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(54) Title: TECHNICAL PLASTIC COMPOSITION		
(57) Abstract <p>A technical plastic composition which comprises: a) approximately 30–98.9 % by weight of polyamide and b) approximately 1–69.9 % by weight of ultra high molecular weight polyethylene has been rendered compatible and melt processible by incorporating into it: c) approximately 0.1–30 % by weight of a copolymer, the macromolecules of which comprise: i) C₂–C₈ alkylene repeating units, ii) C₂–C₆ alkylene repeating units which contain a carboxyl group or a carboxyl derivative group and, preferably, iii) C₈–C₁₀ aralkylene repeating units, such as styrene units.</p>		

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Technical plastic composition

The invention relates to a technical plastic blend which comprises

- 5 a) approximately 30-98.9% by weight of polyamide and
- b) approximately 1-69.9% by weight of ultra high molecular weight polyethylene.

10 Technical thermoplastics are used for many applications in machines, equipment, automobiles and the like, wherein good mechanical properties and good wear properties are required of the product. Furthermore, it is desirable that moving parts have low friction and wear and often self-lubricating capability. Various polyamide grades are commonly used for these applications. Polyamides are polymers which contain repeating amide groups -NHCO- as essential parts in the polymer backbone.

15 Polyamides can be used as such, with additives, or reinforced with fiber. Excellent mechanical properties are achieved with glassfiber reinforcement, although thereby the good properties of the plastic, such as its light weight and impact strength, are partially lost.

20 Polyamides have also been compounded with polyolefins, in which case an attempt has been made to combine the high tensile strength, wear resistance and heat resistance and easy processibility of polyamides with the high impact strength and moisture resistance of polyolefins. The publication Fairley, G. and Prud'homme, R.E., Polym. Eng. Sci. 27 (1987) 1495 presents publications and patents all the way from

25 1960, relating to blends of polyamides and polyolefins. The publication Kim, B.K., Park, S.Y. and Park S.J., Eur. Polym. J. 27 (1991) 349 discloses blends of polyamide and polyethylene, for example, blends of polyamide-6 and low-density polyethylene, of polyamide-66 and high-density polyethylene, and of polyamides and chemically modified polyethylenes, as well as corresponding blends rendered

30 compatible by means of a compatibilizer.

Often two polymers are thermodynamically immiscible with each other, which prevents the production of a truly homogeneous product. This applies in particular to the combinations of polar polymers, such as polyamides, and of non-polar polymers, such as polyolefins, since solvating interaction does not take place between

35 the components. Thus the system is divided into two separate phases. The conditions prevailing at the interface between the two phases often result in problems. In a typical case, high interfacial tension and poor adhesion are produced between the

two phases. Thus the phases tend to separate from each other, whereupon the good properties of the polymers in the blend are not combined in the forming blend.

5 On the other hand, if low interfacial tension and strong adhesion prevail between polar polymers and non-polar polymers, they form a finely-divided and stable dispersion from which there forms a product having the good properties of both components, sometimes even better properties.

10 As was already stated above, the interfacial tension between two polymer phases can be reduced by adding an additive which reduces surface tension, i.e. a compatibilizer. Some typical compatibilizers are segment copolymers, i.e. block and/or graft copolymers, some blocks of which solvate one polymer component or react with it, and some blocks solvate the other polymer block or react with it.

15 The compatibility of polyamides and polyolefins may be improved by means of copolymers the blocks of which are capable of physical or chemical interaction with the components of the polymer blend. It is suggested in the publication Chen, C.C. and White, J.L., Polym. Eng. Sci. 33 (1993) 923 that the compatibilizer used for a binary blend of polyamide-6 and a high-density polyethylene should be a partially
20 zinc-neutralized random copolymer of ethylene and methacrylic acid, a graft copolymer of maleic anhydride with propylene, or a graft copolymer of maleic anhydride with styrene and hydrogenated butadiene. The said copolymer compatibilizers are approximately equally effective, and more effective than the other compatibilizers experimented with.

25 The literature also contains proof that copolymers modified with maleic anhydride react with polyamide and are in solvating interaction with polyolefin.

30 The publication Willis, J.M. and Favis, B.D. Polym. Eng. Sci. 28 (1988) 1416 shows that, when 5% by weight of a compatibilizer is added to blends of polyamide and polypropylene or polyamide and polyethylene, the particle size of the dispersed polymer component is decreased and equalized considerably. This proves that both the polyamide phase and the polyolefin phase are in the molten state in the melt processing apparatus and capable of dispersing into each other like liquids. If one of
35 the polymer components were in the solid state in the melt processing apparatus, the particle size and its distribution would remain unchanged regardless of the compatibilizer addition.

The publication Raval, H., Singh, Y.P., Mehta, M.H. and Devi, S., Polym. Intern. 26 (1991) 105 examines the compatibilization of polyamide-6 and a low density polyethylene with a graft polymer the macromolecules of which consist of a backbone of a low density polyethylene and a branch linked to the backbone, the branch
5 being a copolymer of butylacrylate and maleic anhydride.

The publication Kim, B.K., Park, S.Y. and Park, S.J., Eur. Polym. J. 27 (1991) 349 examines a blend of polyamide-6, a high density polyethylene and a graft polymer the macromolecules of which consist of a maleic anhydride branch linked to a poly-
10 ethylene backbone.

The publication Holsti-Miettinen, R. and Seppälä, J., Polym. Eng. Sci. 32 (1992) 868 examined, among others, polyamide and polypropylene blends to which a graft copolymer had been added and the macromolecules of which consisted of maleic
15 anhydride branches linked to a polypropylene backbone or of maleic acid branches linked to a styrene-ethylene-butadiene-styrene block chain.

As is evident from the above, the investigations so far have focussed on blends of polyamide with low density polyethylene, high density polyethylene and polypropylene. Since conventional polyamide grades and conventional polyolefin grades
20 are easy to process by thermoplastic melt processing methods, such as injection molding, blow molding, thermoforming and extrusion, two molten phases have been produced which, owing to the compatibilizer, have dispersed evenly into each other and have formed products combining the good properties of polyamide and polyolefin. On the other hand, it has not been possible to compatibilize blends of
25 polyamide and ultra high molecular weight polyethylene in the manner stated above. Ultra high molecular weight polyethylene (UHMWPE) is namely a high density polyethylene having a molar mass of at least 3×10^6 . The molar mass of conventional high density polyethylene is seldom above 50,000, whereas the molar mass of ultra
30 high molecular weight polyethylene is, according to the ASTM definition, as high as 3×10^6 - 6×10^6 (ASTM D 4020).

Owing to its extremely high molar mass, ultra high molecular weight polyethylene cannot be processed by thermoplastic melt processing methods such as injection
35 molding, blow molding, thermoforming or extrusion. Long chain molecules will not become plasticized nor flow as do the molecules of thermoplastics. Owing to the absence of melt processibility of ultra high molecular weight polyethylene, its melt dispersion in polyamide has so far been regarded as impossible. In the publications

Gabriele, M.C., Plastics Technol. 36, (1990) 5, 25 and Williams, M.A., Bauman, B.D. and Thomas, D.A., Polym. Eng. Sci. 31 (1991) 992, an attempt has been made to improve the compatibility of ultra high molecular weight polyethylene with polyamides by modifying its surface by a gas treatment. However, such a gas treatment will not produce melt processibility and thus not an uniform dispersion in the polyamide phase.

On the basis of the above technical lesson, ultra high molecular weight polyethylene is thus capable of acting only as a filler in the manner of a metal powder in polyamide. Cf. Buett, J.H. and Allen, C. Tribology International, 25 (1992) 4, 237-246.

The production of compatible blends of polyamides and ultra high molecular weight polyethylene involves the following problems:

a) Effect of molar mass

In general, the molar mass of ultra high molecular polyethylene exceeds 3×10^6 , which is much higher than the molar masses of polyamide and potential compatibilizers. If we take into account the principle generally known in the art, i.e. that the molecules of the basic polymer tend to exclude any different molecules and even molecules of the same type but of a different size, this tendency is especially emphasized when molecules of extremely different sizes are concerned. Cf. Markham, R.L., Adv. Polym. Technol. 10 (1990) 231.

b) Effect of melt viscosity

The viscosity ratio of the basic components at the processing temperature has a crucial effect on the morphology of the forming blend. Cf. the above reference. It is known that ultra high molecular weight polyethylene is not at all melt processible, and therefore melt dispersion seems impossible.

c) Effect of polarity

It is known that polyamide is a polar polymer and that ultra high molecular weight polyethylene is a non-polar polymer. Owing to these different polarities it is very difficult to achieve dispersion in blends of polyamide and ultra high molecular polyethylene. Also, adhesion between polyamide and ultra high molecular weight

polyethylene is minor, and therefore it is difficult to make their blend compact and mechanically strong.

As is evident from the above, the problems concerning the compatibilization and melt dispersion of polyamides and ultra high molecular weight polyethylene have so far not been solved. Furthermore, it is known that ultra high molecular weight polyethylene has very good properties required of a technical plastic, such as low wear, good sliding properties, very high notched impact resistance and resistance to chemicals, and therefore it would be particularly desirable to achieve its blend with polyamide, in which blend the said properties would combine with the good properties of polyamide, stated above.

It is an object of the present invention to solve the problems described above and to provide a technical plastic blend better than previously, the blend comprising polyamide and ultra high molecular weight polyethylene. The invention is thus mainly characterized in what is stated in the characterizing clause of Claim 1. It has thus been realized that a technical plastic blend which comprises

- a) approximately 30-98.9% by weight of polyamide and
- b) approximately 1-69.9% by weight of ultra high molecular weight polyethylene

is melt dispersible and processible into a technical plastic blend of superior properties if it comprises, as a component improving the melt processibility of the ultra high molecular weight polyethylene and the compatibility between the polyamide and the ultra high molecular weight polyethylene,

- c) approximately 0.1-30% by weight of a copolymer the macromolecules of which comprise
 - i) C₂-C₈ alkylene repeating units,
 - ii) C₂-C₆ alkylene repeating units which contain a carboxyl group or a carboxyl derivative group and, preferably,
 - iii) C₈-C₁₀ aralkylene repeating units, such as units of styrene.

Although copolymers of the above-mentioned type have been used as components improving the compatibility of polyamides and polyethylenes having normal-sized molecules, it was completely surprising that it at the same time acted as an agent crucially improving the melt processibility of ultra high molecular weight polyethyl-

ene, i.e. as a processing auxiliary, and thereby enabled a new type of technical plastic with excellent properties to be prepared.

Although the concentration of the copolymer component (c) in a technical plastic blend according to the invention may vary widely, it is preferable for the plastic blend to comprise (käsittää) approximately 1-15% by weight, preferably 2-10% by weight, and most preferably approximately 3-8% by weight, of the said copolymer (c). The word käsittää in this publication (translator's note: the Finnish original) means the same as the English word "comprise", i.e. the blend may contain also components other than the component indicated by the word käsittää (comprise). Cf. Grubb, B.W., Patents in Chemistry and Technology, Clarendon Press, Oxford (1986) 220.

A technical plastic blend according to the invention thus comprises a copolymer (c) the macromolecules of which have repeating units of at least two types. One type, i.e. C₂-C₈ alkylene repeating units (i), consists of bivalent saturated aliphatic hydrocarbon units (-ylene, cf. Römpps Chemie-Lexicon, 8th edition (1988), volume 6, p. 4666), which are assumed to be in interaction with the molecules of the ultra high molecular weight polyethylene. The said C₂-C₈ alkylene repeating units may derive from monomers of highly different types, such as diene monomers which have been hydrogenated to form alkylene repeating units, or olefin monomers of one or several types which have been directly polymerized to form the said C₂-C₈ alkylene repeating units (i).

It is however, advantageous if the C₂-C₈ alkylene repeating units (i) in the macromolecules of the said copolymer (c) are repeating units of a C₂-C₆ olefin. Such repeating units include ethylene, propylene, 1-butene, 4-methylpent-1-ene, 3-methylbut-1-ene, 4,4-dimethylpent-1-ene, and vinylcyclohexane. It is however, most advantageous if the C₂-C₈ alkylene units (i) in the macromolecules of the said copolymer (c) are repeating units of a C₂-C₃ olefin, such as repeating units of ethylene and/or propylene.

The macromolecules of the said copolymer (c) in a technical plastic blend according to the invention contain, as the other repeating unit type, C₂-C₆ alkylene repeating units which contain a carboxyl group or a carboxyl derivative group. These repeating units are thus made up of a bifunctional saturated aliphatic hydrocarbon group having one or several carboxyl groups, i.e. the group -COOH or some other derivative group of the carboxyl group, such as an anhydride, ester, salt or amide group. It

has been presumed that the carboxyl group or the carboxyl derivative group in the said repeating units interacts with the polyamide component in the technical plastic blend, even so that it in some cases reacts with the polyamide.

- 5 According to one embodiment of the invention, the C₂-C₆ alkylene repeating units (ii), containing a carboxyl group or a carboxyl derivative group, in the macromolecules of the said copolymer (c) are repeating units reactive with the said polyamide, and preferably repeating units reactive with the amino end groups of the polyamide. Such a repeating unit containing a carboxyl group or a carboxyl derivative group is
10 formed when an unsaturated carboxylic acid or its derivative is polymerized.

As stated, the C₂-C₆ alkylene repeating units (ii), containing a carboxyl group or a carboxyl derivative group, in the macromolecules of the copolymer (c) in a plastic blend according to the invention may vary widely. It is however, advantageous if the
15 said repeating units (ii) are repeating units of an ethylenically unsaturated C₃-C₈ mono- or dicarboxylic acid or its derivative. Examples of usable C₃-C₈ monocarboxylic acids include acrylic acid, methacrylic acid and ethacrylic acid, and of usable C₃-C₈ monocarboxylic acid derivatives their esters such as methylacrylate, methylmethacrylate, ethylacrylate, ethylmethacrylate, methylethacrylate and ethyl-
20 ethacrylate. Other C₃-C₈ monocarboxylic acid derivatives which form repeating units (ii) include salts such as the zinc salt. Some of the said repeating units (ii) may contain carboxyl groups and some may contain carboxyl derivative groups. Also amide groups are possible.

- 25 In the macromolecules of the copolymer (c) of the plastic composition according to the invention, the C₂-C₆ alkylene repeating units (ii) which contain a carboxylic acid group or a carboxylic derivative group may also be repeating units of a C₃-C₈ dicarboxylic acid or its derivative. Typical usable C₃-C₈ dicarboxylic acids include maleic acid, fumaric acid, itaconic acid (methylene succinic acid), mesaconic acid
30 (methyl fumaric acid) and citraconic acid (methyl maleic acid). The said repeating units (ii) may also be based on C₃-C₈ dicarboxylic acid derivatives, such as esters and salts. According to one preferred embodiment, the said repeating units (ii) in the macromolecules of the copolymer (c) are C₃-C₈ dicarboxylic acid anhydrides, such as maleic acid anhydride or citraconic acid anhydride (methyl maleic acid anhy-
35 dride). One especially preferable C₂-C₆ alkylene repeating unit (ii) which contains a carboxyl group or a carboxyl derivative group is a repeating unit of maleic acid anhydride.

As stated above, a technical plastic composition according to the invention contains polyamide (a), ultra high molecular weight polyethylene (b) and a copolymer (c) having C₂-C₈ alkylene repeating units (i) and C₂-C₆ alkylene repeating units (ii) which contain a carboxyl group or a carboxyl derivative group. The said units (i) and (ii) in the macromolecules of the copolymer may be in any order in the macromolecule chains, and the macromolecule chains may also contain repeating units of other types. Thus the said copolymer (c) may be a random copolymer, an alternating copolymer, a sequential copolymer, a block copolymer, a graft copolymer, or any combination or blend of these copolymer types. It is advantageous if the macromolecules of the copolymer (c) comprise blocks, i.e. chain segments, having repeating units of the same type. Thus it is advantageous if the macromolecules of the copolymer (c) comprise a first block comprising the said C₂-C₈ alkylene repeating units (i) and a second block comprising the said C₂-C₆ alkylene repeating units (ii) which contain a carboxyl group or a carboxyl derivative group. By a "block" is meant a polymer molecule part, made up of several structural units, at least one structural feature of the part not being present in the adjacent parts (IUPAC, Compendium of Macromolecular Nomenclature, Blackwell, Oxford, 1991, p. 17).

It is also clear that the molecules of the said copolymer (c) may contain a plurality of the first and the second blocks, i.e. blocks having the said repeating units (i) and (ii). Furthermore, the blocks may be mutually in any order, i.e. they may be in any order in a linear or branched molecule.

According to one embodiment of the invention, the said copolymer (c) is a block copolymer having, arranged linearly in succession, one or several first blocks of the above-mentioned type having C₂-C₈ alkylene repeating units (i) and one or several second blocks of the above-mentioned type having C₂-C₆ alkylene repeating units (ii) which contain a carboxyl group or a carboxyl derivative group. It is presumed that a copolymer (c) such as this acts so that the said first block interacts with the molecules of the ultra high molecular weight polyethylene and the said second block interacts, or even reacts, with the polyamide, whereupon the ultra high molecular weight polyethylene is plasticized and in the plasticized state the ultra high molecular weight polyethylene disperses effectively and uniformly into the polyamide, and a usable plastic blend is formed.

According to another embodiment, the said copolymer (c) is a graft olefin copolymer in which one of the said first and second blocks of the macromolecules constitutes the principal chain (backbone) of the graft copolymer and the second one

a side chain (branch) linked to the backbone. This takes place preferably so that the first block, i.e. the block having C₂-C₈ alkylene repeating units (i), constitutes the backbone and the second block, i.e. the one having C₂-C₆ alkylene repeating units (ii) which contain a carboxyl group or a carboxyl derivative group, constitutes the
5 branch.

It is especially preferable that the said copolymer (c) is a graft olefin copolymer in the macromolecule of which the first block, i.e. the backbone, is made up of repeating units (i) of an olefin, preferably propylene, at least one other block, i.e.
10 branch, linked to its backbone, consisting of repeating units (ii) of an ethylenically unsaturated carboxylic acid or a derivative thereof, preferably maleic acid anhydride. The branch may also contain repeating units (ii) of ethylenically unsaturated carboxylic acids of various types. If the olefin is propylene and the carboxylic acid derivative is maleic acid anhydride, such a copolymer is called a
15 polypropylene grafted with maleic acid anhydride (PP-g-MA).

It is preferable that, in a graft olefin copolymer of the above-mentioned type, the proportion of repeating units (ii) of an ethylenically unsaturated carboxylic acid or a derivative thereof, such as maleic acid anhydride, is approximately 0.05-5%, more
20 preferably approximately 0.1-1%, most preferably approximately 0.2-0.6%, calculated as maleic acid anhydride, of the total weight of the olefin graft copolymer. It is thus seen that the copolymer (c) used in a technical plastic composition according to the invention does not need to contain more than a small quantity of C₂-C₆ alkylene repeating units which contain a carboxyl group or a carboxyl derivative group in
25 order for the copolymer to act well both as an agent improving the melt-processibility of the ultra high molecular weight polyethylene and as a compatibilizer of the polyamide and the ultra high molecular weight polyethylene.

The above discussion has dealt mainly with copolymers (c) in which the said first
30 and second blocks are of the homopolymeric type and which do not contain any units other than the said repeating units (i) and (ii). However, it is often advantageous to balance the interaction of the copolymer with the ultra high molecular weight polyethylene component and with the polyamide component by adding to the said blocks other repeating units, the interaction of which with the said polymer
35 components is not equally strong. Such modification can be achieved, for example, by copolymerizing into the copolymer C₂-C₆ alkenes which contain carboxyl derivatives and do not interact strongly with the polyamide. Such derivatives include carboxylic acid esters and salts. The copolymer (c) of the plastic composi-

tion may also be subjected to an external treatment, such as esterification and/or neutralization, in order to hinder some of the carboxyl groups and to modify interaction with the polyamide component.

- 5 Another method of modifying the copolymer (c) is to copolymerize into its first block, i.e. the block containing C₂-C₈ alkylene repeating units (i), unsaturated repeating units which are not in solvating interaction with the molecules of the ultra high molecular weight polyethylene. According to one preferred embodiment, the first block of the macromolecules in the said copolymer (c) is made up of linearly
10 arranged sub-blocks, some of which are made up of the said C₂-C₈ alkylene repeating units (i) and some are made up of C₈-C₁₀ aralkylene repeating units.

One preferred C₈-C₁₀ aralkylene repeating unit is a repeating unit of styrene. A typical first block is made up of, for example, a block-type chain segment of olefin
15 repeating units and styrene units, being part of either a block copolymer or a graft copolymer.

According to one embodiment, the said copolymer (c) is a grafted block copolymer, the first block, i.e. backbone, of its macromolecule being made up of linearly
20 arranged sub-blocks the sequence of which is: sub-block of styrene repeating units (iii) - sub-block of unsaturated aliphatic hydrocarbon repeating units, such as olefin repeating units (i) - sub-block of styrene repeating units (iii), and in which at least one other block, i.e. branch, linked to the backbone contains repeating units (ii) of maleic acid anhydride.

25 The proportion of the repeating units (ii) of maleic acid anhydride is preferably approximately 0.05-10%, more preferably approximately 0.5-5%, and most preferably approximately 1-3%, of the weight of the said grafted block olefin copolymer.

30 Copolymers (c) usable in a technical plastic composition according to the invention have been described above in detail. Their detailed description is due to the fact that it is possible to use as the copolymer highly varied polymers, all of which, however, have in common the property that they contain parts which interact strongly with the
35 ultra high molecular weight polyethylene component and the polyamide component, and even react with them. This has been indicated clearly in the above description. More structures of compatibilizing polymers usable in the invention are presented in

the work IUPAC Compendium of Macromolecular Nomenclature, Blackwell, Oxford, 1991, pp. 14-24.

5 A technical plastic blend according to the invention is the first technical plastic to contain polyamide 30-98.9% by weight. Polyamides are polymers which contain repeating amide groups as an integral part of the principal polymer chains. Linear polyamides are formed as condensation products of bifunctional monomers.

10 In reference to amino acid monomers, such as ϵ -caproic acid, or lactam monomers, such as ϵ -caprolactam, the polyamides are called AB-types, A indicating amine groups and B indicating carboxyl groups. If the polyamides are formed by the condensation of diamines and diacids, they are called AABB-types. The numerals in the names of polyamides indicate the number of carbon atoms in the diamine and the number of carbon atoms in the diacid when there are two numerals separated by
15 a comma, and the number of atoms in the amino acid or the corresponding lactam when there is only one numeral in the name.

The most important polyamides appearing in a technical plastic blend according to the invention are PA-6,6, the chemical name of which is
20 poly(hexamethylenediamine-co-adipic acid); PA-6, the chemical name of which is either poly(ϵ -aminocaproic acid) or poly(ϵ -caprolactam); PA-6,12, the chemical name of which is poly(hexamethylenediamine-co-dodecane diacid); PA-4, the chemical name of which is poly(2-pyrrolidone); PA-3, the chemical name of which is poly(β -propiolactam); PA-7, the chemical name of which is poly(ω -
25 enantolactam); PA-8, the chemical name of which is poly(capryl lactam); PA-11, the chemical name of which is poly(ω -aminoundecane acid); PA-12, the chemical name of which is poly(ω -dodecane lactam); PA-4,6, the chemical name of which is poly(tetramethylenediamine-co-adipic acid); and PA-4,2, the chemical name of which is poly(tetramethylenediamine-co-oxalic acid). Also possible may be certain
30 aliphatic-aromatic polyamides, such as PA-6,T, the chemical name of which is poly(hexamethylenediamine-co-terephthalic acid); PA-4,I, the chemical name of which is poly(tetramethylenediamine-co-isophthalic acid); PA-6,I, the chemical name of which is poly(hexamethylenediamine-co-isophthalic acid) and PACM-12, the chemical name of which is poly(bis[4-aminocyclohexyl]methane-co-dodecane
35 diacid). Purely aromatic polyamides are possible only in exceptional cases.

The most preferable polyamides to be used in a plastic blend according to the present invention are PA-6,6, i.e. poly(hexamethylenediamine-co-adipic acid), and

PA-6, i.e. poly(ϵ -caprolactam). A preferable amount of polyamide in a technical plastic blend according to the invention is approximately 40-96% by weight, and the most preferable is approximately 50-90% by weight.

- 5 The second component (b) of a technical plastic blend according to the invention is ultra high molecular weight polyethylene. Polyethylene is a polymer the macro-
molecules of which contain ethylene repeating units. Ultra high molecular weight
polyethylene (UHMWPE), for its part, is a high density polyethylene having a
molar mass above 3×10^6 . By its chemical structure it resembles high density
10 polyethylene, but the molar mass of a conventional high density polyethylene
seldom exceeds 50,000, whereas according to ASTM definitions the molar mass of
an ultra high molecular polyethylene is at least approximately 3×10^6 . According to
ASTM D 4020 it may be as high as 6×10^6 .
- 15 The long molecule chains of ultra high molecular weight polyethylene provide the
following unique combination of properties: its wear resistance is higher than that of
any other thermoplastic; its impact strength is higher than that of any other plastic,
also at low temperatures; it has high corrosion resistance properties and an excellent
resistance to stress-cracking caused by the environment; it has a high resistance to
20 fatigue caused by repeated loading; it attenuates sound and impacts well; its surface
friction coefficient is low; its surface is not sticky; and it resists radiation well.

It is thus clear that the use of ultra high molecular weight polyethylene as a techni-
cal plastic is extremely desirable and that each improvement which increases its
25 usability in technical plastic blends satisfies the need for a technical plastic which
has long prevailed in the field.

However, ultra high molecular weight polyethylene has the disadvantage that it
cannot be melt processed into, for example, machine elements in the manner of
30 conventional thermoplastics. Thus, it has so far been regarded as impossible to
process ultra high molecular weight polyethylene in the molten state by, for
example, injection molding, blow molding, thermoforming or extrusion. Long
molecule chains render ultra high molecular weight polyethylene non-melting and
non-flowing. It has so far been processible only by means of extreme pressure,
35 which consumes energy, limits its uses and limits the shape of the final parts.

The copolymer component (c) of the technical plastic blend according to the inven-
tion has the surprising property that it both compatibilizes polyamide and ultra high

molecular weight polyethylene and acts as a processing auxiliary for ultra high molecular weight polyethylene so that the ultra high molecular weight polyethylene will be melt processible and in fact will form smaller-than-original particles dispersed in the polyamide. Owing to this effective and uniform dispersion, the technical plastic blend formed has the best properties of polyamide and ultra high molecular weight polyethylene, i.e. the blend is clearly synergetic. The proportion of ultra high molecular weight polyethylene (c) in a plastic blend according to the invention is preferably approximately 1.5-52% by weight, and most preferably approximately 2-40% by weight.

10

Since what is in question is a technical plastic blend which can be used for highly varied purposes, other additives (d) known in the art can, of course, be added to it, such as fillers, plasticizers, lubricants, stabilizers, anti-combustion agents, colorants, foaming agents, bridging agents, and UV-shield agents. It is especially preferable to add to a technical plastic blend according to the invention reinforcing additives, such as reinforcement fiber such as carbon and glassfiber; metal powder; glass beads; pigment; rubber powder; and other polymers and compatibilizers or auxiliary compatibilizers. A typical reinforcing fiber is glassfiber, the amount of which in the blend may be approximately 5-40% by weight, and most preferably approximately 10-30% by weight. Advantageously it is possible to add additives which are known to reduce friction, such as polytetrafluoroethylene, molybdenum disulfide or silicon oil.

Since the novelty and usefulness of the plastic blend according to the invention is due to the fact that, deviating from the previous, the ultra high molecular weight polyethylene is easily melt-processible, the invention also relates to a process in which a plastic blend is prepared by melt processing the said polyamide (a), the said ultra high molecular weight polyethylene (b) and the said copolymer (c) in such a manner that all of the components (a), (b) and (c) are in the soft state. This is preferably done so that shear forces typical of melt processing are used at the melt processing temperature of the said polyamide, which is preferably within a range of approximately 200-300 °C. The process according to the invention is otherwise characterized in what is stated above in connection with the description of the technical plastic blend.

35

In a technical plastic blend according to the invention, also its morphology is novel and advantageous, since so far the blends of polyamide and ultra high molecular weight polyethylene have always been such that the ultra high molecular weight

polyethylene is distributed in the polyamide as particles similar to those in the form of which it was when it was added to the polyamide.

5 By means of the copolymer (c) according to the invention, the ultra high molecular weight polyethylene is divided into smaller drops, which are equal in size and disperse very uniformly into the polyamide (cf. examples). The morphology of a technical plastic blend according to the invention is thus preferably such that in the polyamide (a) there are dispersed ultra high molecular weight polyethylene (b) particles having a size of approximately 1-10 μm .

10

Since the present invention relates to a technical plastic blend, it also relates to the use of such a plastic blend for machine parts, such as moving parts, bearings, structural machine elements, slide, friction and wear surfaces, soles of socks, etc.

15 The invention is illustrated below with embodiment examples and experiments, in which reference is made to the following figures:

Figure 1 depicts an SEM micrograph of the fracture surface of a non-compatibilized PA-6/UHMWPE blend, enlarged a) (graph 0060) 500 x and b) (graph 0059) 5000 x;
20

Figure 2 depicts an SEM micrograph of the fracture surface of a CI-compatibilized PA-6/UHMWPE blend, enlarged a) (0063) 500 x and b) (0034) 5000 x;

Figure 3 depicts an electron micrograph of the surface a CII-compatibilized
25 PA-6/UHMWPE blend, enlarged a) (0074) 500 x and b) (0017) 5000 x;

Figure 4 depicts an SEM micrograph of the surface of a CII-compatibilized PA-6,6/UHMWPE blend, enlarged a) (0070) 500 x and b) (0024) 5000 x;

30 Figure 5 depicts the dependence of the tensile modulus of non-compatibilized and compatibilized PA-6/UHMWPE and PA-6,6/UHMWPE blends on the percentage of UHMWPE in the blend;

35 Figure 6 depicts the dependence of the tensile strength of the blends of Figure 5 on the percentage of UHMWPE;

Figure 7 depicts the dependence of the notched impact strength of the blends of Figure 5 on the percentage of UHMWPE;

Figure 8 depicts the friction coefficients of PA, UHMWPE and PA/UHMWPE blends at a pressure of 1 MPa and a velocity of 0.38 m/s;

5 Figure 9 depicts the wear of PA, UHMWPE and PA/UHMWPE blends at a pressure of 1 MPa and a velocity of 0.38 m/s;

Figure 10 depicts the effect of the percentage of UHMWPE on the friction coefficients of PA/UHMWPE blends at a pressure of 1 MPa and a velocity of 0.38 m/s;

10 Figure 11 depicts the effect of the percentage of UHMWPE on the wear of PA/UHMWPE blends at a pressure of 1 MPa and a velocity of 0.38 m/s;

Figure 12 depicts the effects of composition and sliding velocity on the friction coefficients of PA/UHMWPE blends at a pressure of 1 MPa;

15

Figure 13 depicts the effects of composition and sliding velocity on the wear of PA/UHMWPE blends at a pressure of 1 MPa;

20 Figure 14 depicts the friction coefficients of PA/UHMWPE blends at different sliding velocities at a pressure of 1 MPa;

Figure 15 depicts the specific wear rates of PA/UHMWPE blends at different sliding velocities at a pressure of 1 MPa;

25 Figure 16 depicts the friction coefficients of PA/UHMWPE blends at different contact pressures at a velocity of 0.76 m/s;

Figure 17 depicts the specific wear rates of different PA/UHMWPE blends at different contact pressures at a velocity of 0.76 m/s;

30

Figure 18 (0013) depicts an electron micrograph of the worn surface of the test specimen, the wear time being 6 h, the contact pressure 1 MPa, and the velocity of the contact piece 0.38 m/s for specimen N6U (75X);

35 Figure 19 (0023) depicts an electron micrograph of the worn surface of the specimen, the wear time being 6 h, the contact pressure 1 MPa and the velocity of the testing member 0.38 m/s for specimen N6GU (75X);

Figure 20 (0033) depicts an electron micrograph of the worn surface of the specimen, the wear time being 6 h, the contact pressure 1 MPa and the velocity of the testing member 0.38 m/s for specimen N66U (75X);

- 5 Figure 21 (0043) depicts an electron micrograph of the worn surface of the test specimen, the testing time being 6 h, the contact pressure 1 MPa and the velocity of the testing member 0.38 m/s for specimen N66GU (75X).

Examples

10

Materials

The commercial polymer grades used in the examples were as follows:

- 15 (i) BASF ULTRAMIDE PA-6 in binary blends and ICI MARANYL B 114 PA-6 in ternary blends and (ii) ICI MARANYL A 231 PA-6,6 in ternary blends and (iii) Beijing No. 2 Auxiliary Agent Factory M-3 UHMWPE in all blends. Although the PA-6's were different in the binary and the ternary blends, they were comparable to each other, with the exception of elongation at break results.

20

The compatibilizers used were two types of compatibilizers, Exxelor PO 2011 (Exxon) and Kraton X-n 731n (Shell), the first of which, i.e CI, is a polypropylene grafted with 0.4% by weight of maleic anhydride and CII is a triblock copolymer consisting of polystyrene end blocks and polyolefin midblocks and being grafted
25 with 2% by weight of maleic anhydride.

Blending

Before the blending, the polyamide was dried for 16 h at 80 °C. The blending was
30 carried out using a Berstorff ZE 25x33 D double-screw extruder, the operating rotation speed of which was 135 rpm. The temperature was 220-240 °C for PA-6/UHMWPE blends and 250-270 °C for PA-6,6/UHMWPE blends. Blends having PA contents ranging from 55 to 91.1% by weight and UHMWPE contents ranging from 2.9 to 40% by weight were prepared. The compatibilizer content of the
35 ternary blends was maintained constant, at 5% by weight. The extrudates were cooled in water, pelleted, and dried for 16 h at 80 °C. Eventually the dried pellets were injection molded to test specimens. For this purpose, an Arburg 250-275

injection molding machine was used, its temperature being 240-250 °C for PA-6/UHMWPE blends and 270-280 °C for PA-6,6/UHMWPE blends.

Blend characterization

5

The blends were characterized systematically by mechanical, microscopic and thermal analysis. All of the test specimens were conditioned for 3 days in a conditioning room having a temperature of 22 °C and a relative humidity of 50% before the mechanical testing. At least 5 test specimens were tested in order to calculate a mean, and the standard deviation was typically less than ± 10 . The tensile tests were conducted using an Alwetron TYP F5000 testing apparatus according to the standard ISO R 527, by using a drawing speed of 50 mm/min. From the tensile elongation data, the tensile modulus, the tension corresponding to the maximum load, and the maximum elongation percentage were calculated. The Charpy notched impact strength tests were performed using a Ceast Impact Tester in accordance with the standard ISO 179/2B. The morphology of the blend was analyzed using a scanning electron microscope (SEM) JEOL JSM-T100 having a voltage of 15 kV. The specimens were prepared by breaking cast pieces at the temperature of liquid nitrogen and by then coating the fracture surfaces with gold in order to prevent charging under the electron beam.

The thermal analysis was carried out in a nitrogen atmosphere by using a Perkin Elmer DSC-2 differential scanning calorimeter. The temperature was raised from 320 to 580 K at a rate of 20 K/min and was allowed to cool at the same rate. The heating and cooling thermograms were recorded. Crystallization was investigated from the cooling curves.

Results

30 Compatibilization

PA and UHMWPE are usually incompatible and segregate into two separate phases. The interfacial tension between the phases can be reduced by means of polyolefins grafted with maleic anhydride, such as the compatibilizers CI and CII used in the tests. In them the favorable interaction between the UHMWPE and the compatibilizer is based on interaction between the olefin blocks. The favorable interaction between the polyamide and the compatibilizer is probably based on a chemical

reaction between the amino end group of the polyamide and the anhydride group of the compatibilizer.

5 The activity of compatibilizers CI and CII according to the invention was tested by using Molau's test. Cf. Molau, G.E., J. Polym. Sci. (A) 3 (1965) 4235. It was observed that, when pure formic acid was added to a PA/UHMWPE blend not containing the said compatibilizers, the PA component dissolved completely in 2-4 h, whereas UHMWPE precipitated in the form of white flakes. When the same test was performed on a PA/UHMWPE blend containing either compatibilizer CI or 10 CII, a very stable colloidal suspension was obtained. This result indicates that the copolymer compatibilizer present in the PA/UHMWPE blend acted as an effective interfacial agent. Below, non-compatibilized PA/UHMWPE blends are compared with compatibilized PA/UHMWPE blends by measuring their morphology, thermal behavior, and mechanical properties.

15

Morphology

Typical morphologies of PA/UHMWPE blends (UHMWPE: 20-30% by weight) are depicted in Figures 1-4 a,b. In non-compatibilized PA/UHMWPE blends (cf. Figure 20 1 a,b) the PA phase forms the matrix and the UHMWPE phase is segregated as spherical domains. The particle size of the dispersed phase ranges from 5 to 100 μm , the distribution of the dispersed phase thus being very wide. No morphological evidence of adhesion at the interface between the dispersed phase and the matrix is visible. When the dispersed phase is detached from the matrix, smooth 25 traces are left on the matrix surface. This suggests that there are no major adhesive forces between the components and that they are mutually incompatible.

The morphology of compatibilized PA/UHMWPE blends is completely different (cf. Figures 2-4, a,b). The average particle size of the dispersed phase is 5-10 times 30 reduced and ranges from 1-10 μm when a compatibilizer, CI or CII, has been added to the PA/UHMWPE blends. Since UHMWPE is usually non-fusible at the temperatures used, this means that each compatibilizer works, surprisingly, also as a processing auxiliary and enables UHMWPE to become plasticized and dispersed as smaller particles. Of the compatibilizers tested, CII seems to be more effective than 35 CI, because CII yields a structure indicating higher dispersion than does CI. Dispersion is also more uniform, and when the phases are separated from each other, rougher traces are left in the polyamide matrix, indicating stronger adhesion between the phases.

When the compatibilizer CII is used, there even form small fibrils when the phases are separated, which means that the adhesion is so great that the polyamide yields when the phases are being separated.

5 Mechanical properties

The results of the mechanical testing of binary and compatibilized blends are shown in Figures 5-7. Figures 5 and 6 show the corresponding tensile moduli and tensile strengths as a function of the composition. It is seen that the tensile moduli and
10 tensile strengths of all of the PA/UHMWPE blends were lower than those of pure PA. All of the values indicate an even reduction as the UHMWPE concentration increases. An exception to this consists of PA-6/UHMWPE blends with compatibilizer, in which the tensile modulus decreases slowly at lower UHMWPE concentrations (0-10% by weight).

15

Figure 7 shows the notched impact strength of the blends as a function of the composition. It is seen that the effect of the compatibilizers on impact strength is more significant. The effect is dependent on the type and proportion of the blend components.

20

The brittleness of the binary blends is striking as compared with the UHMWPE or PA components. When 5% by weight of compatibilizer CII was added to PH-6/UHMWPE blends, a dramatic increase in the notched impact strength occurred at high UHMWPE concentrations (20% by weight). The improvement in
25 the impact strengths of PA-6,6/UHMWPE blends was not as significant as that of PA-6/UHMWPE blends when the compatibilizer CII was used. However, both PA-6/UHMWPE and PA-6,6/UHMWPE blends which have UHMWPE concentrations above 20% by weight and which contain 5% by weight of CII compatibilizer have even higher notched impact strengths than has pure PA. In contrast, CI
30 compatibilizer does not improve the notched impact strength.

Thermal behavior

DSC thermograms of non-compatibilized and compatibilized blends of polyamide
35 and UHMWPE show that the melting points of the polyamide components do not change in the blend, whereas the melting point of the UHMWPE component drops somewhat when compatibilizers CI and CII are used. This means that the

UHMWPE component melts more readily when it is in interaction with the said compatibilizers.

As judged from the DSC thermograms, a compatibilizer, i.e. copolymer (c), thus improves the melt processibility of ultra high molecular weight polyethylene.

The above mechanical properties of the blends are compiled in Table 1.

Table 1

Property	UHMWPE	PA-6	PA-6,6	PA-6+ 30% UHMWPE	PA-6,6+ 20% UHMWPE	PA-6+ 22.2% UHMWPE + 22.2% glassfiber	PA-6,6+ 14.6% UHMWPE + 26.8% glassfiber
Specimen code	U	N6	N66	N6U	N66U	N6GU	N66GU
Density ISO R1183 g/cm ³	0.928	1.135	1.134	1.056	1.082	1.214	1.259
Hardness ISO868 Shore D	65.2	72.9	74.5	71.8	72.4	73.7	75.2
Tensile strength ISO R527 MPa	21	68	67	31	43	53	83
Tensile modulus ISO R527 X10 ³ MPa	0.71	2.18	2.61	1.30	1.61	3.46	4.62
Elongation at break ISO R527 %	76	25	30	35	25	1.4	4.9
Impact strength (notched) ISO 179/26 KJ/m ²	no fracture	7.4	6.6	7.6	6.6	6.1	8.7

Example

- Test bars the dimensions of which were 110x10x4 mm³ were dried for 3 d at 80 °C, and thereafter their moisture absorption was measured by immersing them for 24 h in distilled water at room temperature. The following water absorption results for the various specimens were obtained:

Table 4

- 10 Water absorption of samples (23 °C, 24 h)

Specimen	Water absorption %		
UHMWPE	0.2	N66	6.7
N6	6.1	N66U(20)CII	2.7
N6U(30)CII	3.5	N666U(20)CII	2.0
N66U(30)CII	3.6		

- According to the results, the decrease in water absorption was in the case of N6U(30)CII 19%, N66U(30)CII 17%, N66U(20)CII 50%, and N666U(20)CII 63%, as compared with a blend of PA and UHMWPE in which the polymers have no interaction with each other.

Tribological properties

- 20 The tribological properties, i.e. wear properties, of PA-6/UHMWPE blends were also investigated; approximately 25% of glassfiber had been added to some bars.

Materials

- 25 Cylindrical pins having contact diameters of 3.5, 7.0 and 10.0 mm were cut out from castings of the said polymer blends. At the same time such test pins were also prepared from pure PA, pure UHMWPE, and non-compatibilized PA/UHMWPE blends. A cylindrical steel disc having a surface roughness $R_a = 0.1 \mu\text{m}$ was selected as the counterpiece.

Testing

Friction, wear and PV-limit tests were carried out with a pin-on-disc tribometer having a horizontal rotating disc. The rotation diameter of the test pin against the disc was 58 ± 1 mm. The plastic pin to be tested was loaded with weights at the end of a lever arm. Before the test, the test pins and the steel disc were cleaned carefully with alcohol. All of the tests were conducted in a conditioned room having a temperature of 20 °C and a relative humidity of 50%, without using an external lubricant. The specimens were kept in the same room during the testing.

Several sliding velocities and contact pressures were selected for the test. A 6 h running-in time was set for the measurement. During this time the friction force seemed to level off at a constant value and the wear $_h$ of the test pin was measurable with a precision of a micron. The pin was also weighed in order to obtain wear data for the specific wear rate K. The K-values are calculated from the sliding distances, the applied loads F, and the volume loss V (by using the density of the material), in which case it is calculated in the following manner:

$$K = V/FS$$

To determine the PV limit for a blend, at least three contact pressures P were selected in order to cover the practical pressure range, e.g. 1, 2 and 8 MPa. A velocity-stepping test was performed at each pressure. The friction torque, which was plotted continuously, was allowed to reach an equilibrium at each velocity. At higher speeds the friction torque no longer stabilized and/or it increased rapidly; this resulted in the failure of the material. The velocity limits at several contact pressures can thus be used for determining the PV limit values for a material.

In order to investigate the probable wear mechanism of the plastic blends tested, the worn surfaces were examined with a scanning electron microscope (SEM), JEOL TSM-T100, operated at 25 kV. Before the examination, the specimens were coated with gold in order to avoid charging and damage under the electron beam.

Effect of composition

Figures 8 and 9 show the coefficient of friction and the wear for each material, measured at a contact pressure of 1 MPa and a sliding velocity of 0.38 m/s. The measuring of the friction force of pure PA-6 was difficult owing to its high value

and instability as compared with the other materials in these testing conditions. PA-6,6 had a lower friction and a higher wear than had pure PA-6. Pure UHMWPE had a much lower coefficient of friction and wear rate than had PA-6 and PA-6,6 in the same testing conditions.

5

The addition of UHMWPE to both PA-6 and PA-6,6 results in a considerable decrease in the coefficients of friction and the wear rates (cf. Figures 10 and 11). The coefficient of friction and wear for PA-6,6/UHMWPE blends decrease rapidly with small amounts of UHMWPE (approximately 10% by weight). Larger
10 additions have very little improving effect on tribological behavior. Approximately 20-30% by weight of UHMWPE in PA-6/UHMWPE blends leads to a dramatic drop in the coefficient of friction and a corresponding improvement in the wear rate.

The incorporation of a compatibilizer into PA/UHMWPE blends emphasizes these
15 favorable effects. Compatibilized blends based on homogeneity and strong interfacial adhesion between the two polymer phases exhibit a better tribological behavior than do blends obtained by blending UHMWPE with molten polyamide PA.

PA-6,6/UHMWPE blends had lower coefficients of friction and higher wear rates
20 than had PA-6/UHMWPE blends.

The same specimens were also tested by using compatibilized PA-6/UHMWPE blends having UHMWPE concentrations of 20% by weight N6U (20) and 30% by weight N6U (30) and compatibilized PA-6,6/UHMWPE blends having a UHMWPE
25 concentration of 20% by weight N66U (20), in order to investigate the effect of higher sliding velocities on tribological properties (Figures 12 and 13). The velocity was raised from 0.38 m/s to 1.0 m/s. All of the tests were conducted at a constant contact pressure and with the same running-in time (6 h).

30 Increasing the sliding velocity from 0.38 m/s to 1.0 m/s did not cause any essential change in the coefficients of friction or wear of specimens N6U (30) and N66U (20). However, a dramatic change occurred in specimen N6U (20) when the sliding velocity was increased from 0.76 m/s to 1,0 m/s. The friction increased rapidly, resulting in the melting of the surface.

35

It can also be seen that the glassfiber-reinforced PA/UHMWPE blends had lower wear rates than the unreinforced blends at $P = 1$ MPa and $V = 0.38$ m/s (Figure 9). The glassfiber addition also led to a considerable increase in the friction force in the

test conditions (Figure 8). The type of the PA did not affect greatly the friction or wear of the glassfiber-reinforced blends.

Effects of sliding velocity and contact pressure

5

The coefficients of friction and wear of pure UHMWPE and of compatibilized PA/UHMWPE blends were also determined at various sliding velocities and contact pressures. Figures 14 and 15 show the effect of the sliding velocity on the coefficients of friction and wear.

10

For the PA/UHMWPE blends tested, no major change in friction and wear was observed as the sliding velocity changed.

15

Figures 16 and 17 show the effect of contact pressure on the coefficients of friction and wear. The result was that the coefficient of friction somewhat decreased and the coefficient of wear somewhat increased as the contact pressure increased.

PV limit

20 Polymers have a PV limit, wherein P is the mean contact pressure and V is the sliding velocity. Above this limit the temperature rises so that the surface melts and the wear rate increases to a very high value. The highest PV value used in the tests was 12 MPa•m/s, and it was reached with the highest contact pressure P value 8 MPa and the highest sliding velocity V value 1.5 m/s on the said tribometer. The
25 PV-limit values for these materials are shown in Table 2.

Table 2

30 PV-limit values obtained using a pin-on-disc tribometer and testing PA, UHMWPE, non-compatibilized PA/UHMWPE blends and compatibilized PA/UHMWPE blends.

Materials	N6	UHMWPE	N6U	N6GU	N66U	N66GU
P at failure, MPa	1	>8	8	>8	>8	>8
V at failure, m/s	0.38	>1.5	1.3	>1.5	>1.5	>1.5
PV limit, MPa•m/s	0.38	>12	10.4	>12	>12	>12

With the exception of the unreinforced PA-6/UHMWPE blend (N6U), the PV limits of all other compatibilized PA/UHMWPE blends were clearly above 12 MPa•m/s. These values are clearly above the PV limits reported in the literature for polymer sliding materials.

5

Micrographs of worn surfaces

Electron micrographs, shown in Figures 18-21, were taken of the worn surfaces of the pins. On the basis of these micrographs it was noted that there were no signs of
10 any glassfiber debonding or pull-out in the materials according to the invention; this indicates high adhesion between the fiber and the matrix.

Compared to the situation described in the literature, in which UHMWPE was used as a filler in PA-6,6, without a compatibilizer, the blends according to the present
15 invention did not exhibit the deformation noted in the literature nor the spreading of the UHMWPE on the composite surface. Thus, the blend according to the invention is clearly superior to the blends described in the literature.

Conclusions from the tribological investigation

20

The results of the tribological investigation revealed, among other things, the following:

Compatibilized PA/UHMWPE blends based on homogeneity and strong interfacial
25 adhesion have clearly better tribological properties than have non-compatibilized blends.

The addition of UHMWPE to both PA-6 and PA-6,6 leads to a considerable decrease in the coefficient of wear and in the wear rate.

30

The strength of glassfiber-reinforced PA/UHMWPE blends is higher than that of unreinforced blends. On the other hand, the addition of glassfiber increases the friction force considerably in the test conditions described.

35 It is surprising that the compatibilized PA/UHMWPE blends not only have lower coefficients of friction but they also have a better velocity dependence of friction than does pure UHMWPE within the entire range examined.

Electron micrographs of the compatibilized PA/UHMWPE blends show that interfacial adhesion between PA and UHMWPE is greater than it is without a compatibilizer.

Claims

1. A technical plastic composition which comprises
 - a) 50-90% by weight of polyamide, and
 - 5 b) approximately 2-40% by weight of ultra high molecular weight polyethylene, **characterized** in that it comprises in the ultra high molecular weight polyethylene, as a component improving the compatibility between the polyamide and the ultra high molecular weight polyethylene and melt processibility:
 - c) approximately 0.1-30% by weight of a copolymer the macromolecules of
 - 10 which comprise:
 - i) C₂-C₈ alkylene repeating units,
 - ii) C₂-C₆ alkylene repeating units which contain a carboxyl group or a carboxyl derivative group, and, preferably,
 - iii) C₈-C₁₀ aralkylene repeating units such as styrene units.
 - 15
2. A plastic composition according to Claim 1, **characterized** in that it comprises approximately 1-15% by weight, preferably approximately 2-10% by weight, and most preferably approximately 3-8% by weight, of the said copolymer (c).
- 20 3. A plastic composition according to Claim 1 or 2, **characterized** in that the C₂-C₈ alkylene units (i) in the macromolecules of the said copolymer (c) are repeating units of a C₂-C₆ olefin, most preferably repeating units of a C₂-C₃ olefin, i.e. repeating units of ethylene or propylene.
- 25 4. A plastic composition according to Claim 1, 2 or 3, **characterized** in that the C₂-C₆ alkylene repeating units (ii) which contain a carboxyl group or a carboxyl derivative group in the macromolecules of the said copolymer (c) are repeating units of an ethylenically unsaturated C₃-C₈ mono- or dicarboxylic acid or of a derivative thereof, preferably repeating units of maleic acid anhydride.
- 30
5. A plastic composition according to any of the above claims, **characterized** in that the macromolecules of the said copolymer (c) comprise a first block, which comprises the said C₂-C₈ alkylene repeating units (i), and a second block, which comprises the said C₂-C₆ alkylene repeating units (ii) which contain a carboxyl
- 35 group or a carboxyl derivative group.
6. A plastic composition according to Claim 5, **characterized** in that the said copolymer is a graft copolymer in the macromolecules of which one of the said first

and second blocks constitutes the backbone of the graft copolymer and the other a branch linked to the backbone, preferably so that the first block constitutes the backbone and the second block constitutes the branch.

5 7. A plastic composition according to Claim 6, **characterized** in that the said
copolymer (c) is a graft olefin copolymer in the macromolecule of which the first
block, i.e. the backbone, consists of repeating units (i) of an olefin, preferably
propylene, and at least one other block, i.e. branch, linked to the backbone
comprises repeating units (ii) of an ethylenically unsaturated carboxylic acid or a
10 derivative thereof, preferably maleic acid anhydride, the proportion of the repeating
units (ii) of the ethylenically unsaturated carboxylic acid or the derivative thereof
being preferably approximately 0.05-5%, more preferably approximately 0.1-1%,
most preferably approximately 0.2-0.6%, calculated as maleic acid anhydride, of the
weight of the graft olefin copolymer.

15

8. A plastic composition according to Claim 5 or 6, **characterized** in that the first
block in the macromolecules of the said copolymer (c) consists of linearly arranged
sub-blocks, some of which consist of the said C₂-C₈ alkylene repeating units (i) and
some consist of C₈-C₁₀ aralkylene repeating units (iii), preferably repeating units of
20 styrene.

9. A plastic composition according to any of Claims 6-8, **characterized** in that
the said copolymer (c) is a grafted block olefin copolymer in the macromolecule of
which the first block, i.e. backbone, consists of linearly arranged sub-blocks the
25 sequence of which is: sub-block of styrene repeating units (iii) - sub-block of
unsaturated aliphatic hydrocarbon repeating units (i), such as olefin repeating units -
sub-block of styrene repeating units (iii), and in which at least one other block, i.e.
branch, linked to the backbone contains repeating units (ii) of maleic acid anhy-
dride, the proportion of the repeating units (ii) of maleic acid anhydride being
30 preferably approximately 0.05-10%, more preferably approximately 0.5-5%, most
preferably approximately 1-3%, of the weight of the said grafted block olefin
copolymer.

10. A plastic composition according to any of the above claims, **characterized** in
35 that it comprises a polyamide (a) or any blend thereof, the polyamide (a) being a
polymerization product of a C₆ diamine and a C₆-C₁₂ diacid, preferably PA6,6, or a
polymerization product of a C₃, C₄ or C₆-C₁₂ amino acid or a derivative thereof,
preferably PA6.

11. A plastic composition according to any of the above claims, **characterized** in that it comprises ultra high molecular polyethylene (b) or a blend thereof, the weight average molar mass of the ultra high molecular weight polyethylene (b) ranging
5 approximately from 3×10^6 to 6×10^6 .

12. A plastic composition according to any of the above claims, **characterized** in that it comprises:

d) an additive, which additive (d) is selected from among the following: reinforcing fiber such as carbon fiber or glassfiber; metal powder; glass beads; pigment;
10 rubber powder; other polymers and other compatibilizers or auxiliary compatibilizers, preferably glassfiber, more preferably approximately 5-40% by weight and most preferably approximately 10-30% by weight of glassfiber, or friction-reducing additives, e.g. polytetrafluoroethylene, molybdenum sulfide, or silicon oil.

15

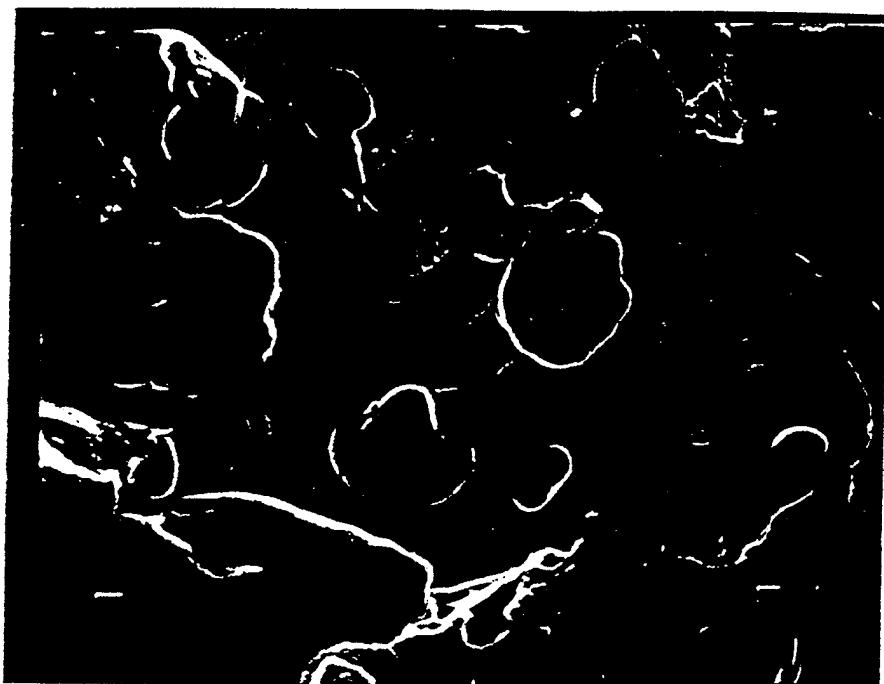
13. A plastic composition according to any of the above claims, **characterized** in that it is prepared by melt processing the said polyamide (a), the said ultra high molecular weight polyethylene (b) and the said copolymer (c) so that all of the components (a), (b) and (c) are in the soft state, preferably by using shear forces at
20 the melt processing temperature of the said polyamide, which is preferably within a range of approximately 200 - 300 °C.

14. A plastic composition according to any of the above claims, **characterized** in that it has such a morphology that there are, dispersed in the polyamide (a), particles
25 of the ultra high molecular weight polyethylene (b) having a size of approximately 1-10 μm .

15. The use of a plastic composition according to any of the above claims for machine parts, such as moving parts, bearings, structural machine elements, slide,
30 friction and wear surfaces, ski bottoms, etc.

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a)



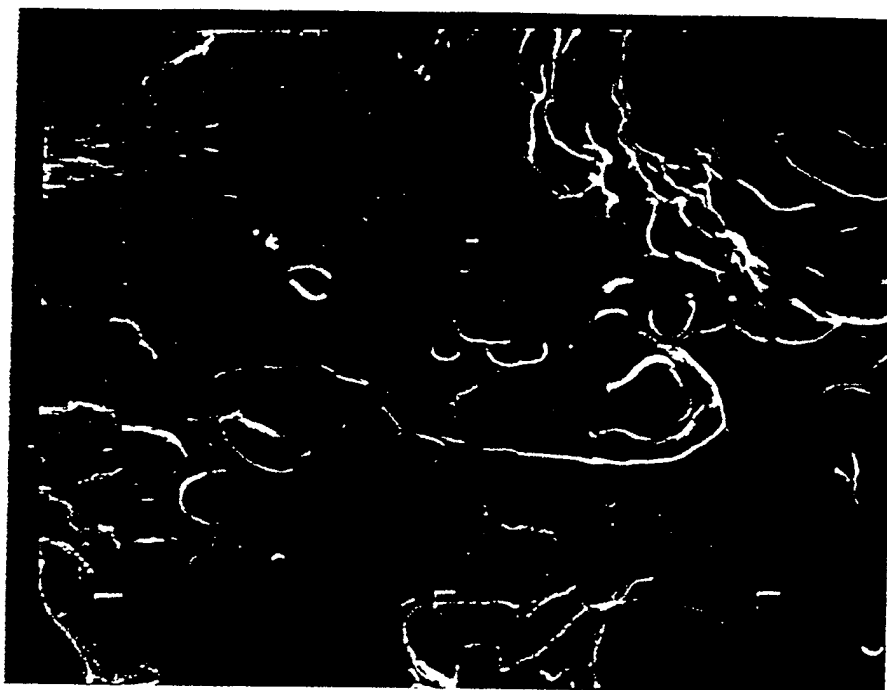
b)

**Figure 1**

SEM micrograph of the fracture surface of a non-compatibilized PA-6/UHMWPE blend, enlarged a) (graph 0060) 500 times and b) (graph 0059) 5000 times.

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a)



b)

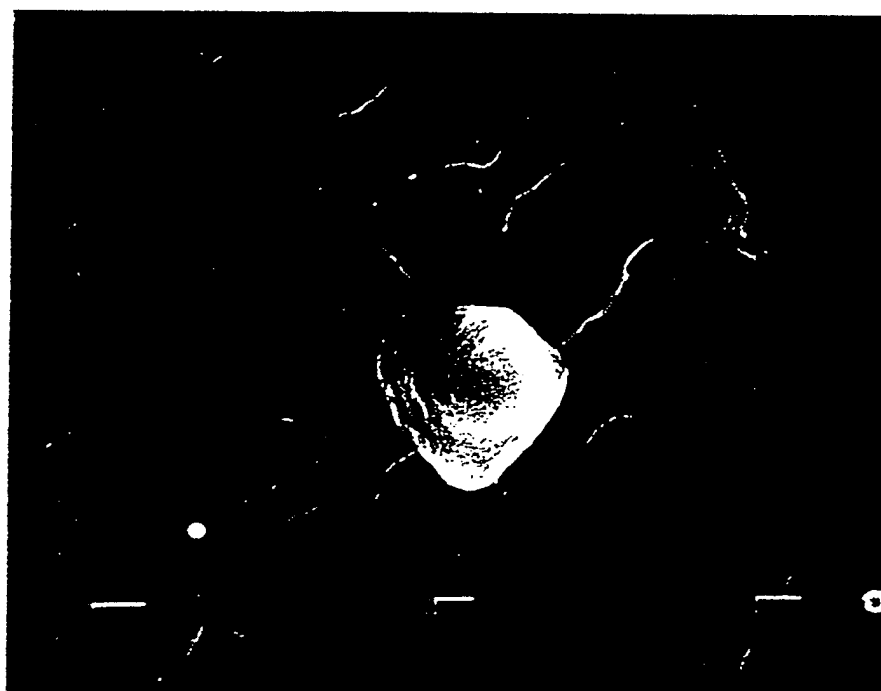
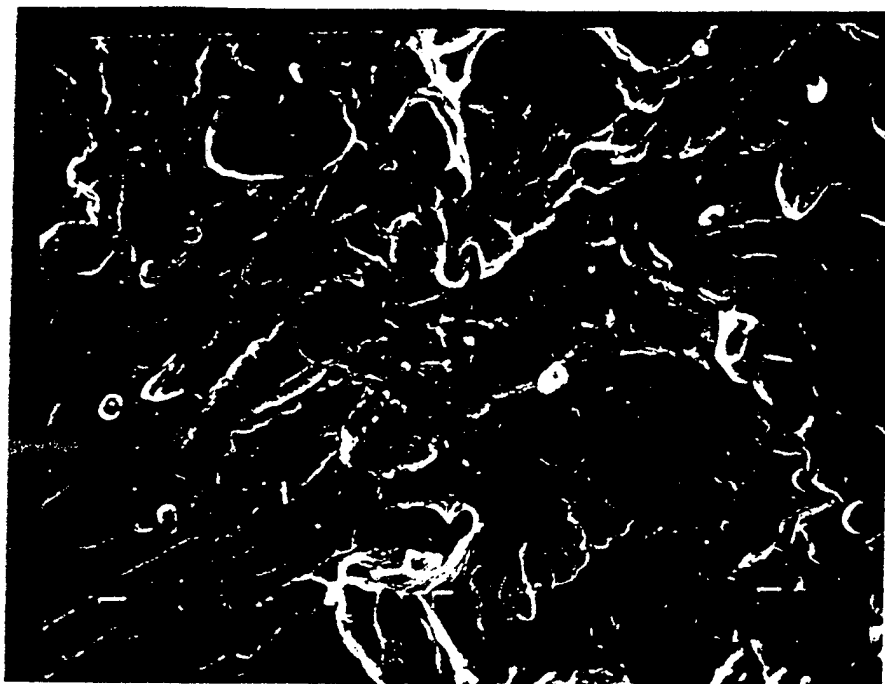


Figure 2

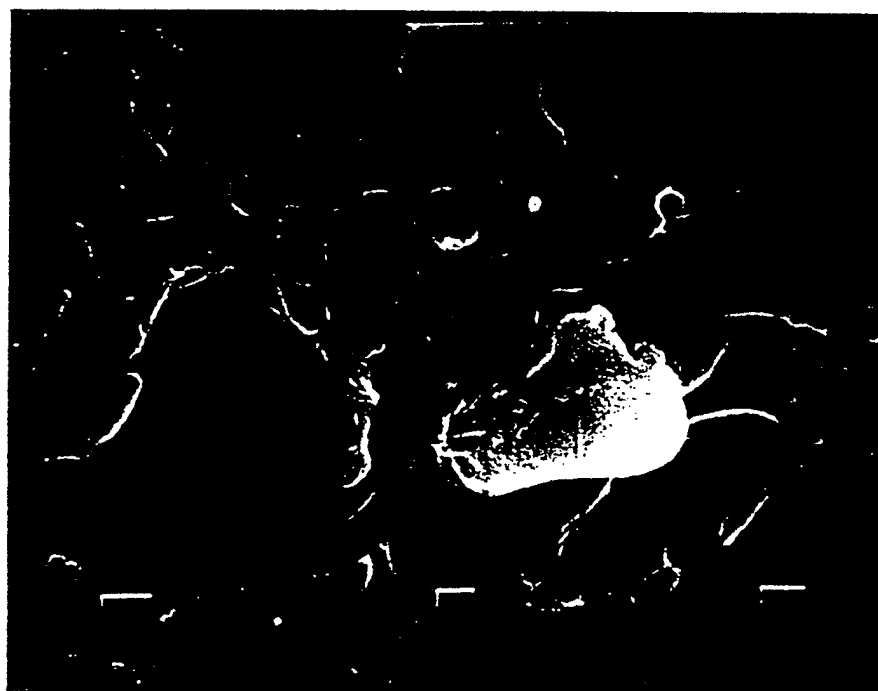
SEM micrograph of the fracture surface of a CI-compatible PA-6/UHMWPE blend, enlarged a) (0063) 500 times and b) (0034) 5000 times.

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a)



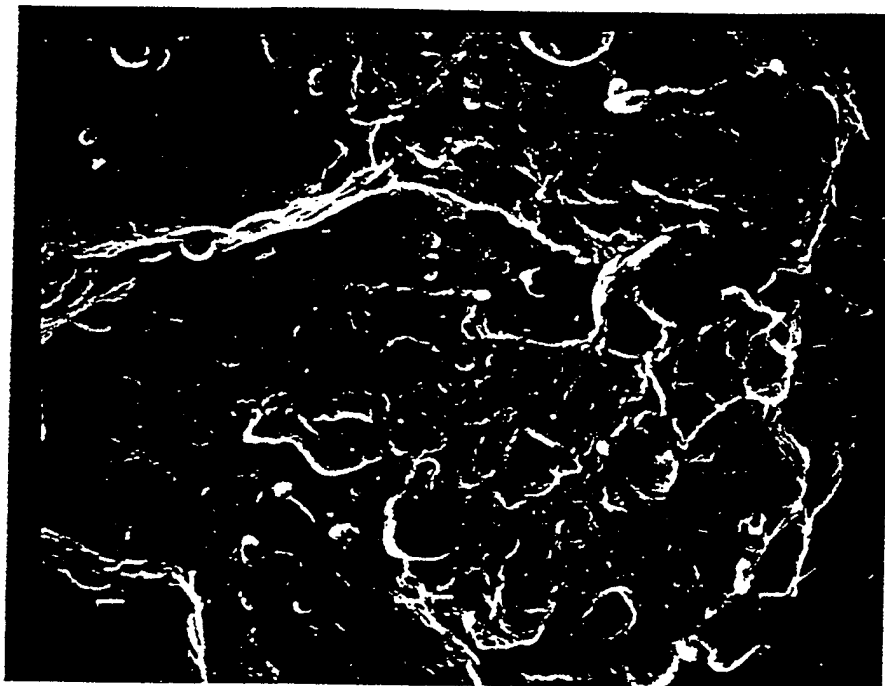
b)

**Figure 3**

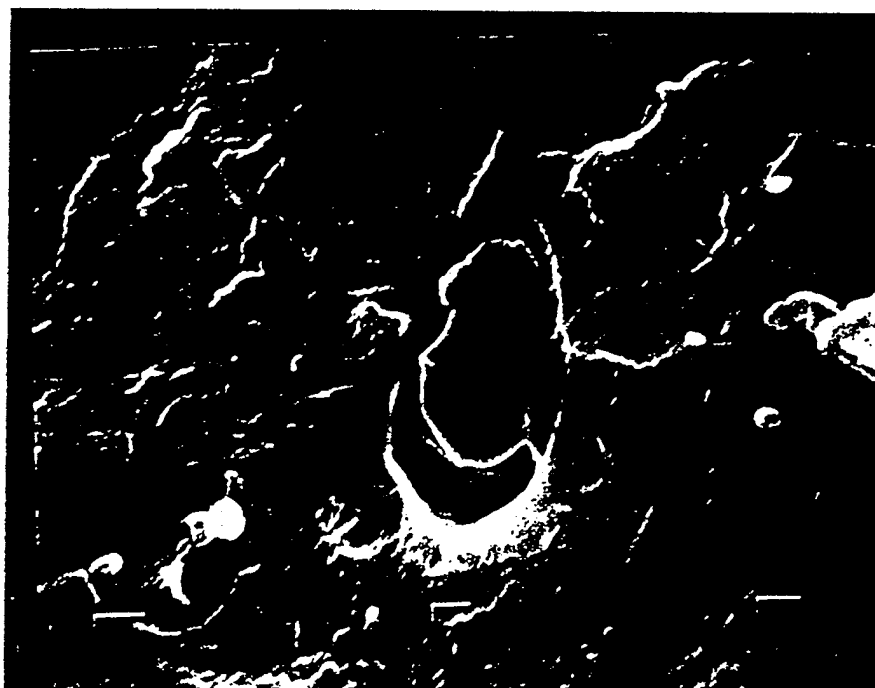
Electron micrograph of the surface of a CII-compatible PA6/UHMWPE blend, enlarged a) (0074) 500 times and b) (0017) 5000 times.

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a)



b)

**Figure 4**

SEM micrograph of the surface of a CII-compatible PA6,6/UHMWPE blend, enlarged a) (0070) 500 times and b) (0024) 5000 times.

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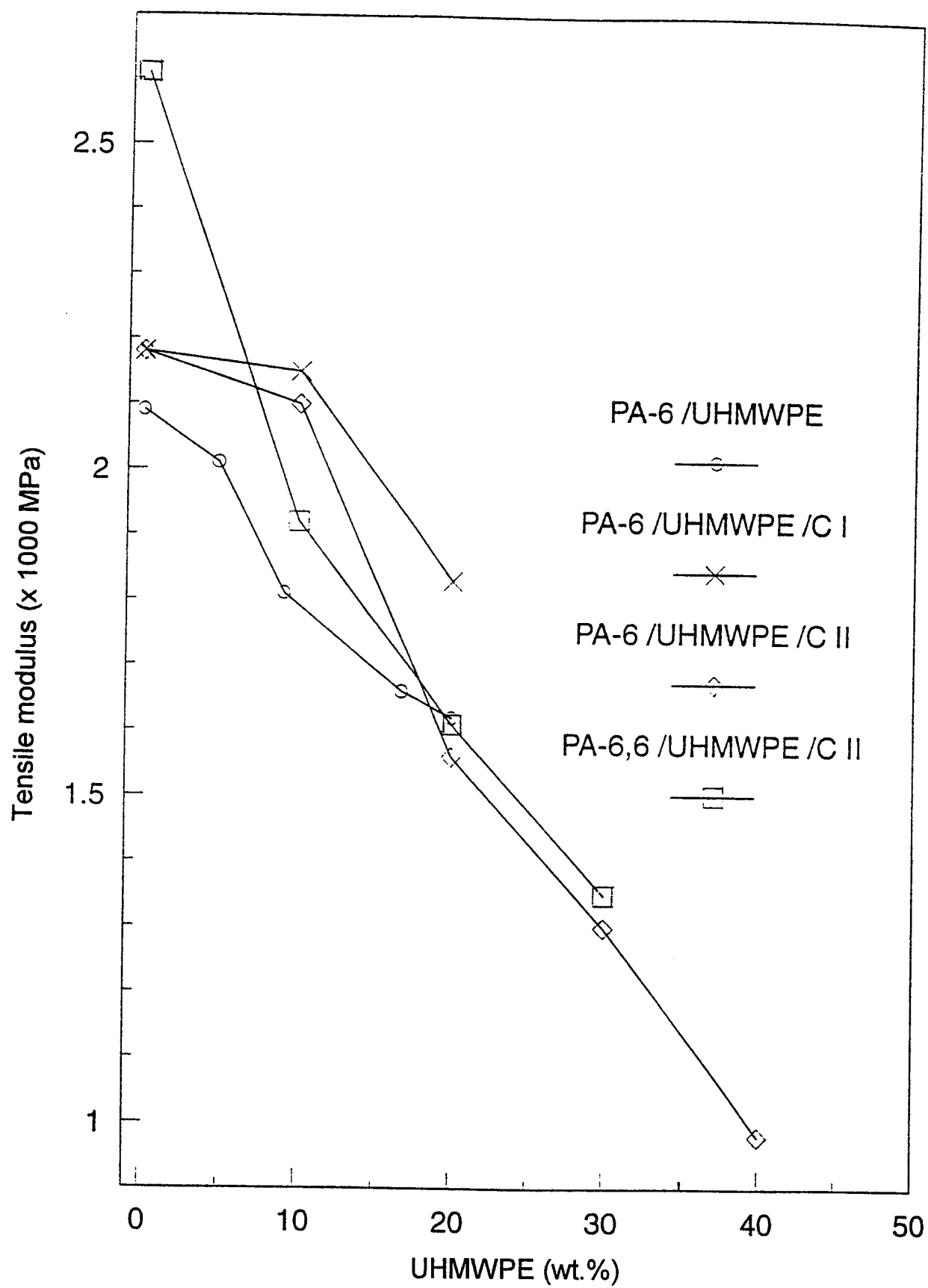


Figure 5

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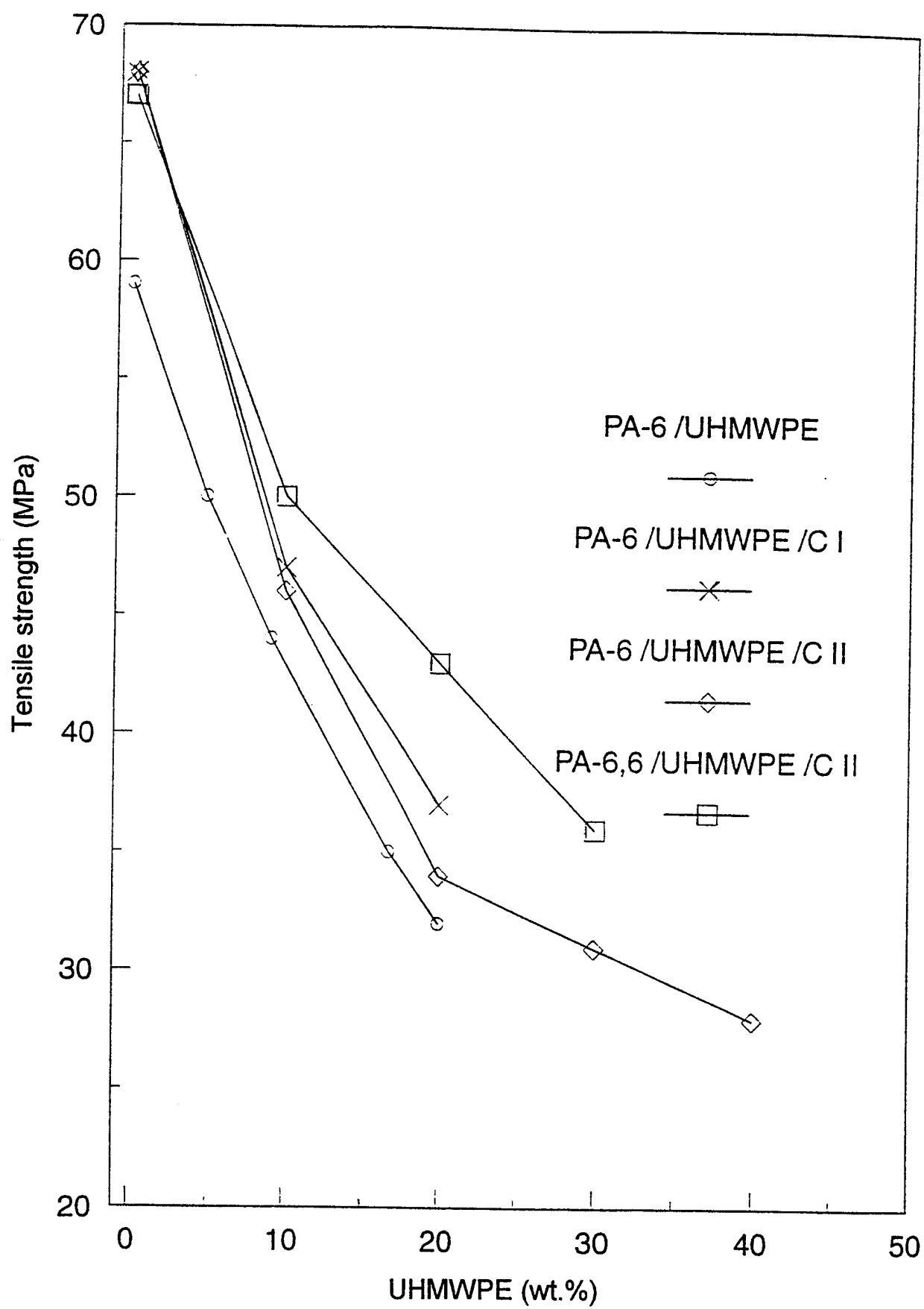


Figure 6

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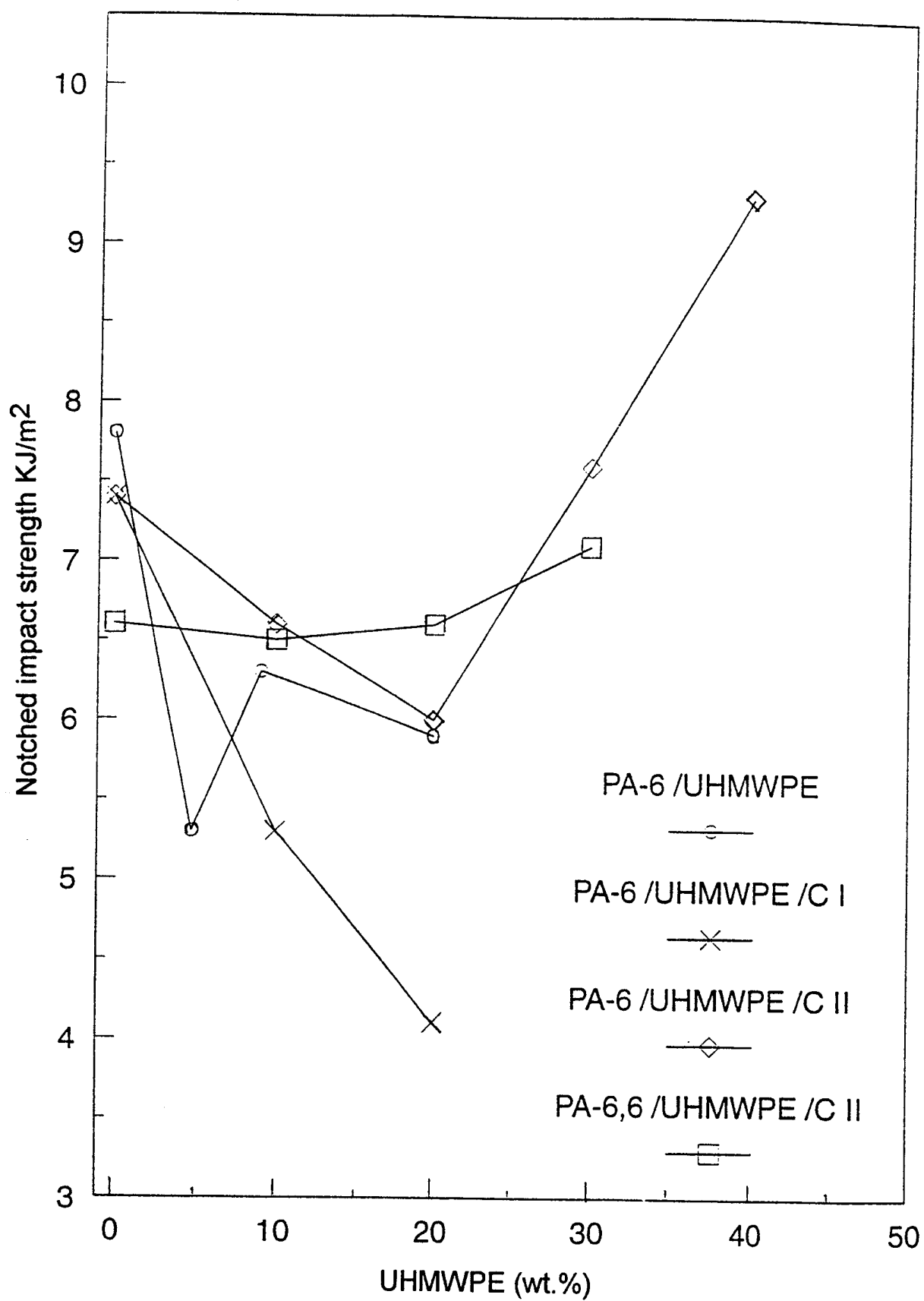
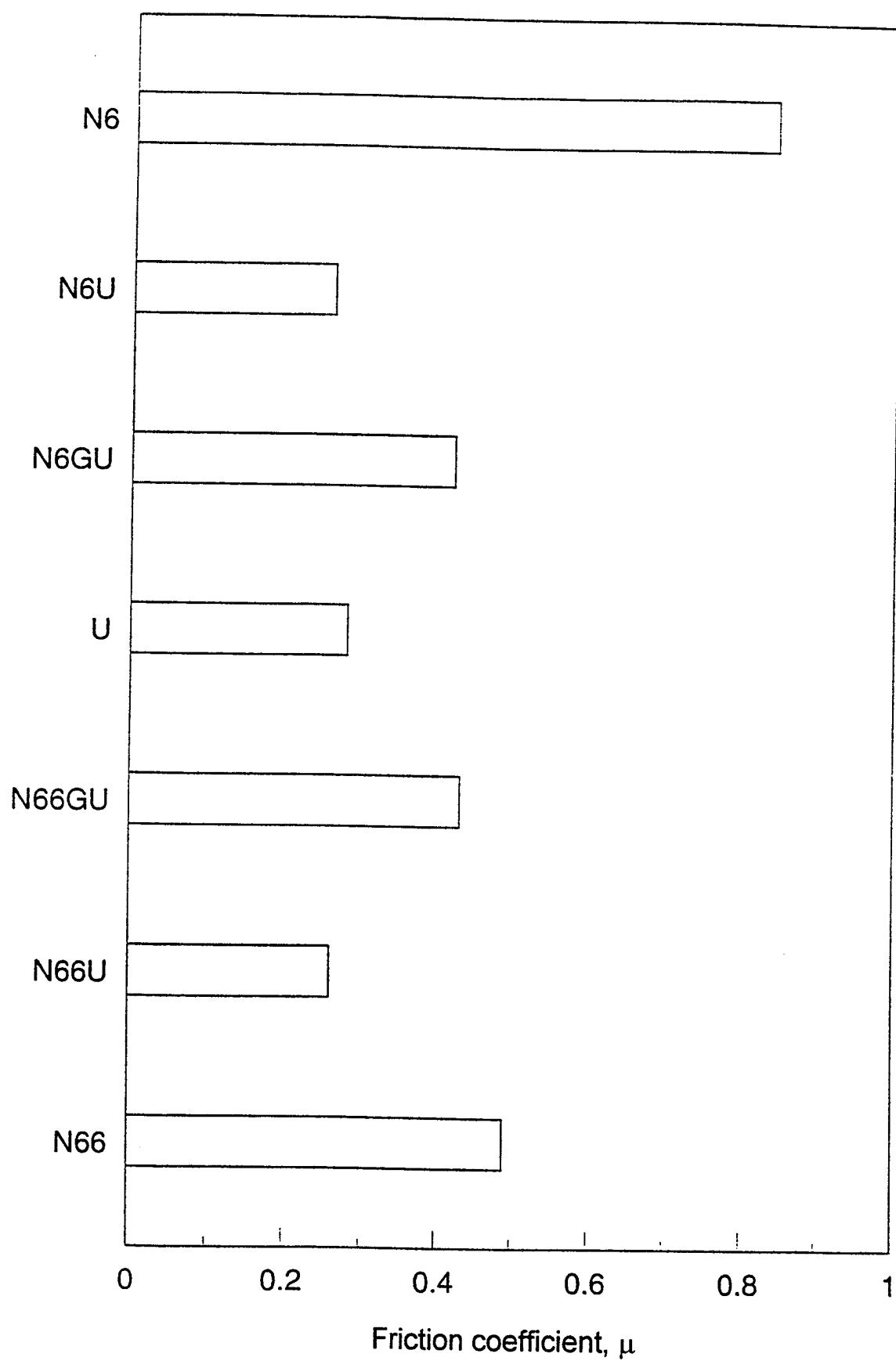


Figure 7

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**Figure 8**

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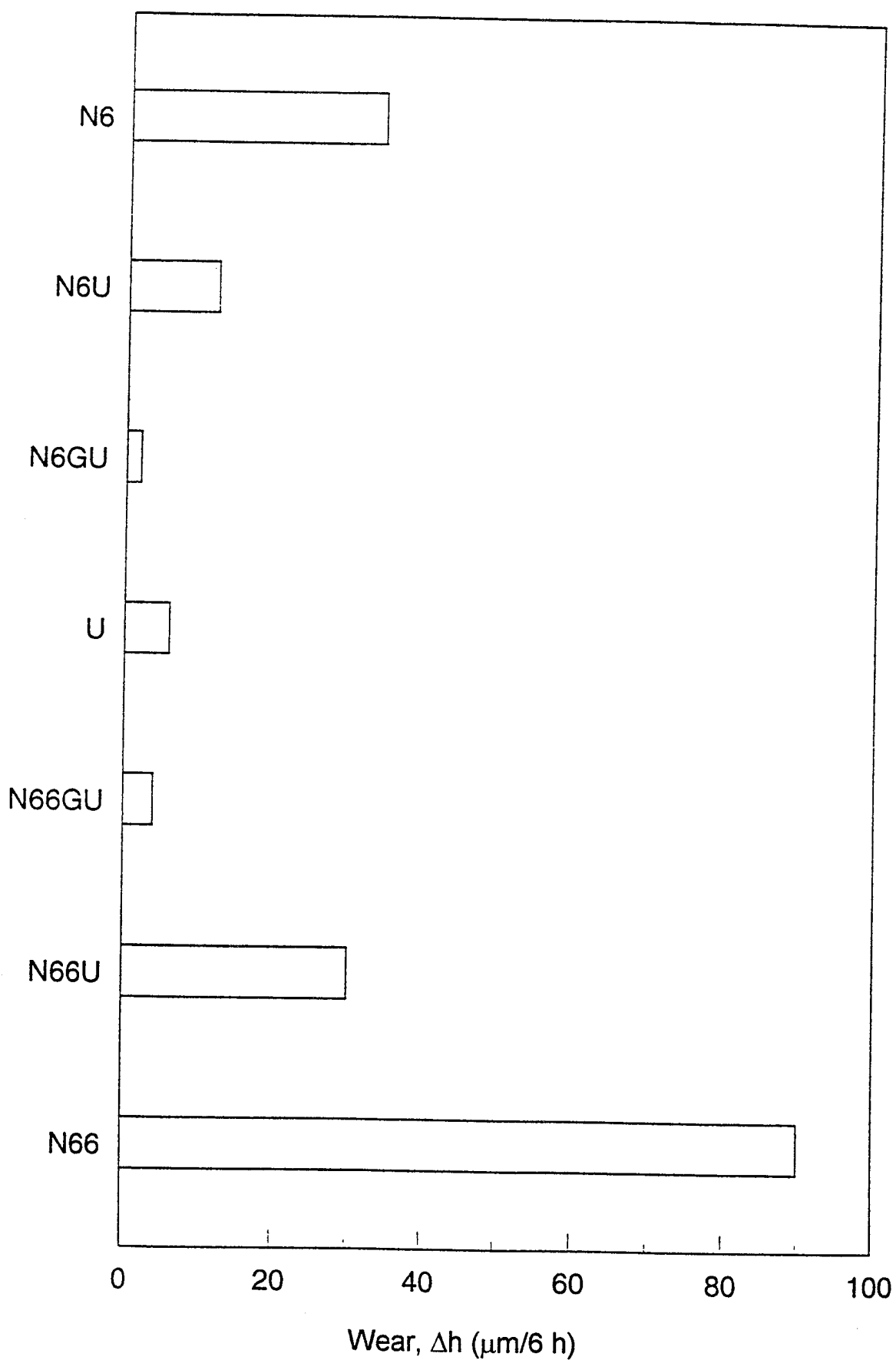


Figure 9

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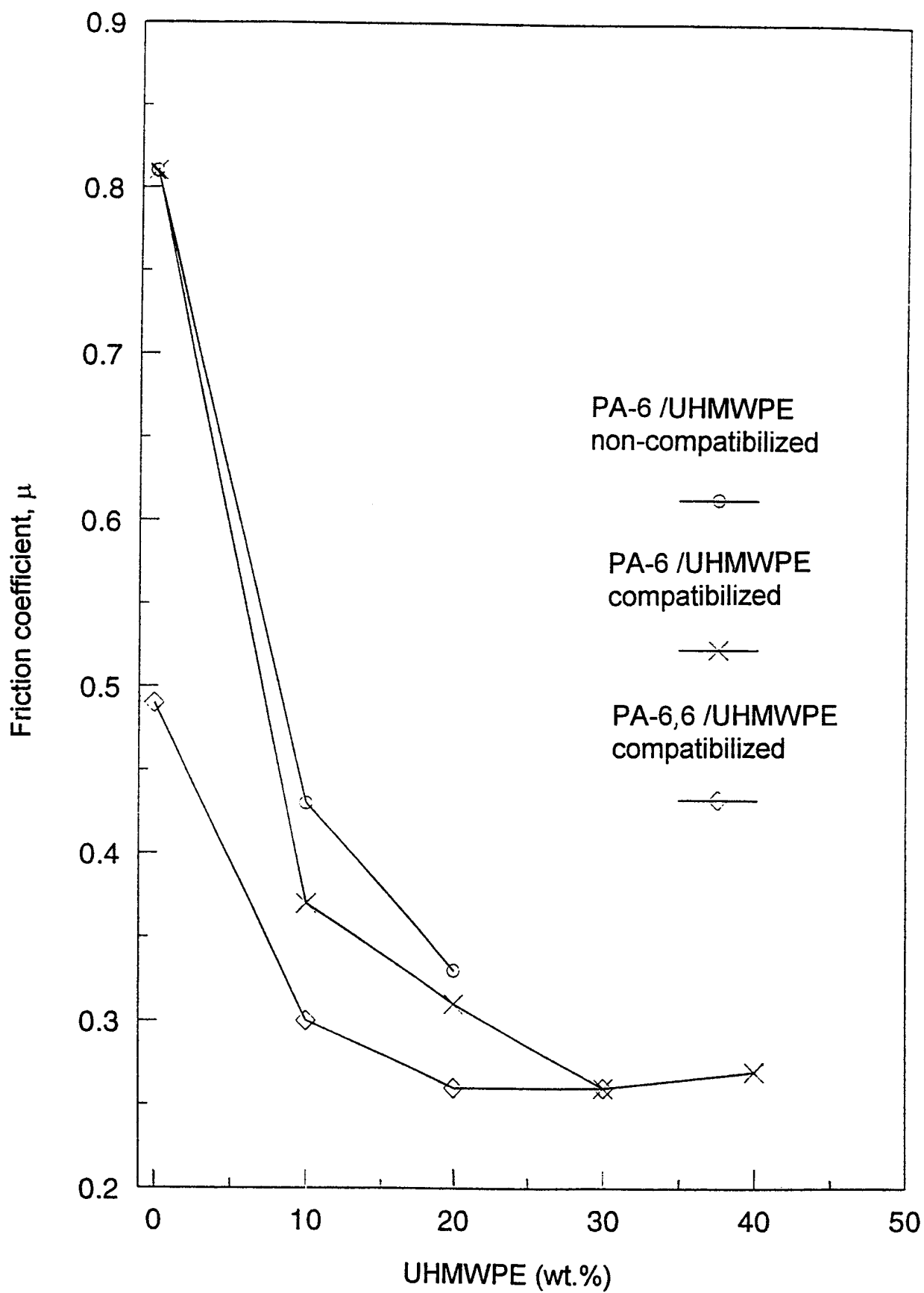


Figure 10

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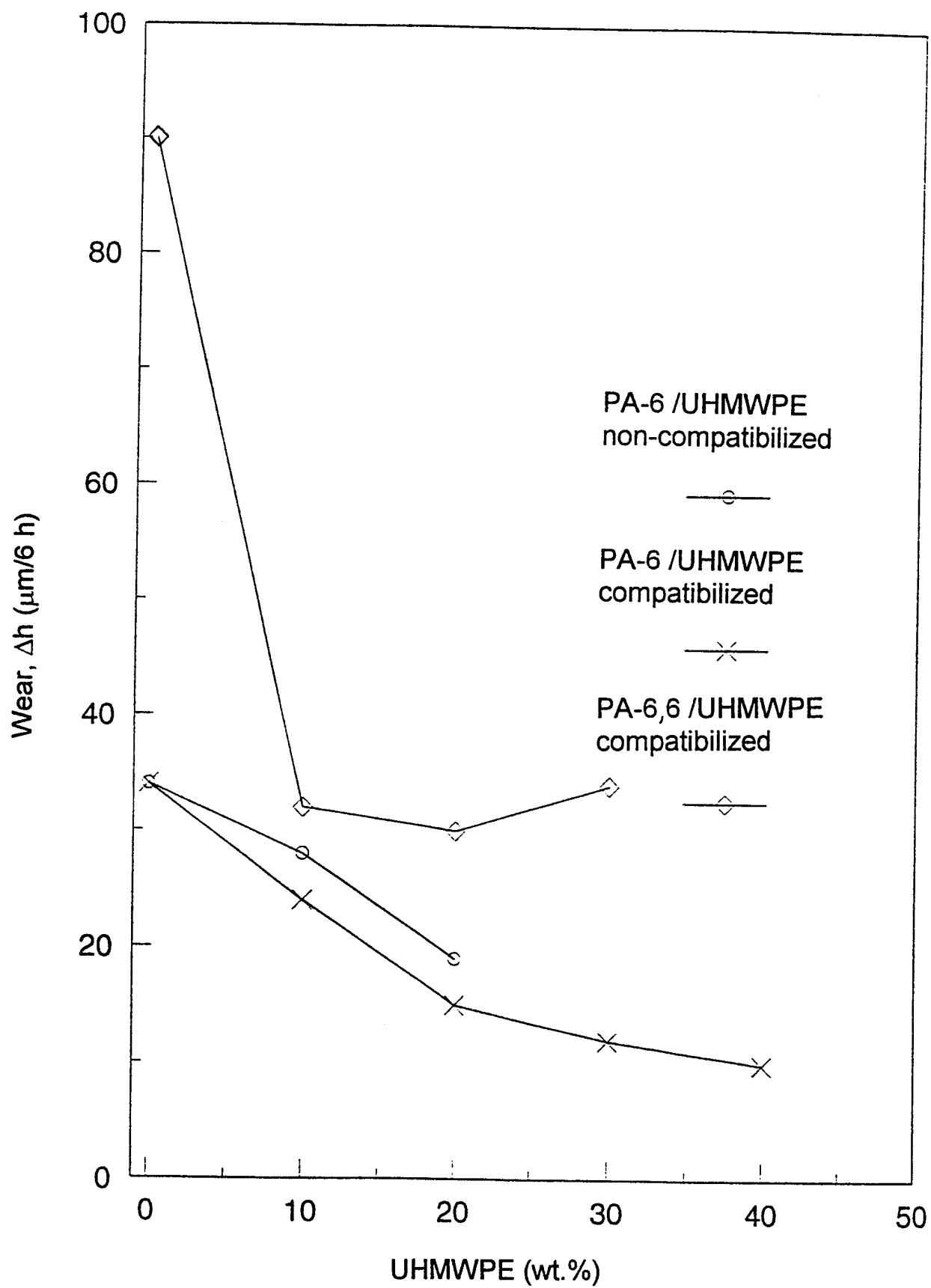


Figure 11

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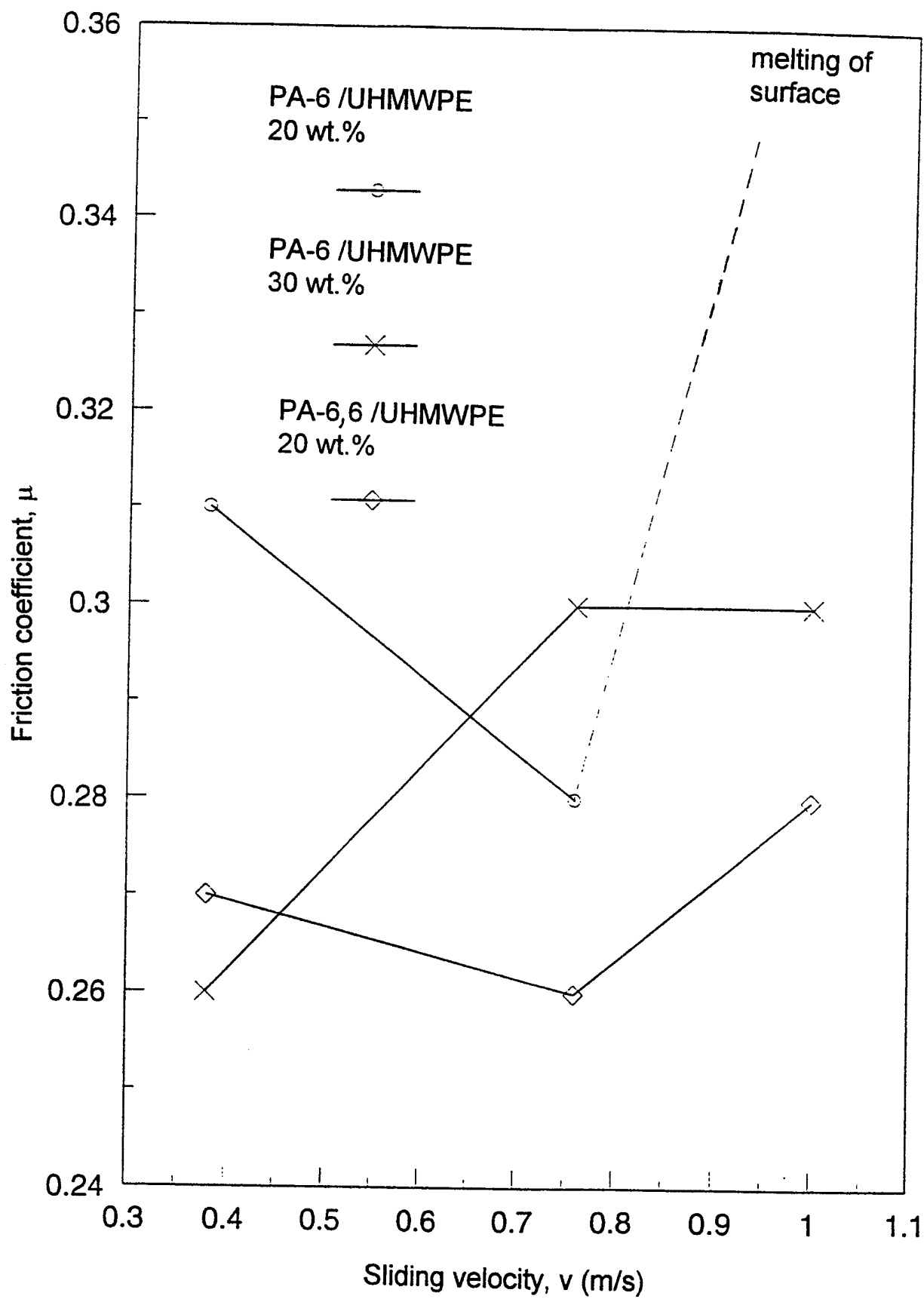


Figure 12

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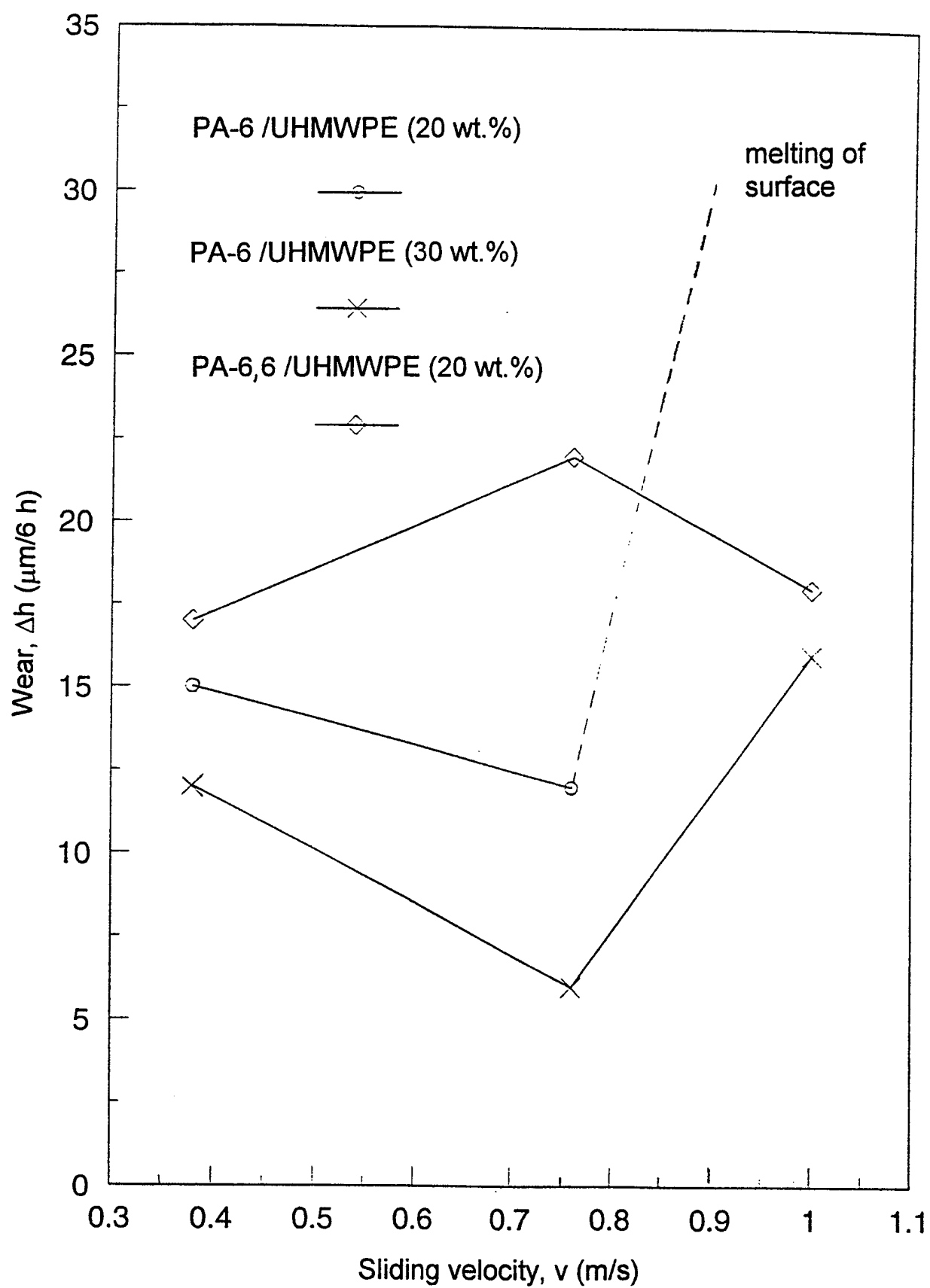


Figure 13

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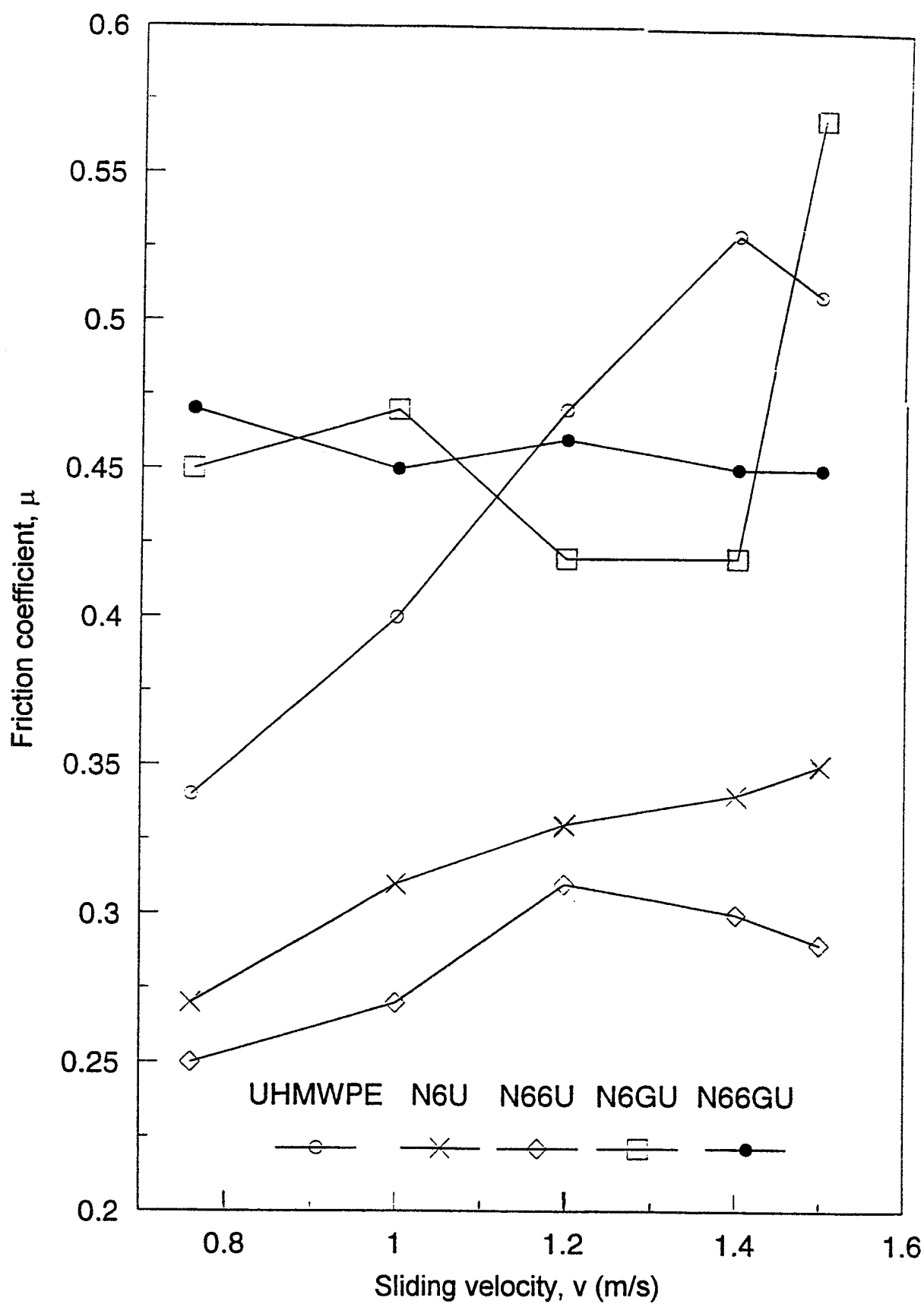


Figure 14

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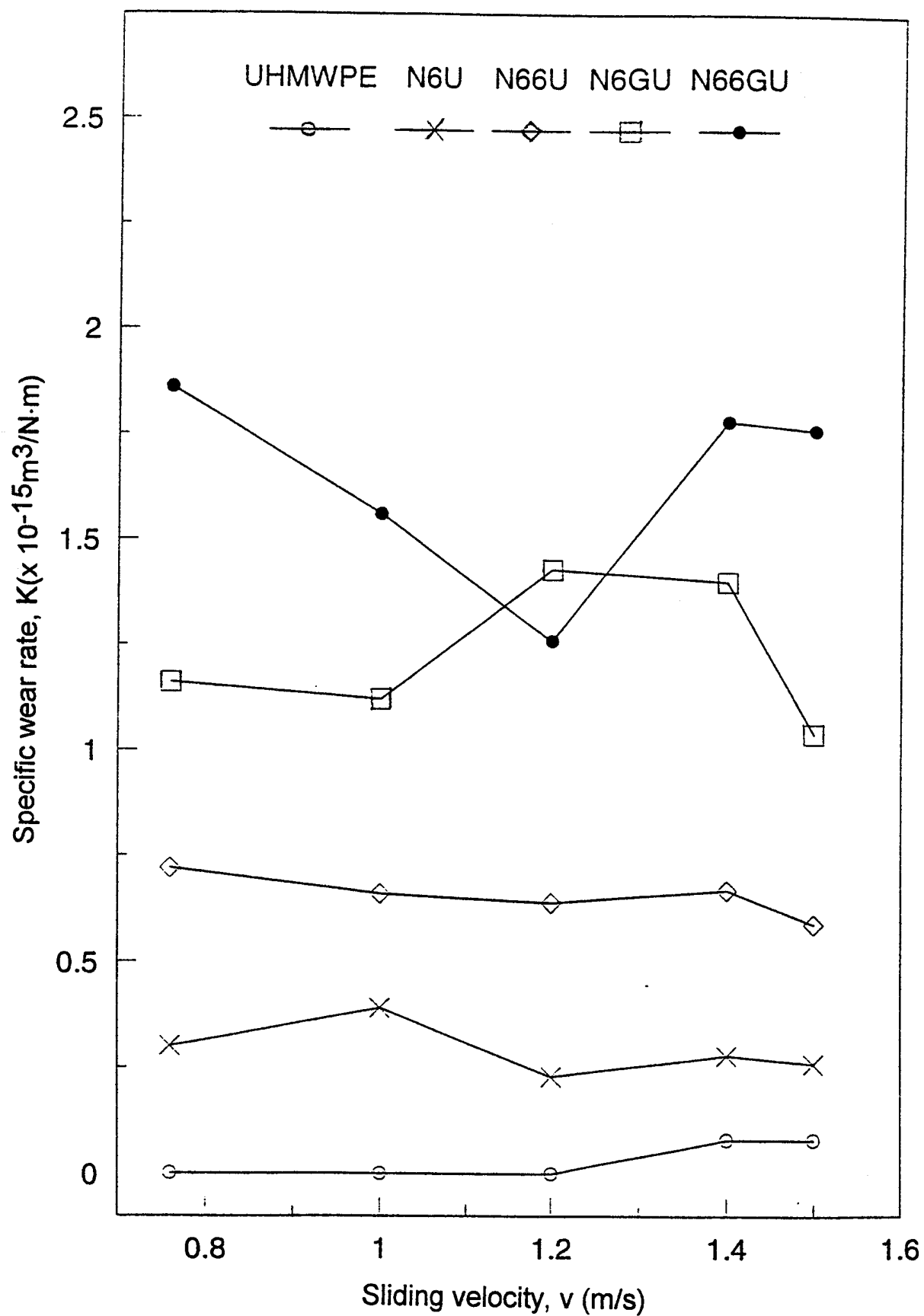


Figure 15

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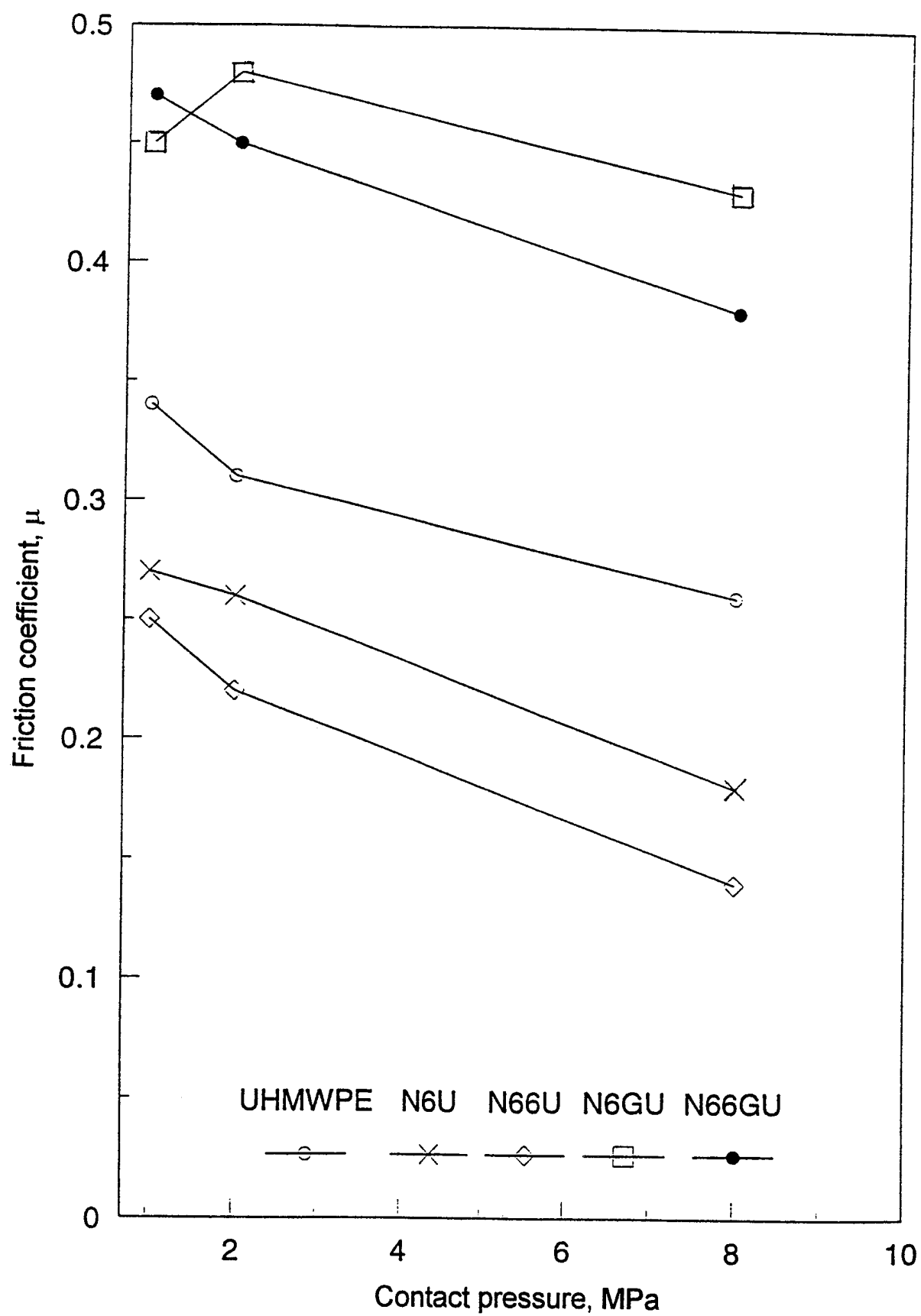


Figure 16

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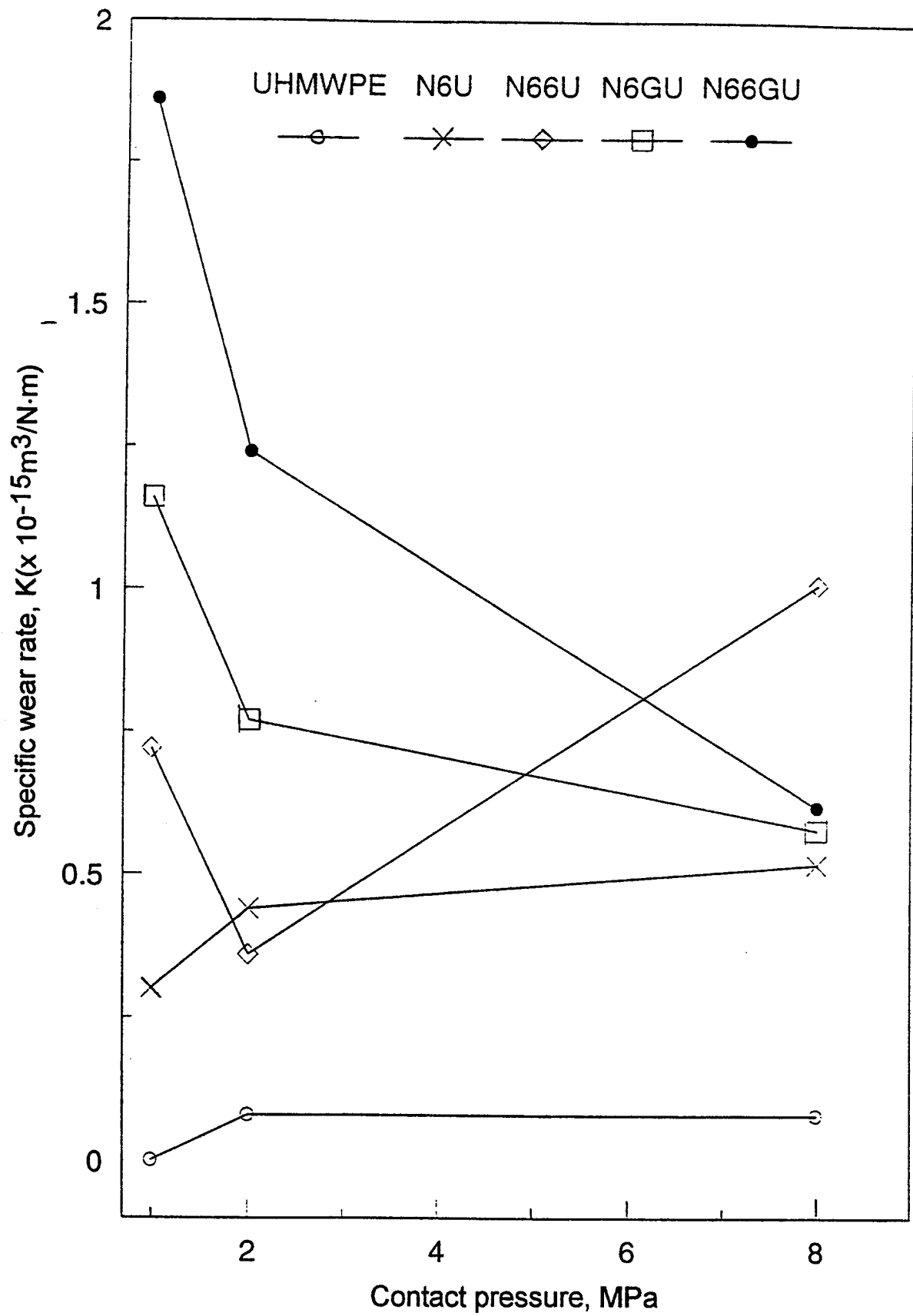


Figure 17

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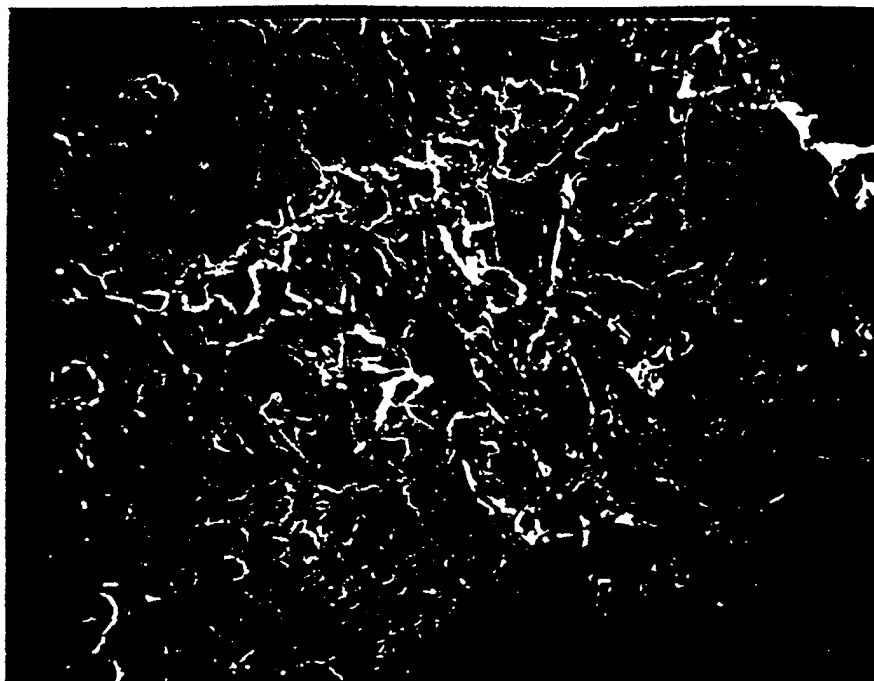


Figure 18 (0013)

Electron micrograph of the worn surface of the test specimen, the wear time being 6 h, the contact pressure 1 MPa, and the velocity of the contact piece 0.38 m/s for specimen N6U (75X).

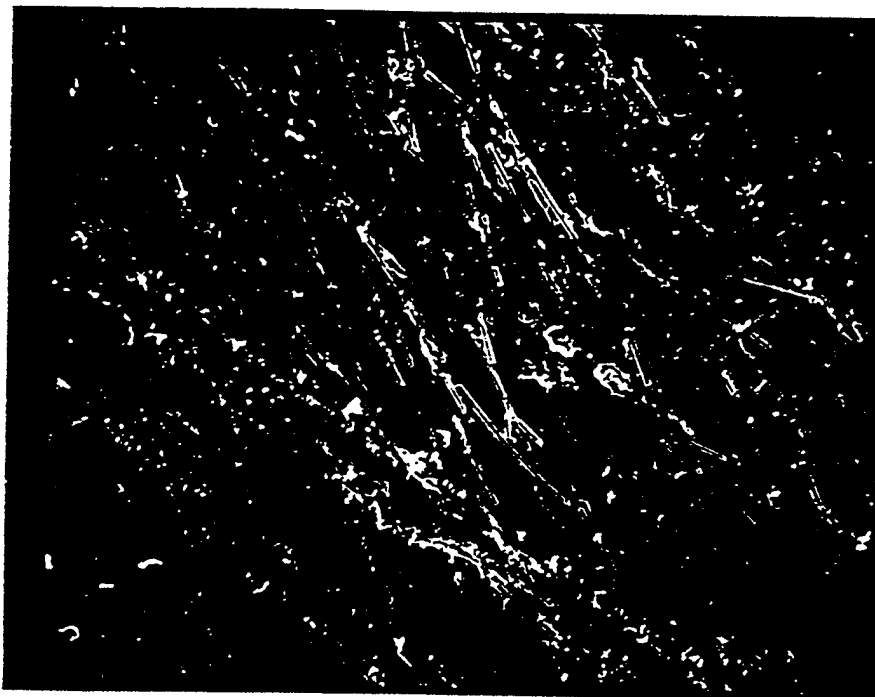


Figure 19 (0023)

Electron micrograph of the worn surface of the specimen, the wear time being 6 h, the contact pressure 1 MPa and the velocity of the testing member 0.38 m/s for specimen N6GU (75X).

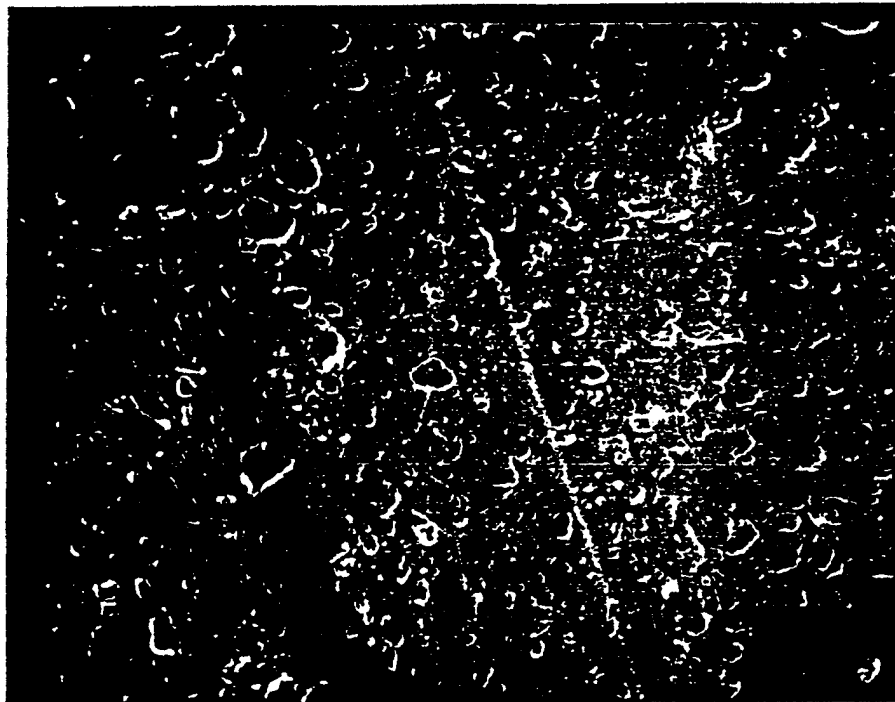


Figure 20 (0033)

Electron micrograph of the worn surface of the specimen, the wear time being 6 h, the contact pressure 1 MPa and the velocity of the testing member 0.38 m/s for specimen N66U (75X).

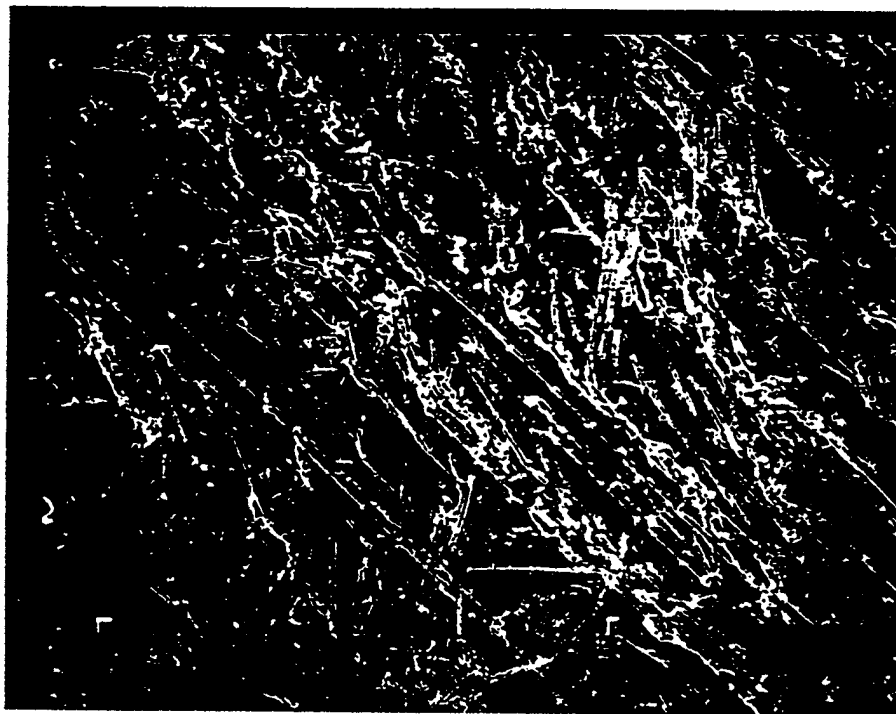


Figure 21 (0043)

Electron micrograph of the worn surface of the test specimen, the testing time being 6 h, the contact pressure 1 MPa and the velocity of the testing member 0.38 m/s for specimen N66GU (75X).

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 97/00172

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 23/04, C08L 77/00, C08F 255/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08L, C08F

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

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAPLUS, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0609892 A1 (GUNZE LIMITED), 10 August 1994 (10.08.94), column 2, line 46 - column 5, line 37, abstract, claims --	1-15
X	File WPI, Derwent accession no. 94-322344, Mitsuboshi Belting Ltd: "Polyamide based resin compsn.- comprises polyamide for cast moulding thermoplastic resin and compatibilising agent", JP,A,6248177, B2 970423 DW9721 --	1-5
X	EP 0335649 A2 (ROHM AND HAAS COMPANY), 4 October 1989 (04.10.89), page 5, line 8 - line 10; page 8, line 60 - line 61, abstract, table XL, XLI, XLII; claims --	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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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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Date of the actual completion of the international search

Date of mailing of the international search report

6 November 1997

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 97/00172

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0583595 A1 (BAYER AG), 23 February 1994 (23.02.94), page 4, line 4 - line 12, claims --	1-15
A	File WPI, Derwent accession no. 96-306798, Teijin Ltd: "Polyamide resin compsn. for min. abrasion of soft non-ferrous metal - comprises nylon resin, silicate powdery inorganic fillers and ultrahigh mol. wt. polyethylene resin powder, useful for sliding on metal", JP,A,8134348, 960528, DW9631 -- -----	1

INTERNATIONAL SEARCH REPORT

01/10/97

International application No.

PCT/FI 97/00172

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
EP	0609892	A1	10/08/94	CA	2115000 A	06/08/94
				JP	6226893 A	16/08/94
				US	5403638 A	04/04/95
<hr/>						
EP	0335649	A2	04/10/89	AT	141933 T	15/09/96
				AU	3171689 A	05/10/89
				BE	1003120 A	03/12/91
				CN	1041765 A	02/05/90
				CN	1092782 A	28/09/94
				DE	3910062 A	26/10/89
				DE	68927018 D,T	20/03/97
				DK	149389 A	30/09/89
				FR	2629462 A,B	06/10/89
				GB	2216892 A,B	18/10/89
				JP	2022316 A	25/01/90
				NL	8900757 A	16/10/89
				NO	175537 B,C	18/07/94
				NO	941044 A	27/12/89
				US	4957974 A	18/09/90
				US	5128410 A	07/07/92
				US	5202380 A	13/04/93
				US	5229456 A	20/07/93
				US	5433984 A	18/07/95
				US	4997884 A	05/03/91
				US	5035933 A	30/07/91
				US	5147932 A	15/09/92
				US	5300570 A	05/04/94
<hr/>						
EP	0583595	A1	23/02/94	SE	0583595 T3	
				DE	4223864 A	27/01/94
				DE	59302667 D	00/00/00
				ES	2086832 T	01/07/96
				JP	6192570 A	12/07/94
				DE	4310850 A	06/10/94
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