

58749.324

Field of the Invention

The invention relates to thermoplastically workable
5 solvent-resistant plastics mixtures consisting of
mixtures of polymethyl-, ethyl-, propylacrylate, or
polyvinyl acetate, polyvinyl propionate, grafted onto a
chemically cross-linked elastomer having a glass
transition temperature $< 0^{\circ}\text{C}$, on the one hand, and
10 polyvinylidene fluoride, on the other hand.

Prior Art

The compatibility of polymethylacrylate as well as
polyethylmethacrylate with polyvinylidene fluoride
15 (PVDF) in mixtures has been known for a long time. (Cf.
S. Noland et. al. Polym. Prepr. Amer. Chem. Soc., Div.
Polym. Chem. 11, 355 (1970); US-A 3 253 060).

Such mixtures meet the criterion of a single glass
transition temperature T_g of the polymer components and
20 also exhibit complete transparency over a wide range of
mixing.

It has also been found that polyvinylidene fluoride
(PVDF) is compatible with a whole number of different
polyvinyl compounds. Thus D.R. Paul et al. have
25 disclosed mixtures of PVDF with polymethylacrylate,
polyethylacrylate, polymethylmethacrylate,
polyethylmethacrylate, polyvinylacetate and
polyvinylmethylketone. (D.R. Paul et al. Polymer
Engineering and Science, 18, No. 16, 1225 - 1234
30 (1978)). Compatible mixtures of polymethylmethacrylate
with copolymers of vinylidene fluoride and
hexafluoroacetone are disclosed by S. Miyata et al. and
Maeda et al. (S. Miyata et al., Polym. Propr. Jpn. 34,
1074 (1985) and Maeda et al. US-P 4 617 350 (1986).
35 The miscibility of polyvinylidene fluoride-
hexafluoroacetone copolymers and ethylene vinyl acetate
copolymers is described by Hasegawa (Masatoshi Hasegawa

and Saburo Akiyama, Polymer Journal, 20, 471 - 476 (1988)).

The crystallisation behaviour of PVDF-PMMA blends is described by various authors (Wendorff et al.

- 5 Makromol. Chem., Rapid Commun. 7, 591 - 597 (1986), B.R. Hahn et al., Polymer 28, 201 - 208 (1987) and J.L. Halary et al. Macromolecules 21, 2988 - 2994 (1988)).

It has been found empirically that the crystallisation tendency of PVDF clearly decreases when
10 PMMA is added [T. Nishi, T.T.Wang Macromolecules 8, 909 (1975)]. This is based on the observation that the crystalline PVDF dissolves in the amorphous polymethacrylate melt and that the PVDF which is now amorphous acts as a plasticiser for the glass-like
15 polymethacrylates (cf. S. Noland et al. in N.A. Platzer, Multicomponent Polymer Systems, Advances in Chemistry Series 99, American Chemical Society 1971).

Thus, PVDF may be added, in smaller amounts, to polymethylmethacrylate (PMMA) as polymeric plasticiser
20 (cf. US-A 3 458 391), whereas, on the other hand, PMMA may be added, in small amounts, to PVDF as processing aid (US-A 3 253 060). It has, however, been shown that there is no distinct improvement in the properties of PMMA, when about 2 to 20 wt.% of PVDF is added to PMMA.

25 Patent Abstracts of Japan, Volume 7, No. 201(C184) (1346) or JP-A-5898352 disclose thermoplastic plastics compounds with a core-shell character. In marked contrast to the teaching of this invention, the grafted-on shell, in which alkyl methacrylates having up to 4
30 carbon atoms in the alkyl group are polymerised, is a "hard" shell. By contrast, the monomers of the shell portion, used according to the invention, are "soft" monomers.

35 Object and Solution

It is possible to produce blends with improved properties, in particular, improved mechanical and

optical properties, improved workability and stability, by mixing compatible polymers. This has already resulted in a number of commercially successful products (cf. H.F. Mark et al. Encyclopedia of Polymer Science & Engineering 2nd Ed., Vol. 12, pg. 399 - 461, J. Wiley & Sons, New York 1988).

The efforts to utilise the known miscibility between PMMA and PEMA, which are representative of acrylate plastics, on the one hand, and PVDF, on the other hand, for producing technically advanced products have so far been less successful.

It was, in particular, the aim to substitute, in part, the relatively costly PVDF by mixing it with a less expensive polymer component, without, if possible, impairing the favourable properties of PVDF.

It has now been found that plastics with excellent performance characteristics are obtained if PVDF is mixed with such polyvinyl esters and polyvinyl acrylates which are grafted, at least partially, onto a chemically cross-linked elastomer, on the one hand, and exhibit a glass transition temperature of $< 50^{\circ}\text{C}$, on the other hand. Of special interest are such mixtures that contain elastomers which have a clearly lower compatibility with PVDF than the polyvinylesters and polyvinylacrylates grafted on these elastomers.

According to the invention, thermoplastically workable polymer mixtures are obtained in this way which contain almost the entire PVDF content in crystalline form even if only small amounts of PVDF e.g. about 5 to 20 wt.% are present. There are even indications that in these "blends" the crystalline PVDF part of the total amount of PVDF contained in the mixture has become greater than the pure PVDF part. The determination of the crystallisation degree may be carried out by "Differential Scanning Calorimetry" (DSC, cf. H.F. Mark et al. Encyclopedia of Polymer Science & Engineering 2nd Ed. Vol. 4, 488, J. Wiley & Sons 1986). The polymer

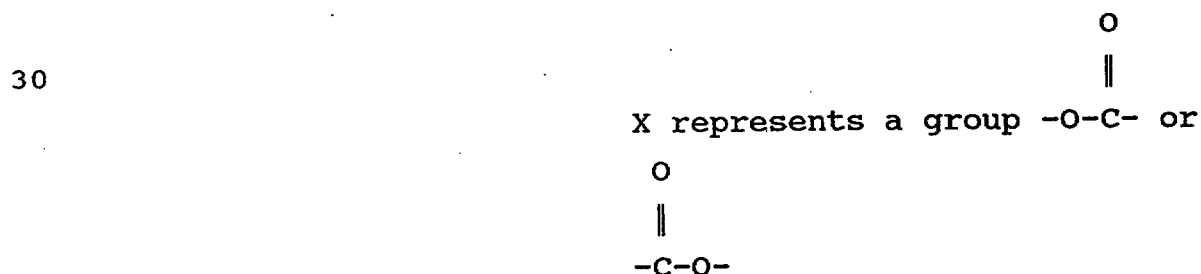
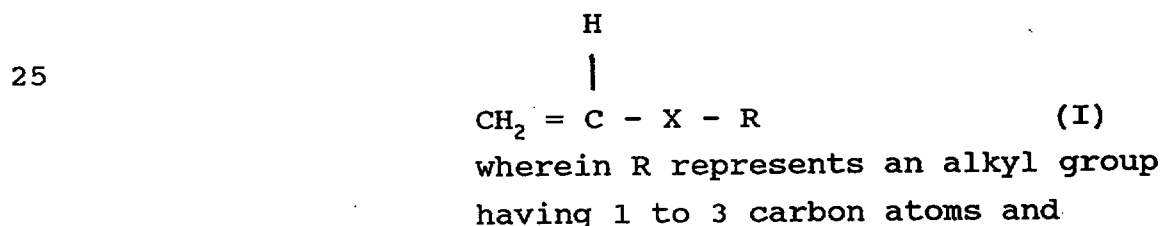
mixtures, according to the invention, are noted for their high mechanical stability and excellent solvent resistance.

Characteristics of particular interest in industry are achieved if the polymers grafted onto the elastomers are polymethylacrylate or polyethylacrylate and the viscous phase (i.e. the elastomer), on which polymethylacrylate or polyethylacrylate contained in the mixture is, at least partially, grafted, is completely incompatible with PVDF.

Thus, the invention relates to thermoplastically workable plastics mixtures KM with an excellent solvent resistance which are synthesised from

A) 2 - 98 wt.% , preferably 4-50 wt.%, of a polymer formed, in an amount of at least 80 wt.%, of monomers of the Formula $\text{CH}_2 = \text{CF}_2$,

B) 98 - 2 wt.% , preferably 96-50 wt.%, of a polymer which consists, in an amount of
 α) 20 - 90 wt.%, of a monomer of Formula I



and, in an amount of
 β) 80 - 10 wt.%, of a chemically cross-linked polymer KP with a glass transition temperature T_g below 0°C , preferably below -10°C , which is

covalently bound with at least 5 wt.% of the polymer formed from the monomers of Formula (I).

5 According to present findings, particularly favourable characteristics are obtained if a typical commercially available PVDF is used as polymer component A) in the plastics mixtures KM and if polymers composed of a core and shell, in particular core-shell polymers
10 produced by emulsion polymerisation, are used as component B.

 Elastomers (lattices) known per se (Ullmanns Encyclopädie der Technischen Chemie, 4th ed. vol. 13, 595 - 635, Verlag Chemie), mainly chosen from the group
15 of polyacrylates, polysiloxanes, polyolefins, more particularly polybutadiene, polyisoprene, ethylene-propylene-elastomers (EPM, EPDM, EPTM), are used as core material KP with a glass transition temperature $< 0^{\circ}\text{C}$, preferably $< -10^{\circ}\text{C}$.

20 The monomers of Formula I are, preferably, ethylacrylate, methylacrylate, propylacrylate, isopropylacrylate and vinylacetate as well as vinylpropionate or mixtures thereof. Normally, it can be assumed that the graft components synthesised from
25 the monomers of Formula I are compatible with PVDF i.e. the polymers synthesised from the monomers of Formula I must form a compatible polymer melt within the temperature range above the melting point of PVDF up to $> 200^{\circ}\text{C}$, preferably up to $> 250^{\circ}\text{C}$.

30
Component A)

 By definition, Component A is synthesised, in an amount of up to 100 wt.%, from monomers of 1,1-
35 difluoroethylene.

 The polymerisation is normally carried out as emulsion or suspension polymerisation in an aqueous medium under peroxide catalysis, for example with di-tert-butylperoxide within the range of 50 to 150°C and

at pressures of approximately 25 to 150 bar. (Ullmanns
Encyclopädie der Technischen Chemie, 4th ed. vol. 19,
103 - 104, Verlag Chemie; H.F. Mark et al. Encyclopedia
of Polymer Science and Technology, Vol. 14, 600 - 616,
5 Wiley Interscience, K.U. Bühler, Spezialplaste, Akademie
Verlag, Berlin 1978). The homopolymer PVDF is a highly
crystalline plastics with a linear molecular structure.
The average molecular mass is, as in the commercial
types, within the range of 100,000 to 300,000, the
10 melting point is normally within the range of 160 to
180°C, more particularly 168 to 172°C. (DTA). The
temperature range suitable for applications is -30 to
150°C.

The solvent, weather and radiation-resistance of
15 PVDF is particularly notable. Powdery PVDF types with a
grain diameter of about 100 μm are also commercially
available. It is also advantageous if commercially
available PVDF dispersions are used for mixing. Poorly
crystallising copolymers of vinylidene fluoride are,
20 therefore, less favoured. This applies in particular,
to copolymers of vinylidene fluoride and
hexafluoroacetone.

Component B)

25 Component B) is, advantageously, prepared by
emulsion polymerisation (cf. Houben-Weyl, 4th ed. vol.
XIV/1, 133 - 194, Georg Thieme Verlag 1961; H.F. Mark et
al. Encyclopedia of Polymer Science and Engineering, 2nd
Ed., Vol. 6, pp 1 - 51, J. Wiley 1986; H. Rauch-
30 Puntigam, Th. Völker Acryl- und Methacrylverbindungen,
Springer Verlag, Berlin 1967). The glass transition
temperature of the homo- or copolymers formed from the
monomers is known or may be calculated (cf. Brandrup-
Immergut, Polymer Handbook, 2nd. Ed., J. Wiley 1975;
35 Vieweg-Esser, Kunststoff-Handbuch, vol. IX, pg. 333 -
340, Carl-Hanser Verlag 1975).

In a preferred embodiment, the method used is to

graft the monomers of Formula I on an elastomer B β) incompatible with Component A. Here, the emulsion polymerisation is of particular interest, the elastomeric particle being produced in a first process step and the polymer B α) being grafted onto the elastomer in a second step.

The preparation of such core-shell lattices of the acrylate type used as Component B) may be carried out e.g. according to US-A 199 486, EP 0 065 069 or US-A 4 710 525 and US-A 3 787 522, US-A 3 943 190, US-A 3 914 338, US-A 4 052 525, US-A 3 985 703.

The syntheses of polymers B) from a core material KP and the shell material based on acrylate are carried out in a manner known per se, using a specific method:

Here, the monomers forming the core material are polymerised in an aqueous emulsion in the first process step. When the monomers of the first step are largely polymerised, the monomer components of the shell material are added to the emulsion polymer such that the formation of new particles is avoided. In this way, the polymer formed in the second step is placed around the core material in a shell-type fashion. An advantageous ratio of the shell thickness to the size of the core is obtained if the weight of the core material to the shell material is 1 : 3 to 3 : 1. By choosing a suitable amount of emulsifier, the particle size may be influenced according to the principle, the larger the particles, the smaller the amount of emulsifier. The particle diameters may, for example, be in the region of from 0.05 to 5 μm .

In this case, butyl acrylate and 2-ethylhexylacrylate are, preferably, used as monomers for the core material KP. Advantageously, the core material KP is prepared by using monomeric cross-linking agents known per se, preferably in amounts of 0.1 to 6 wt.%, more particularly 0.2 to 3 wt.% based on the monomers forming the core material.

The cross-linking agents used are normally those compounds which contain at least 2 vinylic double bonds in the molecule, for example the (meth)acrylic ester of multivalent alcohols such as glycol dimethacrylate, butanedioldiacrylate, triethyleneglycoldimethacrylate, tetraethyleneglycoldiacrylate, trimethylolpropanetriacrylate, pentaerythrittetraacrylate, etc. The core material used is, advantageously polymethylacrylate or polyethylacrylate.

In the first polymerisation stage, in which the core material is produced, 0.1 to 1 wt.% of anionic, cationic or non-ionic emulsifiers are used, based on the water phase, such as sodium laurylsulphate, alkyl benzene sulphonates, oxethylation products of alkylated phenols or the neutralised sulphurisation products thereof. The polymerisation is, preferably, initiated at temperatures of between 40 and 100°C using water-soluble radical-forming substances such as potassium or ammoniumpersulphate or hydrogen peroxide. Before the beginning of the second polymerisation stage, an initiator may again be added, but only very little or no additional emulsifier is used in the second stage.

If desired, the mainly 30 to 60% dispersions thus obtained may be transformed into a dry powder by carrying out the drying in a manner known per se namely drying up thin layers in flat containers or on rollers or preferably by spray drying at temperatures of between 50 and 100°C.

Preferably, the core material KP, itself, may be "filled" again.

Particularly interesting technical characteristics are observed in an emulsion polymer which has the following composition.

Core: Copolymer consisting of butylacrylate, allylmethacrylate, trimethylolpropanetriacrylate in a weight

ratio of 98 : 1 : 1

Shell: Polymethacrylate 100 wt.%.

A suitable polymer Component B) is also obtained by
5 using ethylene-propylene elastomers such as EPDM or EPTM
as Component B β).

The ethylene-propylene elastomers, which may be
used according to the invention, are known per se. Cf.
Ullmanns Encyclopädie der Technischen Chemie, 4th ed.
10 vol. 13, 619 - 620, Verlag Chemie 1977; H.F. Mark et al.
Encyclopedia of Polymer Science and Engineering 2nd Ed.
Vol. 6, 523 - 564. J. Wiley & Sons 1986. In general,
ethylene and propylene are present here in a molar ratio
of 5 : 1 to 1 : 3. The molecular weight is normally
15 within the region of 200,000 to 500,000. The
(simultaneous) use of further α -monoolefins having up to
16 carbon atoms is also possible. Furthermore, between
0.1 and 10 mol% of a linear diene or an unsaturated,
bridged cyclic hydrocarbon having at least a carbon-
20 carbon double bond is, preferably, copolymerised, for
example unsaturated derivatives of bicyclo-(2,2,1)-
heptane such as alkylidene-2-norbornene,
dicyclopentadiene, bicyclo-(2,2,1)-heptadiene. The
number of double bonds is generally 3 to 20, preferably
25 5 to 12 double bonds per 1,000 C-atoms; EPDM elastomers
are, for example, disclosed by US-A 2 933 480, 3 211
709, 3 093 620, 3 093 621, 3 113 115 and 3 300 450.

The grafting of ethylene-propylene elastomers may
be carried out in different ways, for example in organic
30 solvents or in the monomer.

In the first case, ethylene-propylene-diene
elastomer (EPDM) [e.g. the commercial products $\circ$ EPSYN
55 (product of Messrs Copolymer) or $\circ$ Polysar 585] are,
for example, used in a suitable solvent such as toluene,
35 chlorobenzene, butyl acetate.

The process is, preferably, carried out under a
protective gas such as nitrogen or carbon dioxide in the

usual polymerisation vessels equipped with stirrers. The initiators used may be known per se, for example peroxidic initiators such as benzoylperoxide, tert.-butylperoxctoate, di-tert-butylperoxide, in an amount of
5 normally about 0.01 to 2 wt.% based on the monomers. In most cases, the polymerisation is started by increasing the temperature, e.g. to above 60°C and up to the boiling point of the solvent and normally also carried out at an elevated temperature. Monomers and initiator
10 may, preferably, be added proportionally to the elastomers contained in the preparation mixture. Normally, total polymerisation takes several hours or lasts more than one working day. Solvents and any non-reacted monomer, may, advantageously, be removed under
15 reduced pressure, particularly advantageously by using a Leistritz-extruder. The analysis of the grafted portions may be carried out by means of the "Reprecipitation-chromatography" technique (cf. J. Ma, D. Pang & B. Huand, J. Polym. Sci. A, Polym. Chem. 24,
20 2853 - 2866 (1986); A. Gadkari & M.F. Farona, Polym. Bull 17, 299 - 306 (1987)). So called "soluble rubber", which is, to some extent, analagous to EPDM/EPTM, may, moreover, also be used as elastomer.

Furthermore, the following elastomers B β) may be
25 used within the scope of this invention:

Butyl caoutchouc (IIE, cf. Ullmann loc.cit. vol. 13, p. 621 - 623; H.F. Mark et al. Encyclopedia of Polymer Science and Engineering 2nd Ed. Vol. 8, 423 - 487, J. Wiley & Sons, 1987).

30 Polyisoprene (IR, cf. Ullmann, loc.cit. vol. 13, p. 617 - 621, H.F. Mark et al. Encyclopedia of Polymer Science and Engineering, 2nd Ed. Vol. 8, 487 - 564, J. Wiley & Sons, 1987).

Polybutadiene (BR, cf. Ullmann loc.cit. vol. 13, p.
35 602 - 605; H.F. Mark et al. Encyclopedia of Polymer Science and Engineering 2nd Ed. Vol. 2, 537 - 590, J. Wiley & Sons 198.).

Elastomers produced by polycondensation such as silicon caoutchouc (Q, cf. Ullmann loc.cit. vol. 13, 628 - 631); H.F. Mark et al. Encyclopedia of Polymer Science & Technology, Vol. 12, 464 - 569, J. Wiley Interscience) may also be used.

The preparation of the mixtures is carried out in a manner known per se, for example by mechanical mixing of the particles, advantageously already crushed or while crushing during the mixing process, and melting the mixture. The mixing may, advantageously, be carried out in the extruder. (cf. German Patent Application No. P 37 43 199.4 of 19.12.1987).

The mechanical mixing is started by mixing the components based on substances advantageously already particle-like, normally using slowly rotating mixers such as drum mixers, continuous flow mixers or double chamber plough mixers. The slowly rotating mixers produce a mechanical mixing without doing away with the phase boundaries (cf. Ullmanns Encyklopädie der Technischen Chemie, 4th ed. vol. 2, pg. 282 - 311, Verlag Chemie). Then, the thermoplastic working-up is carried out by homogenous mixing in the melt, using heatable mixers at suitable temperatures for example 150 to about 300°C, in kneaders, or preferably extruders such as single- or multiple-screw extruders or, optionally, in extruders with oscillating screw and shear pins (e.g. in a BUSSCO-kneader).

By using these methods, it is possible to obtain uniform granules (e.g. chips, granules in cubic form, round grain). The grain size of the granules here is 3 to 5 mm. Another advantageous aspect is the mixing of dispersions (emulsions) of the components and the subsequent removal of the liquid phase, for example by squeezing out in an extruder.

35

Advantageous Effects of the Mixtures KM

The advantageous effects of the mixtures KM are

demonstrated by the following example, using PVDF as Component A) and a core-shell polymer as Component B) (B β : Copolymer consisting of butylacrylate, allylacrylate and trimethylolpropanetriacrylate (98 : 1 : 1 parts by weight as described above), B : polymethylacrylate or polyethylacrylate).

Even with a low content of PVDF, such a mixture of core-shell polymer and PVDF exhibits a high crystallinity of the PVDF part. This fact is likely to contribute, at least significantly, to the observed resistance of the mixtures to solvents.

Thus, a mixture consisting of 10 wt.% of PVDF and 90 wt.% of an emulsion polymer of the above composition is resistant to toluene, acetone, chloroform and ethylacetate.

Surprisingly, when only 10 wt.% is added to the above emulsion polymer, a clear improvement of the thermal stability is also achieved. This is in contrast to the results obtained with PVDF-PMMA mixtures in which a small amount of PVDF already clearly reduces the thermal stability of PMMA.

Of particular importance of the applicational properties of the plastics mixtures KM is the balanced presence of all three components of the plastics mixture KM.

- A) PVDF or a crystalline vinylidene fluoride copolymer
- B α) a vinyl polymer compatible with PVDF, having a glass transition temperature $< 50^{\circ}\text{C}$, preferably $< 30^{\circ}\text{C}$, which is grafted, at least partially, on a third polymer species
- B β) incompatible with PVDF, B β also being incompatible with B α in the temperature range of -50°C to $+100^{\circ}\text{C}$, chemically cross-linked and having a glass transition temperature $T < 0^{\circ}\text{C}$.

Of particular interest are those plastics mixtures KM which contain 4 to 40 wt.% of PVDF. Mixtures containing 5 to 30 wt.% of PVDF are particularly preferred. The proportion of the Component B β in the component B is, preferably, within the range of 40 to 90, more particularly preferred within the range of 55 to 75 wt.%.

Those mixtures KM are also of interest which consist of 75 to 95 wt.% of PVDF as Component A and of 25 to 5 wt.% as Component B, a proportion of 55 to 75 wt.% of the Component B β in B being preferred.

The following Examples serve to explain the invention:

The determination of the melt viscosity (η_s) is carried out according to DIN 54 811 process B.

The particle diameter is determined using a * Coulter Nano-Sizer. The particle diameter may also be determined by means of light scattering.

The breaking elongation and tensile strength are determined according to DIN 53 455.

The Shore-hardness is determined according to DIN 53 505.

EXAMPLES

25

Example 1

Preparation of an emulsion polymer with a core-shell structure (Component B).

30 1.0 g of potassiumperoxodisulphate as initiator
 and
 0.06 g of triisobutylphenyl, ethoxylated with 7 mol
 of ethyleneoxide, sulphated, in sodium salt
 as emulsifier are introduced into
35 630.0 g of distilled water and heated to 80°C

in a polymerisation vessel equipped with stirrer,

reflux cooler and thermometer.

An emulsion I consisting of

5 1631.0 g of butylacrylate,
 16.6 g of allylmethacrylate
 16.6 g of propanetrimethyloltriacylate,
 3.0 g potassiumperoxodisulphate
 5.0 g of the above emulsifier and
10 1877.0 g of distilled water is added uniformly by
 metering to this initial mixture, while
 stirring, within 2½ hours.

15 (A sample is taken for the purpose of analysis: the
 polymer dispersion thus prepared has a particle diameter
 of 346 nm).

 Immediately after adding Emulsion I an Emulsion II
is added by metering within 1½ hours at 80°C, said
emulsion consisting of:

20 900.0 g methylacrylate
 2.0 g potassiumperoxodisulphate
 1.5 g of the above emulsifier
 1345.0 g of distilled water

25 After cooling to ambient temperature a polymer
dispersion is obtained which has a solid content of
39.8%. Particle diameter: 386 nm.

 In order to recover the polymer solid, the
dispersion is frozen at -16°C for 48 hours. After
30 thawing, the solid is separated, washed three times with
 water and dried in vacuo at 50°C.

Example 2

35 A method is used as in Example 1, but a different
 composition of Emulsion I is chosen:

 1648.0 g of butylacrylate

8.3 g of allylmethacrylate
8.3 g of trimethylolpropanetriacrylate
1.6 g of potassiumperoxodisulphate
5.0 g of the emulsifier mentioned in Example 1
5 1877.0 g of distilled water

Result:

Diameter of polymer dispersion after adding
Emulsion II: 446 nm.

10 Solid content of the dispersion: 40 wt.%
Working up to recover the polymer solid according
to Example 1.

Example 3

15 The method used is as in Example 2, but a different
composition of monomers is chosen for Emulsion I:

1597.0 g of butylacrylate
33.3 g of allylmethacrylate
20 33.3 g of trimethylolpropanetriacrylate.

After adding Emulsion II, a polymer dispersion is
obtained which has a particle diameter of 448 nm.

25 Example 4

Preparation and characterisation of the plastics
mixtures KM.

Component A: PVDF
30 Component B: emulsion polymer with a core-shell-
composition
Component B β : polybutylacrylate cross-linked with 1%
of allyl-methacrylate and 1% of
trimethylolpropanetriacrylate.
35 Component B α : polymethylacrylate, partially grafted on
B β .

PDVF ([®] Solef 1010 of Messrs. Solvay) is mixed, in different proportions, with the polymer solid, according to Example 1, on the extruder (see Table 1).

Table 1 lists, in each case, in addition to PVDF contained in KM, the lowest glass transition temperature detectable by means of DSC as well as the melting peak (T_{max}) of the PVDF contained in the mixture, the melting heat/g and the melting heat/g of PVDF.

10 Table 1

Characterisation of KM consisting of PVDF and polymer according to Example 1

15	No.	Proportion of PVDF in KM (wt.%)	T _g (Elastomer) (°C)	T _{max} °C	Melting heat J/g KM J/g PVDF	
	4-a	100	(-40)	192	57.0	57.0
	4-b	80	-43	181	36.0	46.0
	4-c	50	-45	176	33.4	66.9
	4-d	20	-46	170	13.8	68.9
20	4-e	10	-43	163	6.4	64.3
	4-f	5	-44	155	2.4	47.0
	4-g	-	-40	-	-	-

As is apparent, the melting heat/g of PVDF, even in mixtures with only 10 to 20% of PVDF, is substantially equal to or greater than in the PVDF, itself, i.e. PVDF is mainly crystallised in the KM.

KM 4-b to 4-f may be worked up thermoplastically in an excellent manner.

30 4-d (20 wt.% of PVDF) exhibits a η_s of 1925 Pa s at 180°C. This material may also be extruded to form a smooth, non-undulated, non-porous strand.

The tensile strength and breaking elongation of the strands are measured:

	Sample 4-d	Sample 4-e
Tensile strength MPa	5.2	3.1
Breaking elongation (%)	200	180

5 Test laminae were sprayed from KM 4-d and 4-e.
Laminae with an excellent solvent-resistance to toluene
and acetone are obtained (in particular Sample 4-d).

Shore-hardness A of the samples: 4-d : 71
4-e : 59

Examples 5a, b

KM with a high content of PVDF

15 (80) 90 wt.% of PVDF (®Solef 1010 of Messrs. Solvay) is mixed with (20) 10 wt.% of the polymer solid according to Example 2, granulated and then sprayed to form the specimen.

20 Sample 5a, 90 wt.% of PVDF:

VST (°C) : 130

Impact strength (standard small test bar) : without rupture

Notched impact strength (standard small test bar) : 28.9

 $\text{KJ/m}^2 \text{ S}$

25

Sample 5b, 80 wt.% of PVDF:

VST (°C) : 100

Impact strength (standard small test bar) : without rupture

Notched impact strength (standard small test bar) : 39.7

30 KJ/m² T



Claims

1. Thermoplastically workable plastics mixtures with a high resistance against solvents, using polymers of vinylidene fluoride, characterised in that the plastics mixtures KM are synthesised from

10 A) 2 - 98 wt.% of a polymer formed, in an amount of at least 80 wt.%, of monomers of the Formula $\text{CH}_2 = \text{CF}_2$,

15 B) 98 - 2 wt.% of a polymer which consists, in an amount of 20 - 90 wt.%, of a monomer of Formula I



wherein R represents an alkyl group having 1 to 3 carbon atoms and

20 X represents a group $-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-$ or $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$

or of mixtures of monomers of Formula I and,

25 in an amount of 80 - 10 wt.%, of a chemically cross-linked polymer KP with a glass transition temperature T_g below 0°C , which is covalently bound with at least 5 wt.% of the polymer formed from the monomers of Formula (I).
30

2. Thermoplastically workable plastics mixtures KM according to Claim 1, characterised in that the polymer KP is selected from the group of elastomeric polyacrylates, polysiloxanes, polyolefins.



- 19 -

3. Thermoplastically workable plastics mixtures KM according to Claim 1, characterised in that polymers with a structure consisting of a core and shells are used as component B).

5

4. Thermoplastically workable plastics mixtures KM according to Claims 1 to 3, characterised in that ethyl acrylate, methyl acrylate, propyl acrylate, isopropyl acrylate, vinyl acetate or vinyl propionate are used as monomers of Formula I.

10

5. Thermoplastically workable plastics mixtures KM according to Claim 1, characterised in that the component B) is produced by emulsion polymerisation.

15