mixing, correlates with the blend morphology. If the mixing conditions such as screw RPM and feed rate are such that the SEC is high the size of the dispersed particles of modifier will be low, corresponding to a volume fraction of particles with a diameter greater than 1 µm of less than 15%. A lower SEC will increase this volume fraction and produce a less refined particle size distribution which leads to improved toughness and DBTT. The screw configuration of a twin screw extruder may be used to alter the mixing efficiency of the extruder. At very high mixing efficiency the particle size distribution results in the particles being below 1 µm in diameter. The impact strength is improved by lowering the mixing efficiency of the extruder to give a coarser distribution and consequently an improved impact strength.

If a nucleated polyamide 6 is used the volume fraction of particles with a diameter greater than 1 µm is greater than 15% over a much broader range of mixing conditions and the impact reversion phenomenon is not observed.

The following examples illustrate the invention. If not otherwise indicated, all parts and percentages are by weight. In the examples the volume fractions of particles of diameter greater than 1 µm, and the minimum number average diameter, have not been measured for all blends. However it is reasonable to conclude from the physical property measurements that the blends with comparable physical properties to those known to have diameters with the claimed ranges also have diameters within the claimed ranges.

The method used for particle size determination is well known and widely described in the literature (e.g. S.Wu, POLYMER, 1985, Vol. 26, November, pp. 1855-1863, particularly p. 1856). At first a scanning electron microscope picture is taken of the blend at a magnification of 5 000. Then a grid is used having squares equivalent to 1 square µm to count the number of particles having diameters < 0.25, 0.25-0.5, 0.5-0.75, 0.75-1.0, 1.0-1.25, 1.25-1.5, etc. The average diameter for each range and hence the volume fraction of that size range assuming spherical particles are calculated. From these data the number average particle diameter and the volume fraction of particles within a certain size range are calculated.

EXAMPLES 1 TO 6 and 101

Compositions were prepared by mixing the polyamide 6 and impact modifier (an ethylene-propylene copolymer grafted with maleic anhydride) in dry form in a corotating intermeshing twin screw extruder. Extruder barrel temperatures were set at about the melting point of the polyamide with melt temperature being in the range of 10 to 40°C above this melting point.

The ethylene propylene rubbers grafted with maleic anhydride, as used in these examples, were produced by melt grafting the EP rubber in the presence of maleic anhydride, using a free radical initiator to promote grafting. EP-MANH 1, 2, 3, 4, 5, 6 contain 75, 68, 44, 68, 75, 75 wt % ethylene respectively; and 0.7, 0.5, 0.6, 0.7, 0.53, 0.59 wt % maleic anhydride respectively. EP-MANH 1, 2, 3, 4 and 6 were prepared using a peroxide initiator having a high decomposition temperature (half life 10 hours at 150°C); EP-MANH 5 was prepared using a peroxide initiator having a low decomposition temperature (half life 10 hours at 60°C).

Each blend was injection moulded and specimens tested according to ASTM norms as follows:

Flexural Modulus - ASTM D 790 (d=3.2; b< 1/4 (16 x d);
(span = 16 x d)
Tensile Strength - ASTM D 638
Izod Strength - ASTM D 256 Method A 64/18.7
Charpy - DIN 53453, ISO 179-1982 (E)
MFR - ASTM D 1238-85

Morphological analysis was done on microtomed or fracture surfaces. Details of the blend components are contained in Tables I and II. The viscosity ratio of modifier to polyamide is shown in Table III. The specific energy consumption used in producing the blends is indicated in Table IV, together with details of the impact strength and DBTT of the resulting blends. It can be seen from Table IV that decreasing the specific energy given to the blend (and hence producing 15-60% volume fraction of particles >1μm in diameter) surprisingly improves the impact strength and DBTT.

EXAMPLES 7 To 12 AND 102

The blends and test samples were produced as described in Examples 1 to 6 and details of the materials used are given in Table V. Increasing the specific energy consumption again results in a decrease in impact strength, and in particular a worsening impact strength at room temperature compared with that at 0°C.

EXAMPLES 13 To 18

These examples illustrate how variation of the viscosity ratio (modifier/polyamide matrix) may be used to control the blend morphology and hence the impact performance of the blend. The blends and test samples were prepared as described in Examples

1 to 6. Details of the components used and the properties of the blends produced are given in Table VI. By increasing the modifier viscosity, the viscosity ratio is altered to result in a less refined morphology. This less refined morphology shows surprising impact improvement. Particularly, the toughness of the blend at room temperature is improved and the impact strength at room temperature is comparable with that at 0°C. (see eg. Example 17).

EXAMPLES 19 TO 25

Blends were prepared from samples produced using the methods of Examples 1 to 6, and tests were prepared thereon, again as described in Examples 1 to 6.

In Examples 19 to 23 modifiers of different viscosity were used and in some instances two modifiers of different viscosity were mixed. By mixing modifiers of different viscosities the blend morphology can be controlled to result in blends in which the volume fraction of modifier particles greater than 1 μm is 15 to 60%. Details of the blends produced are given in Table VII.

In Examples 24 and 25, modifiers produced by using different free radical initiators were used. The blend morphology and impact properties are compared in Table VIII. The modifier EP-MANH 5 obtained using a different free radical initiator provides much less refined morphology (volume fraction of particles above 1 μm greater than 15%) and correspondingly improved impact strength properties. This less refined morphology is the consequence of the higher modifier viscosity and the different grafting mechanism.

EXAMPLES 26 AND 27

The methods used to obtain the blends were as described in Examples 1 to 6. Two polyamides of different viscosity were used to illustrate the effect of improving the viscosity ratio using these differing polyamides. With the increasing molecular weight of the matrix material increasing toughness would be expected. However, the increasing molecular weight leads to a more refined morphology of particles (i.e. more than 85% volume of the modifier is in the form of particles whose diameter is less than 1μm) and this leads to a dramatic reduction in blend toughness. The results are shown in Table IX.

EXAMPLES 28 AND 29

These examples illustrate another way of optimising the blend toughness by controlling the blend morphology by altering the mixing efficiency of the extruder. This is done by altering the screw configuration of the extruder. The blends and test samples were produced using the methods of Examples 1 to 6 and details of the blends and their properties are given in Table X. The higher the screw configuration number the less efficient the mixing is.

EXAMPLES 30 TO 36 AND 103

These examples iilustrate the use of nucleated polyamide 6 to obtain the necessary blend morphology. The blends and test samples were produced using the method of Examples 1 to 6 (except Examples 35, 36 and 103 which were mixed on the counterrotating tangential twin screw extruder used for Examples 7 to 12) and details of the blends and their properties are given in Table XI.

When nucleated polyamide 6 is used the blend morphology is less refined with the volume fraction of particles with diameter above 1 μm being greater than 15%. Again a surprising impact strength improvement is obtained, as shown by Examples 35 and 36.

When nucleated polyamide 6 is used, the blend morphology obtained is less sensitive to the processing parameters, as shown by Examples 30 to 34.

EXAMPLES 37 AND 38

The blends according to these examples were prepared by mixing the polyamide 6 and the impact modifier in dry form in a corotating twin screw extruder. The extruder barrel temperatures were set at about the melting point of the polyamide with the melt temperature being in the range 10 to 40°C above this melting point.

EP-MAN 7 contains 48% ethylene and 1,8% maleic anhydride, while EP-MAN 8 contains 44% ethylene and 2,8% maleic anhydride. These modifiers were prepared using a peroxide initiator having a high decomposition temperature (half life 10 hours at 150°C). Test specimens were produced as described in Examples 1 to 6 and the test results are shown in Table XII. These blends show how particle size can be controlled according to this invention by varying the proportion of adhering sites in the modifier.

Details of the blend components are contained in Table XII.

<u>FIGURE 1.</u> Shows the relationship between temperature and notched Izod Impact strength for the blends of Examples 1, 9, 11 and 12.
<u>FIGURE 2.</u> Shows the Notched Izod Impact strength at room temperature and the number average particle size of the blends of Examples 1, 9, 11, 12, 101, 102 and 103.
<u>FIGURE 3.</u> Shows the Notched Izod Impact strength at room temperature and the number average particle size (when particles of size greater than 1 µm are not considered).
<u>FIGURE 4.</u> Shows the Notched Izod Impact strength at room temperature and the volume fraction (%) of particles greater than 1 µm for Examples 1, 9, 11, 12, 101, 102 and 103.

Figure 1 shows a plot of the Notched Izod Impact strength of a blend of 80% polyamide and 20% maleic anhydride grafted EP rubber over a range of temperatures from -40°C to room temperature. As may be seen from Figure 1, the blends of Examples 9 and 11 show a clear and pronounced impact strength reversion at temperatures from 0°C to room temperature. Both of these have a zero volume fraction of particles which are greater than 1 µm in size. The blend of Example 1 also shows an impact strength reversion as room temperature is approached, but not so pronounced as for Examples 9 and 11. Again, the volume fraction of particles having particle size greater than 1 µm is 13.3, that is below the invention limit of 15%. In contrast, Example 12, which contains 22.4% (volume fraction) of particles greater than 1 µm in diameter shows no impact strength reversion between 0°C and room temperature.

It may be concluded from Figure 1 that a volume fraction of at least 15% of particles having diameter greater than 1 µm is required to give the improved impact strength properties. It will be noted from Example 9 that in general the impact strength is poor over the whole of the temperature range measured. This is believed to be because the modifier particles in the blend are extremely small.

Figure 2 is a plot of the Notched Izod Impact strength of various blends, versus the number average particle size in µm, the strength being measured at room temperature. This figure shows that (Examples 1, 9, 11 and 12) as the number average particle size of the modifier in the blend decreases, there is a corresponding decrease in room temperature impact strength. Below a level of about 0.2 µm, the impact strength reaches an undesirably low level.

Also in Figure 2, the results for Examples 101, 102 and 103 demonstrate that for blends where the number average particle size is greater than 0.2 µm, the volume fraction of particles having a diameter greater than 1 µm is important with regard to the impact strength at room temperature. All are above 15%, but once the volume fraction exceeds about 60% there is a tailing off in impact strength. Hence this figure demonstrates that the blends of the invention require both a number average particle size of at least 0.2 µm, and a volume fraction of particles having a diameter greater than 1 µm of from 15 to 60%.

Figure 3, plots the same data as are shown in Figure 2, except that the particles of size greater than 1 µm have been excluded from the particle size distribution of each blend. This shows that the increase in impact strength at room temperature, and the maximum value reached, is largely dependent on the volume fraction of particles greater than 1 µm in diameter, rather any change in the number average particle size.

Figure 4 shows essentially the same data as are shown in Figure 2 except here the Figure is of room temperature Notched Izod strength versus the volume fraction of particles greater than 1 µm in diameter. The conclusions are substantially the same.

TABLE I

POLYAMIDE RESINS

MATRIX	CHEMICAL COMPOSITION	Mn	RELATIVE VISCOSITY g/dl	MELT VOLUME INDEX CM^3/10 MIN	MELT VISCOSITY (4) Pa.sec
Polyamide 1	Polyamide 6	18.000	2.69	120	140
Polyamide 2	Polyamide 6 (high viscosity)	42.000	5.0	4	520
Polyamide 3	Polyamide 6 (nucleated)	18.000	2.67	120	140

TABLE II

IMPACT MODIFIER POLYMERS

IMPACT MODIFER	CHEMICAL COMPOSITION	MELT FLOW RATE (1) g/10 min	CRYSTALLINITY (2) cal/g	MANH LEVEL (3) wt %	MELT VISCOSITY (4) Pa.sec
EP-MANH 1	C2 - C3 - MANH	9	9.9	0.7	830
EP-MANH 2	C2 - C3 - MANH	8	3.5	0.5	620
EP-MANH 3	C2 - C3 - MANH	35	1.1	0.6	430
EP-MANH 4	C2 - C3 - MANH	5	1.0	0.7	1100

NOTE:
(1) 10 kg/230°C
(2) by DSC
(3) by IR
(4) at 250°C/250 sec^{-1}

TABLE III

BLEND COMPONENT VISCOSITY RATIO (MODIFIER/PA MATRIX)

	POLYAMIDE 1 (PA 6)		
	235°C	260°C	285°C
EP-MANH 1	2.4	3.8	5.7
EP-MANH 3	1.1	2.3	2.9
EP-MANH 4	-	5.0	-

At 250 sec^{-1} shear rate

TABLE IV

Example No	1	2	3	4	5	6	101
Polyamide 1 (PA 6)	80	80	80	80	80	80	80
EP-MANH 3 (amorphous/high flow)	20	20	20	-	-	-	-
EP-MANH 1 (semicrystalline/low flow)	-	-	-	20	20	20	-
EP-MANH 2 (low crystalline/low flow)	-	-	-	-	-	-	20
Specific Energy Consumption (NET)							
Kwh/kg	0.18	0.27	0.33	0.24	0.36	0.42	0.40
Notched Izod Impact							
(conditioned 3 days/RT/50%R.H.) J/m							
23°C	650	465	384	628	758	643	909
0°C	781	675	541	716	705	595	829
-10°C	753	662	581	648	601	546	703
-20°C	756	733	605	530	228	207	267
-30°C	669	678	285/510	216	217	199	215
-40°C	218	220	205	168	188	140	148
Ductile/brittle Transition °C	-35	-35	-30	-25	-15	-15	-15
Volume Fraction % Greater Than 1µm	13.3	-	-	-	-	-	28.9
No. Average Particle Size (µm)	0.30	-	-	-	-	-	0.3

TABLE V

Example No	7	8	9	10	11	12	102
Polyamide 1 (PA 6)	80	80	80	80	80	80	80
EP-MANH 3 (amorphous/low viscosity)	20	20	20	20	20	-	-
EP-MANH 1 (semi-crystalline /high viscosity)	-	-	-	-	-	20	-
EP-MANH 2 (low crystalline/low flow)	-	-	-	-	-	-	20
Specific Energy Consumption (Gross)							
Kwh/kg	0.67	0.92	1.53	1.07	0.63	0.86	-
Notched Izod Impact							
(conditioned 3 days/RT/50%RH) J/m							
23°C	456	373	296	343	453	839	914
0°C	640	520	409	491	672	842	841
-10°C	613	516	484	417	594	781	712
-20°C	673	596	235	551	693	717	561
-30°C	596	247	210	234	635/258	557	212
-40°C	175	175	162	165	179	161	151
Ductile/brittle Transition °C	-35	-25	-15	-25	-30	-35	-25
Volume Fraction % Greater than 1µm	-	-	0	-	0	22.4	54
no. Average Particle Size (µm)	-	-	0.20	-	0.22	0.37	0.3

Note: counterrotating tangential twin screw extruder

TABLE VI

POLYAMIDE 6 MODIFICATION / MODIFIER VISCOSITY EFFECT

	Semicrystalline EP-MANH				Amorphous EP-MANH	
Example No	13	14	15	16	17	18
Polyamide 1 (PA 6)	80	80	80	80	80	80
EP-MANH	20	20	20	20	20	20
Modifier Melt Flow Rate (10 kg/230°C, g/10')	8	16	21	33	5	35
Notched Izod Impact (conditioned 3 days/RT/50%RH)						
23°C	557	361	311	227	839	296
0°C	632	521	437	379	842	409
-10°C	488	443	345	349	781	484
-20°C	156/218	206	167	178	717	235
-30°C	173	139	128	128	557	210
-40°C	119	118	115	110	161	162
Ductile/brittle Transition °C	-20	-15	-15	-15	-35	-15
Volume Fraction % Greater Than 1μm					22.4	0
No. Average Particle Size (μm)					0.37	0.2

Note: Corotating intermeshing twin screw extruder.

TABLE VII

POLYAMIDE 6 MODIFICATION / MODIFIER AT DIFFERENT VISCOSITY

Example No	19	20	21	22	23
Polyamide 1 (PA 6)	80	80	80	80	80
EP-MANH 1 (MFR 8/semicrystalline)	20	15	10	5	-
EP-MANH 3 (MFR 35/amorphous)	-	5	10	15	20
EP-MANH 5 (MFR 6.0)	-	-	-	-	-
EP-MANH 6 (MFR 12)	-	-	-	-	-
Notched Izod Impact					
(conditioned 3 days/RT/50%R.H.) J/m					
23°C	776	740	709	522	456
0°C	753	791	821	756	684
-10°C	673	685	750	720	679
-20°C	557	592	616	671	646
-30°C	219	461/257	231	486/268	571
-40°C	172	174	190	192	157

Note: Corotating intermeshing twin screw extruder

TABLE VIII

EFFECT OF MODIFIER FREE RADICAL INITIATOR TYPE

Example No	24	25
Polyamide 1 (PA 6)	80	80
EP-MANH 1 (MFR 8/semicrystalline)	-	-
EP-MANH 3 (MFR 35/amorphous)	-	-
EP-MANH 5 (MFR 6.0)	20	-
EP-MANH 6 (MFR 12)	-	20
Notched Izod Impact (conditioned 3 days/RT/50%R.H.) J/m		
23°C	862	612
0°C	687	640
-10°C	584	545
-20°C	216	240
-30°C	177	168
-40°C	164	153

Note: Counter-rotating tangential twin screw extruder

TABLE IX

POLYAMIDE 6 MODIFICATION / EFFECT OF POLYAMIDE VISCOSITY

Example No.	26	27
* Polyamide 1 (PA 6)	80	-
**Polyamide 2 (PA 6 high viscosity)	-	80
EP-MANH 1	20	20
NOTCHED IZOD IMPACT (Conditioned 3 days/RT/50% RH) J/m		
23°C	531	314
0°C	655	530
-10°C	470	435
-20°C	191	152

Notes:

* Ultramid B3 : RV 2.69 /Mn 18.000
**Ultramid B5 : RV 5.00 /Mn 42.000
Counter-rotating tangiental twin screw extruder.

Table X

POLYAMIDE 6 MODIFICATION/ EXTRUDER SCREW CONFIGURATION EFFECT

	Low Flow/Semicrystalline	EP-MANH
Example No.	28	29
Polyamide 1 (PA 6)	80	80
EP-MANH 1	20	20
Screw Configuration No	14	10
Specific Energy Consumption (Gross) KWH/kg	0.57	0.67
Notched Izod Impact (Conditioned 3 days/RT/50% RH)		
23°C	751	490
0°C	725	634
-10°C	636	593
-20°C	576	510
-30°C	257	312
-40°C	229	273
Ductile/brittle transition °C	-25	-25

NOTE: Counter-rotating tangential twin screw extruder

TABLE XI

POLYAMIDE 6 MODIFICATION (NUCLEATED) / EFFECT OF BLENDING CONDITIONS

Example No.	30	31	32	33	34	35	36	103
Polyamide 1 (PA6)	-	-	-	-	-	80	-	-
Polyamide 3 (PA 6 nucleated)	80	80	80	80	80	-	80	80
EP-MANH 3	20	20	20	20	20	20	20	-
EP-MANH 2	-	-	-	-	-	-	-	20
Specific Energy Consumption (NET)								
Kwh/kg	0.26	0.27	0.17	0.36	0.27	-	-	-
Notched Izod Impact								
(Conditioned 3 days/RT/50% RH) J/m								
23°C	1048	1028	988	974	1014	562	1070	971
0°C	955	988	965	949	984	749	995	792
-10°C	863	856	876	826	862	778	940	685
-20°C	738/295	774	818	705	776	803	915	243
-30°C	304	657	651	368/591	705	784	812	195
-40°C	-	-	-	-	-	403	215	139
Ductile/brittle transition °C	-20	-35	-35	-30	-35	-35	-35	-15
Volume Fraction(%) greater than 1μm	-	-	-	-	-	-	-	74
No. Average Particle Size	-	-	-	-	-	-	-	0.55

TABLE XII

POLYAMIDE 6 MODIFICATION/EFFECT OF CONTROL OF FUNCTION OF ADHERING SITES

Example No:	37	38
Polyamide 1	80	80
EP-MAN 7	2.5	
EP-MAN 8		2.5
EP [1]	11.65	17.5
HDPE [2]	5.85	
Specific Energy Consumption (NET) KWH/kg	0.25	0.25
Notched izod impact J/m (conditioned 3 days RT/50% RH)		
23°C	965	940
RT	955	680
-10°	875	640
-20°	315	640
-30°	-	196
Ductile brittle transistion °C	-15	-25
Volume fraction (%) greater than 1 μ	45	50
Number average particle size	0.26 μ	0.32 μ

1) VISTALON 606 (an ethylene-propylene rubber with 44 wt.% ethylene) available from EXXON CHEMICAL INTERNATIONAL MARKETING, Brussels, Belgium

2) ESCORENE HD 6950 YN (high density polyethylene, 8 M.I. (7.16 kg, 190°C)) available also from EXXON CHEMICAL INTERNATIONAL MARKETING

CLAIMS:

1. A polymer blend which comprises from 5 to 40% by weight of an amorphous or semi-crystalline polyolefin modifier which contains sites which adhere to polyamide 6, dispersed as particles in 95 to 60% by weight of polyamide 6, in which blend the dispersed particles have a number average diameter of at least 0.2 µm and the volume fraction of particles having a diameter greater than 1 µm is 15 to 60%.

2. A blend as claimed in claim 1 in which the adhering site on the polyolefin is an unsaturated dicarboxylic acid or anhydride.

3. A blend as claimed in claim 2 in which the dispersed material is an ethylene/propylene rubber grafted with maleic anhydride.

4. A blend as claimed in any one of the preceding claims in which the volume fraction of particles having a diameter greater than 1 µm is 25 to 50%.

5. A blend as claimed in any one of the preceding claims in which the number average diameter of the dispersed particles is 0.2 to 1 µm.

6. A blend as claimed in any one of the preceding claims comprising 15 to 25% by weight of dispersed particles and 85 to 75% by weight of polyamide 6.

7. A blend as claimed in any one of claims 2 to 6 in which part of the amorphous or semi-crystalline polyolefin modifier is replaced by ethylene based homo- and/or copolymers which do not contain adhering sites and in which the amorphous or semi-crystalline polyolefin modifier and the ethylene based homo- and/or copolymers are present as a blend.

8. A blend as claimed in claim 7 in which the modifier blend consists of highly grafted ethylene propylene rubber and ungrafted ethylene propylene rubber or highly grafted ethylene propylene rubber, ungrafted ethylene propylene rubber and polyethylene.

9. A blend as claimed in claim 8 in which the highly grafted ethylene propylene rubber comprises 10 to 20% by weight of the modifier blend and contains 1.5 to 3.5% by weight dicarboxylic acid or anhydride.

10. A blend as claimed in any one of claims 7 to 9 in which the ethylene based homo- and/or copolymer component of the modifier blend contains high density polyethylene (HDPE) and/or very low density polyethylene (VLDPE).

11. A process for preparing a blend as claimed in any one of the preceding claims comprising mixing 95 to 60% by weight of polyamide 6 with 5 to 40% by weight of a modifier which is an amorphous or semi-crystalline polyolefin containing sites which adhere to polyamide 6 or a modifier blend as defined in claim 7, the viscosities of the polyamide 6 and modifier being selected to result in a blend in which the volume fraction of dispersed modifier particles having a diameter greater than 1 µm is 15 to 60% and the number average diameter of the dispersed modifier particles is at least 0.2 µm.

12. A process for producing a polymer blend as claimed in any one of claims 1 to 10 comprising mixing 95 to 60% by weight of polyamide 6 with 5 to 40% by weight of a modifier which is an amorphous or semi-crystalline polyolefin containing sites which adhere to polyamide 6 or a modifier blend as defined in claim 7, the specific energy consumption of the mixing process being such that the volume fraction of dispersed modifier particles in the blend having a diameter

greater than 1 µm is 15 to 60% and the number average diameter of the dispersed modifier particles is at least 0.2 µm.

13. A process for producing a polymer blend as claimed in any one of claims 1 to 10 comprising mixing 95 to 60% by weight of nucleated polyamide 6 and 5 to 40% by weight of a modifier which is an amorphous or semicrystalline polyolefin containing sites which adhere to polyamide 6 or a modifier blend as defined in claim 7.

14. A process for producing a polymer blend as claimed in any one of claims 1 to 10 comprising mixing 95 to 60% by weight of polyamide 6 with 5 to 40% by weight of a modifier system comprising at least two amorphous or semi-crystalline polyolefins each containing sites which adhere to polyamide 6, the concentration levels of adherent sites in the two or more polyolefins being such as to result in a blend having a volume fraction and minimum number average diameter as defined in claim 1.

15. A process according to claim 14 wherein the concentration level of adherent sites in each polyolefin is in the range of 0.1 to 2.0% by weight of each respective polyolefin.

16. A moulded article produced using a blend according to any one of claims 1 to 10.

FIG. I

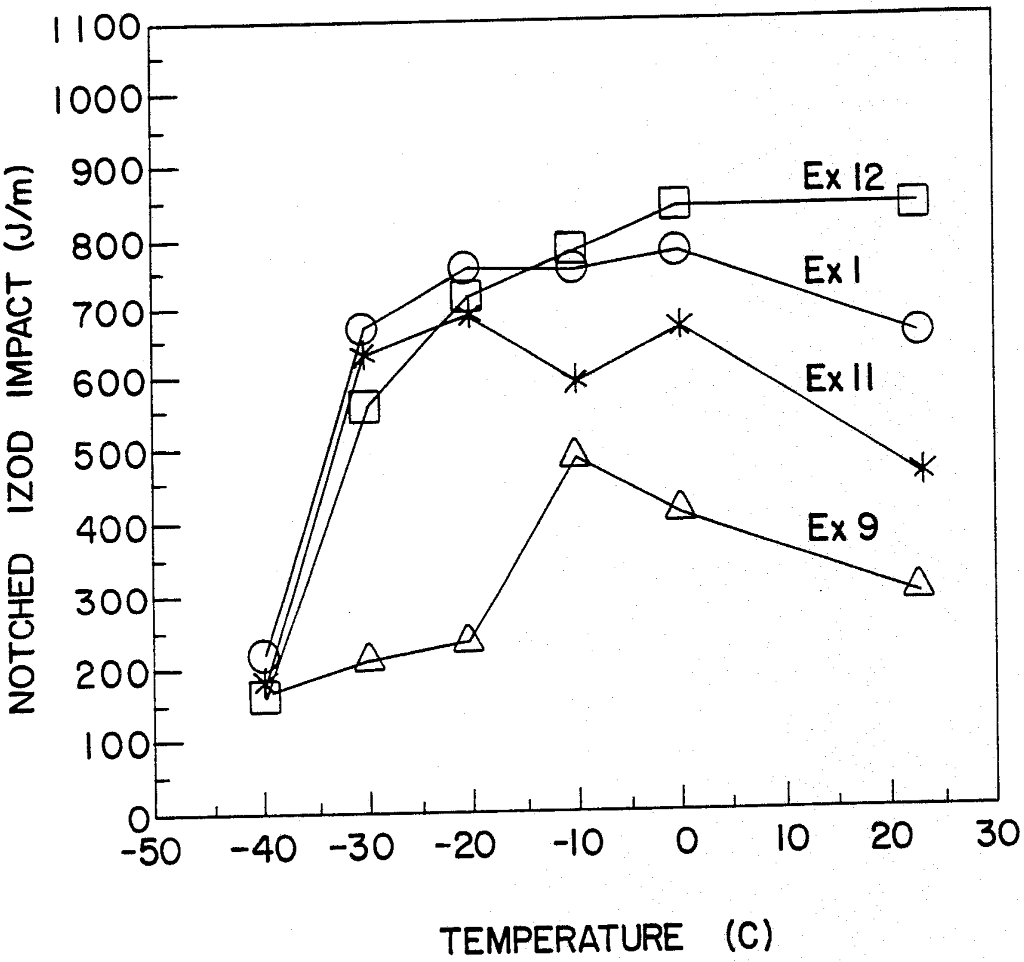
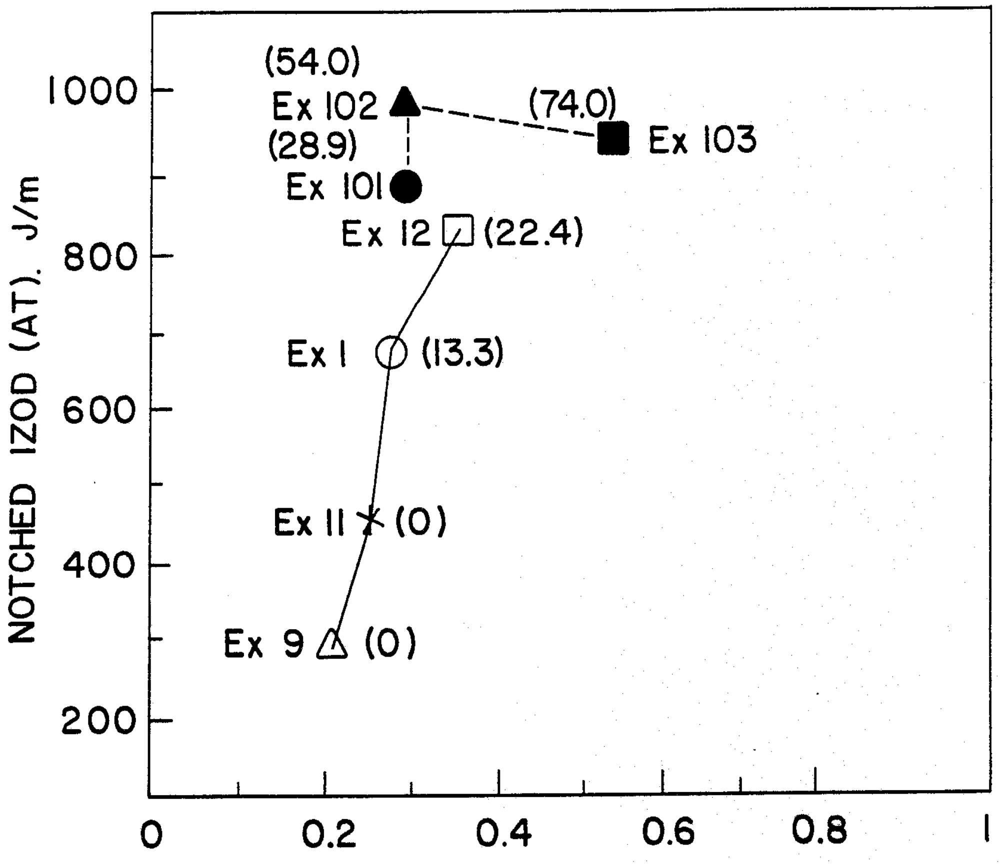
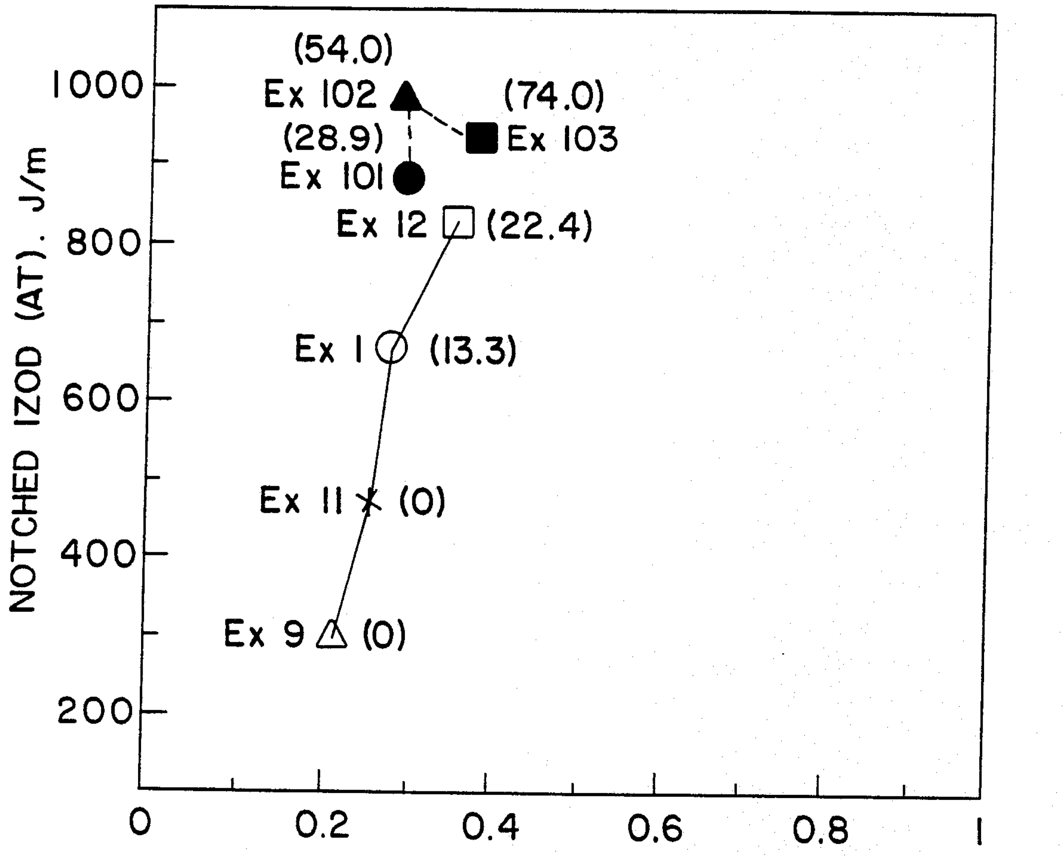

NOTCHED IZOD IMPACT (J/m)
1100
1000
900
800
700
600
500
400
300
200
100
0
-50
-40
-30
-20
-10
0
10
20
30
TEMPERATURE (C)
Ex 12
Ex I
Ex II
Ex 9

FIG. 2



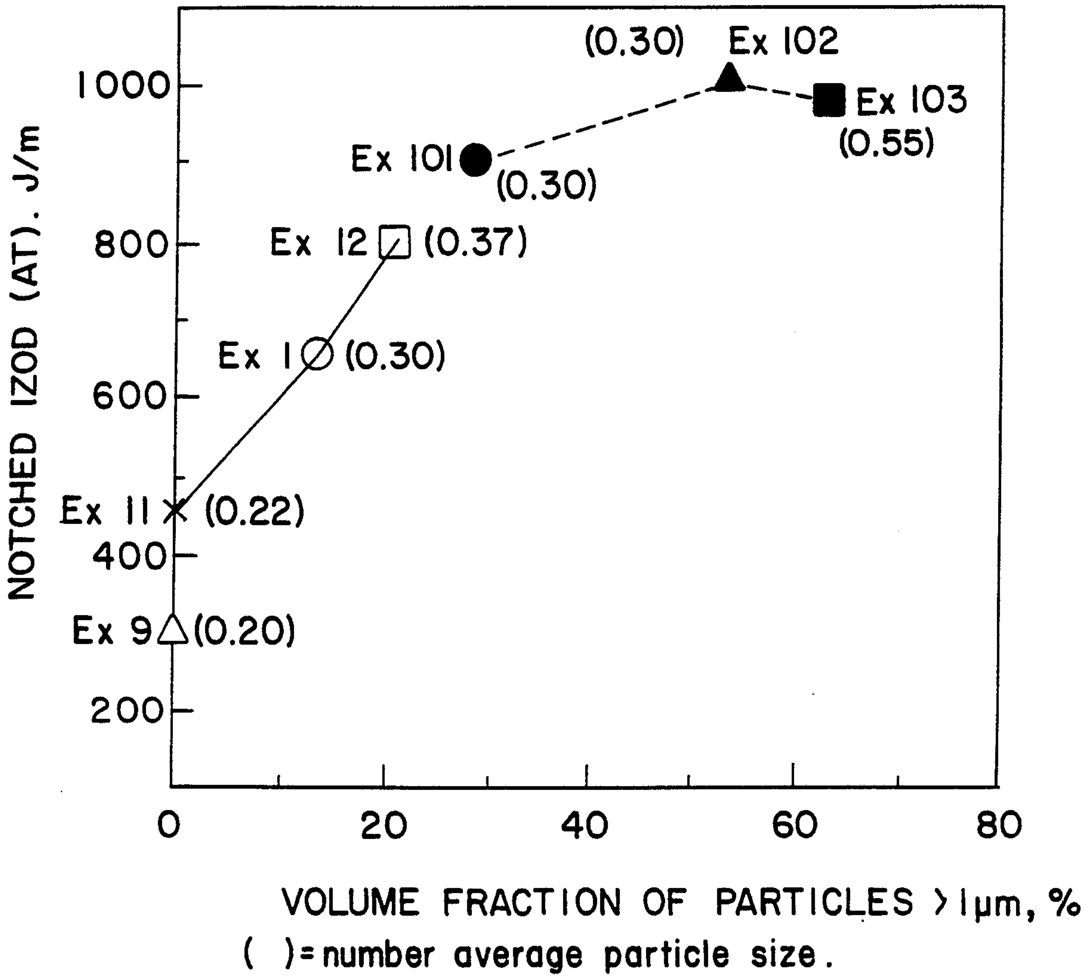
Number average particle size µm
( )= volume % of dispersed phase in particle size > 1 µm

FIG. 3



Number average particle size μm of particles < 1μm
( ) = volume % of dispersed phase in particle size > 1μm

FIG.4


NOTCHED IZOD (AT). J/m
1000
800
600
400
200
0
20
40
60
80
VOLUME FRACTION OF PARTICLES >1μm, %
( )=number average particle size.
Ex 9 (0.20)
Ex 11 (0.22)
Ex 1 (0.30)
Ex 12 (0.37)
Ex 101 (0.30)
(0.30) Ex 102
Ex 103 (0.55)

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/06744

I. CLASSIFICATION OF 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: C 08 L 77/06 // (C08 L 77/06, L 51:06)

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^5	C 08 L

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 *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 4174358 (B.N. EPSTEIN) 13 November 1979 cited in the application ---	
A	Die Makromolekulare Chemie Macromolecular Symposia, volume 16, March 1988, Hüthig & Wepf Verlag, H. Höcker et al.: "Influence of structure on the impact behaviour of nylon-rubber blends", pages 195-207 ---	
A	Chemical Abstracts, volume 107, no. 18 2 November 1987, (Columbus, Ohio, US), R.J.M. Borggreve et al.: "Brittle-tough transition in nylon-rubber blends: effect of rubber concentration and particle size", see page 37, abstract no. 155282v & Polymer 1987, 28(9), 1489-96 -------------	

* Special categories of cited documents: [10]

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

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

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

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"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.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 3rd March 1991	Date of Mailing of this International Search Report 11. 04. 91
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer Nuria TORIBIO

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9006744

SA 42527

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 03/04/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4174358	13-11-79	CA-A- 1133164	05-10-82
		CH-A- 649566	31-05-85
		DE-A,B 2622973	09-12-76
		FR-A,B 2311814	17-12-76
		GB-A- 1552352	12-09-79
		JP-C- 1344392	29-10-86
		JP-A- 51143061	09-12-76
		JP-B- 55044108	10-11-80
		JP-C- 1554624	23-04-90
		JP-A- 59131649	28-07-84
		JP-B- 63054308	27-10-88
		NL-A- 7605495	25-11-76

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82