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Calorimetric study of fluorinated methacrylic and vinyl polymer blends: 1. Binary systems: determination of miscibility domains and correlation of glass transition temperatures with blends composition—application to plastic optical fibre cladding

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This paper reports a calorimetric study of binary polymer blends prepared by solution mixing of fluoroalkyl methacrylic ester–methyl methacrylate (MMA) copolymers with poly(vinylidene difluoride) (PVDF) or VDF–hexafluoropropene (HFP) (or VDF–trifluoroethylene) copolymers and examines their use as materials in plastic optical fibres (POF) technology. Some interesting blends were also obtained through mechanical mixing in the molten state. As compared to the well known PVDF–poly(methyl methacrylate) (PMMA) system, miscibility domains in copolymer blends become wider when less crystalline VDF copolymers are used in place of PVDF, whereas the opposite is found for the introduction of fluorinated alkyl ester side chains in PMMA. Correlation of the observed glass transition temperatures of homogeneous phases to their compositions failed with the Fox and Gordon–Taylor relations, whereas good fits could be observed using both Kwei and Jenckel–Heutsch relations. The q and b (specific interactions) parameters in these relations are well correlated to the chemical composition, indicating the influence of strong intermolecular interactions. In fluoroalkyl methacrylic ester-containing polymers, internal interactions are competing efficiently with intermolecular ones, thus limiting the miscibility of these polymers with VDF-homo- and copolymers. Some blends of the MMA–trifluoromethyl methacrylate with VDF–HFP copolymers give good performances as POF cladding material. A more simple solution lies in the use of VDF–HFP copolymers themselves. © 1997 Elsevier Science Ltd.

(Keywords: polymer blends; PVDF; VDF–HFP copolymers)

INTRODUCTION

The need for homogeneous highly transparent polymeric materials has been driven by plastic optical device developments. Light transmission over short distances (*ca* 1–15 m) can be obtained readily by the use of plastic optical fibres (POFs), which were predicted and described first by Kaino and co-workers[1–6]. They consist of concentric cylinders of transparent materials; the core material must be highly pure and the best way to achieve this purpose is obviously continuous mass polymerization of thoroughly distilled and filtered monomers or oligomers.

POF cladding material must meet two criteria: low refractive indices and elevated glass transition temperatures. The low refractive index is required to obtain high values of the POFs' optical characteristics, determined particularly through the so-called numerical aperture (N.A.)* whereas the high T_g (namely above 60°C or 333 K) is correlated to the service temperatures.

Synthesis of new fluorine-containing polymers has been investigated extensively[7], particularly for POF cladding applications, but is often an expensive solution for such a problem. We have devoted more attention to looking for blends of commercial polymers either alone or in association with polymers and copolymers readily available, e.g. through free-radical suspension polymerization of commercial monomers.

This series of papers will report our results in a study on the miscibility of various fluorine-containing homo- and copolymers: a vinylic polymer associated with an acrylic one, the miscibility of which is based first on the

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* For the POF made of materials having refractive indices n_1 (core) and n_2 (clad): N.A. = $(n_1^2 - n_2^2)^{1/2} = sin\theta_{max}$, where, θ_{max} is the maximum incidence angle value for light entering the fibre and propagating without transmission loss, according to geometrical optics (from air, $n_0 = 1$)

Table 1 Main characteristics of homo- and copolymers used in blends

Polymer	MF (wt%)	Reference used in text	T_g (K)	T_C (K)	T_m (K)	$-\Delta H_m$ ($J g^{-1}$)	$M_n{}^a$ ($g mol^{-1}$)	$M_w{}^a$ ($g mol^{-1}$)	n_D	MVI (ml/10min)
PVDF	Homopolymer	X8N	245.0		448.1	66			1.4200	4.2
VDF/HFP	9/1	11008	250.8		434.7	30			1.4200	6.9
VDF/HFP	4/1	21508	259.5		408.9	22			1.4200	5.1
PTrFE	Homopolymer		nd		470.7	22			1.3890	2.7
VDF/TrFE	3/1	DA 419125	nd	411	424.0				1.4125	1.6
VDF/TrFE	1/1	DA 419150	nd	339	428.0	26			1.4050	2.3
PMMA	Homopolymer	PMMA	391.0						1.4290	
PMATRIFE	Homopolymer	PMATRIFE	346.0				60 300	108 200	1.4200	
MATRIFE/MMA	33.3/66.6	MAT 33	379.4				59 400	98 400	1.4679	
MATRIFE/MMA	66.6/33.3	MAT 66	370.0				75 600	118 000	1.4440	
MATRIFE/MMA	74.0/26.0	MAT 74	365.2				87 200	130 400		
MATRIFE/MMA	81.3/18.7	MAT 81	360.9				73 700	117 600		

[a] Size exclusion chromatography (s.e.c.): PMMA standards; tetrahydrofuran; T_g: glass transition temperature; T_C: Curie temperature (if any); T_m: melting temperature; M_n: number-average molecular mass (s.e.c. using polystyrene standards); M_w: weight-average molecular mass; n_D: refractive index; MVI: melt volumetric index (at 503 K under 2.16 kg); MF: (mass fraction) (weight percent in monomer units); ΔH_m: enthalpy of melting; nd: not determined

For other abbreviations: see text

existence of specific interactions between polarized C–H bonds in the vinylic structural units and carbonyl groups afforded by the acrylic ester units and then on dipole–dipole associations.

The well-known poly(methyl methacrylate)–poly(vinylidene difluoride) (PMMA–PVDF) mixtures were extensively studied since the early works. The main methods used for characterization are: differential scanning calorimetry (d.s.c.)[8–11], infra-red (i.r.) spectroscopy[12–14], crystallography[15], dilatometry[8], dielectric relaxation[16,17] and nuclear magnetic resonance (n.m.r.)[18–20].

The blends we have examined were analogous to PMMA–PVDF mixtures; derivatization was formally obtained by substituting some hydrogen atoms into these polymers by more or less fluorinated species such as F atoms or CF_3 radicals. Some advantages were expected from this kind of substitution as the copolymers of vinylidene difluoride with hexafluoropropene (HFP) or trifluoroethylene (TrFE) are less crystalline than PVDF itself, thus allowing a probable enlargement of the miscibility domain in such mixtures.

However, substitution of some ester methyl groups in MMA copolymers by fluorine-containing alkyl chain might introduce a competition between these new polar groups and PVDF polarized H–C bonds in their specific interactions with PMMA carbonyl double bonds. Although the extent of the last modification must be less important than the (favourable) crystallinity loss resulting from the use of VDF copolymers instead of PVDF, it might work in the opposite direction and thus a detailed study seemed to be necessary to determine the exact miscibility domains in these copolymer mixtures.

This paper reports a calorimetric study of binary polymer blends obtained by solution mixing of side-chain fluorinated methacrylic copolymers with PVDF and commercially available VDF–HFP and VDF–TrFE copolymers. A limited number of blends were also prepared through mechanical mixing in the molten state. Some aspects of application as POF cladding materials are also described. Ternary mixtures will be described in a forthcoming paper.

EXPERIMENTAL

Materials

Atactic PMMA was kindly supplied by Röhm GmbH (PMMA OF 104S), and the fluorinated vinyl polymers; (PVDF homopolymer, VDF–HFP copolymer and VDF–TrFE) copolymer, were provided by Solvay.

Side-chain fluorinated methacrylic homo- and copolymers were synthesized by free-radical suspension polymerization.

Monomers were purified by filtration through an activated basic alumina column, then saturated with dry nitrogen during 1 h and stored under N_2 at 5°C. Vacuum-distilled dodecanethiol (DDT) was used as chain transfer agent and azobisisobutyronitrile (AIBN), recrystallized from ethanol, as polymerization initiator. The aqueous phase, consisting of distilled water (3.5 L), polyacrylic acid (5 g) and Na_2HPO_4 (45 g), was placed in a 5-L Pyrex reactor at the polymerization temperature (between 55 and 65°C according to the composition) and saturated with nitrogen for 2 h; then, under stirring, monomers (1500 g), AIBN (0.3%) and DDT (0.3%) were rapidly introduced. The progress of polymerization was followed by temperature evolution. An exothermic period was observed after 5–6 h. The reactor was still kept at 55°C for 10 h, then heated to 70°C for 10 h. Polymer beads were separated onto a sintered glass filter and washed several times with distilled water. After drying under vacuum at 55–60°C for 48 h, *ca* 1 mm diameter polymer beads were obtained. The main characteristics of these polymers are listed in *Table 1*.

Analysis for remaining monomer indicated less than 0.2% volatile materials.

Sample preparation

Solution mixing. Blending of fluorinated vinylic polymers and fluorinated methacrylic polymers was carried out by solution mixing followed by fast precipitation. Polymers were dissolved at room temperature in dry dimethylformamide, as 5% (w/w) solutions, then solutions were mixed in the appropriate volumes. After 24 h stirring, the blend solutions were poured into a 100-fold excess volume of distilled water under shaking. The blends were filtered off, washed several times with water and dried *in vacuo* at 70°C to constant weight.

Bulk mixing. Some particular blends were obtained from the melt using an industrial opened two-rolls mixer. Blends of 100 g were prepared and used to determine exact refractive indices and to compare the d.s.c. diagram with the results obtained for precipitated mixtures.

Pellets of PVDF (or a VDF copolymer) and methacrylic copolymers with nearly the same granulometry were molten at 210°C under 200 bar pressure; these mixtures were then placed between rolls heated at 210°C for 10 min mixing. Such polymer blends were then pressed under 200 bars at 210°C during 5 min in a small circular mould and cooled. Samples were removed from the mould and cut into adequate pieces for refractive index measurements and thermal analysis.

D.s.c.

Thermal analysis was performed on a Perkin-Elmer DSC 7 differential scanning calorimeter equipped with an Intracooler II cooling system, under a nitrogen atmosphere, at a heating rate of 20 K $\min^{-1}$ (sample weight in the range 10–15 mg). Temperature and enthalpy calibrations were performed using indium. Powdered blends were compressed at room temperature before thermal analysis.

Glass transition temperatures were read on thermograms as the midpoint of the heat capacity jump. Melting and crystallization temperatures were considered as the maxima of the endothermic and exothermic peaks, respectively. Each sample was analysed twice. The same temperature program was applied to all samples: first heating to 483 K at 20 K $\min^{-1}$ followed by a 5 min isotherm, quenching at 200 K $\min^{-1}$ to 218 K and finally heating to 483 K at a 20 K $\min^{-1}$ rate.

Refractive indices

Refractive indices were determined at 23°C on solid samples using a RL-1 type refractometer from PZO (Warzaw, Poland).

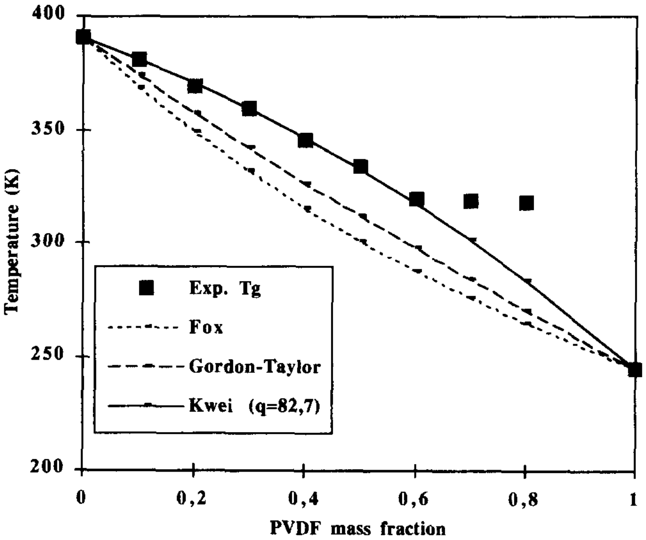

Figure 1 Evolution of T_g in PMMA/PVDF blends: correlation with Fox, Gordon–Taylor and Kwei equations

RESULTS AND DISCUSSION

Binary mixtures from solution blending

PMMA/PVDF systems. PMMA/PVDF blends are well known to give homogeneous phases for the lowest PVDF contents.

We have first done a short study of the commercial PVDF samples we should use for blending with other polymers. Results reported in *Table 2* indicate a behaviour of these samples and of PMMA similar to that previously described: complete miscibility up to 40% (w/w) PVDF content. For blends containing 50 and 60% PVDF, crystallization occurred above the glass transition temperature (T_g). In biphasic blends containing 70% or more PVDF, T_g remains constant at 318–319 K, whereas the melting temperature is slightly increased when the PMMA content is lowered.

Attempts to correlate the observed T_g to blend composition were made according to the following relations:

Table 2 Characteristics of PMMA/PVDF blends

									T_g (K) calculated according to		
PMMA (MF)	PVDF (MF)	PMMA (VF)	PVDF (VF)	T_g (K)	T_c (K)	T_m (K)	Physical state	N_D	Fox[21]	Gordon–Taylor[22]	Kwei ($q = 82.7$)
1.0	0.0	1.000	0.000	391.0			A	1.4920	391.0	391.0	391.0
0.9	0.1	0.931	0.069	381.5			A	1.4870	369.0	374.1	381.5
0.8	0.2	0.857	0.143	369.5			A	1.4817	349.4	357.8	371.0
0.7	0.3	0.778	0.222	359.5			A	1.4760	331.7	342.1	359.5
0.6	0.4	0.692	0.308	346.2			A	1.4698	315.7	326.8	346.6
0.5	0.5	0.600	0.400	333.8	412.1	436.9	M	1.4632	301.2	312.1	332.8
0.4	0.6	0.500	0.500	319.5	368.4	439.1	M	1.4560	288.0	297.8	317.6
0.3	0.7	0.391	0.609	319.0		441.5	C	1.4482	275.9	284.0	301.4
0.2	0.8	0.273	0.727	318.0		443.0	C	1.4397	264.8	270.6	283.8
0.0	1.0	0.000	1.000	245.0		448.1	C	1.4200	245.0	245.0	245.0

VF: volume fraction; A: amorphous; M: metastable; C: crystalline (partially); n_D: refractive index calculated from volume fractions of each polymer introduced into the blends. T_c: crystalline temperature

For other abbreviations: see footnotes to *Table 1*

Fox equation[21]

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

Gordon–Taylor equation[22]

$$T_g = \frac{T_{g1} W_1 + k T_{g2} W_2}{W_1 + k W_2}$$

where T_g, T_{g1} and T_{g2} are, respectively, the glass transition temperature of the blend, pure PVDF and PMMA, W_1 and W_2 are the respective weight fractions of PVDF and PMMA in the blend, and the k parameter corresponds to the ratio of thermal expansion coefficient differences between the two polymers in their rubbery and glassy states at T_g; here, $k = 0.85$. As can be seen in *Figure 1*, the experimental values do not fit well with these models.

Kwei and co-workers[24,25] have introduced into the Gordon–Taylor expression[22] a corrective term (qW_1W_2) that quantifies specific interactions between the two polymers:

$$T_g = \frac{T_{g1} W_1 + k T_{g2} W_2}{W_1 + k W_2} + q W_1 W_2$$

Another equation, the Jenckel–Heusch relation[26] introduces the constant b:

$$T_g = W_1 T_{g1} + W_2 T_{g2} + b(T_{g2} - T_{g1}) W_1 W_2$$

If we apply the Kwei equation to the PMMA/PVDF system with $q = 82.7$, we obtain good correlations of experimental results with theoretical values (*Figure 1*). A similar good fit is observed using the Jenckel–Heusch equation with $b = 0.40$.

The gap observed for blends with high PVDF contents is correlated with their partial crystallization during cooling, thus giving an homogeneous amorphous phase saturated in semi-crystalline polymer with a nearly constant glass transition temperature.

PMMA/(VDF–HFP) copolymer systems. We have studied blends, obtained by substituting PVDF by its copolymers with HFP or TrFE and PMMA by copolymers of MMA and 2,2,2-trifluoroethyl methacrylate (MATRIFE), respectively.

Bulky side-chain groups may be introduced into the PVDF chain by comonomers such as HFP. As described by Bonardelli *et al.*[27], a glass transition temperature increase is observed for these VDF–HFP copolymers.

Commercial VDF–HFP copolymers and with, respectively, 10 and 20% (w/w) HFP units were used as received. As previously described[27] we can observe in these copolymers (*Table 1*) both an increase in the glass transition temperatures and a decrease in the crystallinity contents and melting temperatures as a function of the number of HFP units.

The d.s.c. results obtained for PMMA/VDF–HFP (9/1) copolymers and PMMA/VDF–HFP (4/1) copolymer mixtures are presented in *Tables 3* and *4*. We have supposed that in these blends the k value is the same as for PMMA/PVDF blends ($k = 0.85$). Yet, as was seen for the PMMA/PVDF system, the T_g–composition variations of the two blends show a T_g decrease correlated with the VDF copolymer content of the blends. The poor correlations displayed by T_g values with both the Fox[21] and the Gordon–Taylor[22] relations can be attributed to strong specific interactions between the PMMA and fluorinated copolymers structural units.

The Kwei[24,25] and Jenckel–Heusch[26] relations have been used to correlate T_g and composition of these blends until a good fit was observed, thus allowing q and b interaction parameters to be estimated. The observed decrease in these parameters as a function of the VDF–HFP copolymer compositions shows that the interactions efficiency is influenced by the HFP units content of the different blends (*Table 5*).

However, it can be observed that the VDF–HFP (4/1) copolymer, which is the less crystalline polymer with the lowest melting enthalpy, affords the largest miscibility domain in blends with PMMA. It can also be noticed that this system gives T_g values slightly higher than the T_gs of PMMA/PVDF and PMMA/PVDF–HFP (9/1) copolymer systems.

Trifluoroethyl methacrylate homo and copolymers/PVDF and VDF–HFP copolymer systems. Our study was further extended to blends with substitution of PMMA by MMA–fluoroalkyl methacrylate copolymers.

Table 3 Characteristics of PMMA/VDF–HFP (9/1) copolymer blends

PMMA (MF)	VDF–HFP 9/1 (MF)	PMMA (VF)	VDF–HFP (9/1) (VF)	T_g (K)	T_c (K)	T_m (K)	Physical state	n_D	Fox eq. (K)	Gordon–Taylor eq. (K)
1.0	0.0	1.000	0.000	391.0			A	1.4920	391.0	391.0
0.9	0.1	0.931	0.069	381.7			A	1.4870	370.3	374.8
0.8	0.2	0.857	0.143	370.6			A	1.4817	351.7	359.1
0.7	0.3	0.778	0.222	360.0			A	1.4760	334.8	344.0
0.6	0.4	0.692	0.308	347.1			A	1.4698	319.5	329.4
0.5	0.5	0.600	0.400	334.7			A	1.4632	305.6	315.2
0.4	0.6	0.500	0.500	320.6	361.0	422.5	M	1.4560	292.8	301.5
0.3	0.7	0.391	0.609	306.8	353.6	425.1	M	1.4482	281.0	288.2
0.2	0.8	0.273	0.727	309.9	348.7	428.5	M	1.4397	270.2	275.4
0.1	0.9	0.143	0.857	nd		433.6	C	1.4303	260.1	262.9
0.0	1.0	0.000	1.000	250.8		434.7	C	1.4200	250.8	250.8

Abbreviations: see footnotes to *Tables 1* and *2*

Table 4 Characteristics of PMMA/VDF-HFP (4/1) copolymer blends

PMMA (MF)	VDF-HFP (4/1) (MF)	PMMA (VF)	VDF-HFP 4/1 (VF)	T_g (K)	T_c (K)	T_m (K)	Physical state	n_D	Fox eq. (K)	Gordon-Taylor eq. (K)
1.0	0.0	1.000	0.000	391.0			A	1.4920	391.0	391.0
0.9	0.1	0.931	0.069	382.7			A	1.4870	372.1	375.8
0.8	0.2	0.857	0.143	372.0			A	1.4817	355.0	361.1
0.7	0.3	0.778	0.222	360.9			A	1.4760	339.4	346.9
0.6	0.4	0.692	0.308	349.9			A	1.4698	325.1	333.2
0.5	0.5	0.600	0.400	336.4			A	1.4632	312.0	319.9
0.4	0.6	0.500	0.500	323.9			A	1.4560	299.8	307.1
0.3	0.7	0.391	0.609	309.1			A	1.4482	288.6	294.6
0.2	0.8	0.273	0.727	292.3	355.7	401.9	M	1.4397	278.2	282.5
0.1	0.9	0.143	0.857	nd	335.0	405.4	M	1.4303	268.5	270.8
0.0	1.0	0.000	1.000	259.5		408.9	C	1.4200	259.5	259.5

Abbreviations: see footnotes to *Tables 1* and *2*

Table 5 Evolution of Kwei parameter q and Jenckel-Heusch parameter b values in fluorinated acrylic-vinylic polymer blends

	Vinylic polymer		
Acrylic polymer	PVDF homopolymer	VDF-HFP (9/1) copolymer	VDF-HFP (4/1) copolymer
PMMA	$q = 82.7$	$q = 76.0$	$q = 68.2$
	$b = 0.400$	$b = 0.375$	$b = 0.363$
MAT 33	$q = 65.1$	$q = 58.3$	$q = 51.3$
	$b = 0.312$	$b = 0.288$	$b = 0.270$
MAT 66	$q = 45.3$	$q = 35.1$	$q = 26.7$
	$b = 0.200$	$b = 0.126$	$b = 0.074$

Table 6 PMATRIFE/VDF-HFP (9/1) copolymer blends T_g and T_m *versus* VDF-HFP (9/1) copolymer mass fraction

PMATRIFE (MF)	VDF-HFP (9/1) (MF)	T_{g1} (K)	T_{g2} (K)	T_m (K)
1.0	0.0		350.5	
0.8	0.2	253.1	347.3	431.2
0.6	0.4	250.3	345.5	431.7
0.4	0.6	249.9	346.2	432.5
0.2	0.8	251.2	342.5	432.7
0.0	1.0	250.8		434.7

Results obtained for mixtures containing copolymers of MMA and 1,1,3,3-tetrafluoropropyl methacrylate were quite similar to those obtained for copolymers of MMA and MATRIFE. Therefore, only these results are reported here.

Trifluoroethyl methacrylate homopolymer/PVDF and VDF/HFP copolymer systems. Blends of MATRIFE homopolymers with PVDF and its VDF-HFP (4/1) and VDF-HFP (9/1) copolymers have been studied first. The d.s.c. scans recorded after quenching show two glass transitions near the T_gs observed for each polymer present in the blends (*Table 6*). A melting peak corresponding to the partially crystalline vinylic polymer was also observed. These systems are obviously not miscible although we can notice a slight decrease in the PMATRIFE-rich phase T_{g2} as the VDF-HFP copolymer content increases, indicating a slight miscibility of some VDF-HFP copolymer macromolecules in this homopolymer.

The excellent compatibility of PVDF with ethyl methacrylate homopolymer (PEMA) has been previously described[28]; thus, our results on PMATRIFE/PVDF blends give evidence of the influence of the fluoroalkyl lateral chain on the miscibility decrease in these systems. Other considerations based on fluorine electronegativity could also explain that these polymers are not miscible. In PMMA/PVDF or PEMA/PVDF systems, miscibility occurs from attractive intermolecular interactions (hydrogen bond between PMMA carbonyl group and PVDF hydrogen atoms); the use of fluorinated methacrylate polymers necessarily introduces new but repulsive dipolar interactions (unfavourable to miscibility) between fluorine atoms present in both polymer chains. Moreover, the high electronegativity of fluorine atoms influences the vicinal hydrogen atoms of fluoroalkyl chain CF_3 or CF_2 groups through C-H bond polarization; therefore, these hydrogen atoms become more acidic and can enter in competition for *intra*molecular bonds as well as *inter*molecular hydrogen interactions between methacrylic units.

As shown in *Figure 2*, these intramolecular interactions can take place either between vicinal monomers units such as MMA and a fluorine-containing methacrylate unit or in the last type of monomer units through a five-membered ring. A third possibility of intramolecular interaction between successive fluorine-containing methacrylate units was also examined from entropy consideration, although MMA is probably a stronger acceptor in such weaker bondings than its

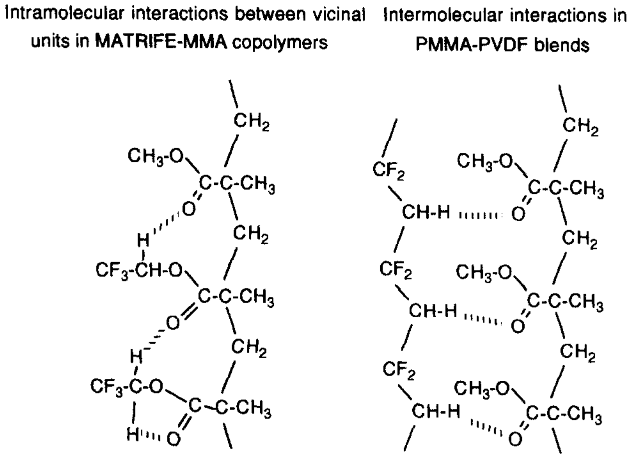

Figure 2 Intra- and inter-molecular interactions

Table 7 Characteristics of MAT 66/PVDF blends

MAT 66 (MF)	PVDF (X8N) (MF)	T_g (K)	T_c (K)	T_m (K)	Physical state	n_D
1.0	0.0	370.0			A	1.4440
0.9	0.1	360.8			A	1.4422
0.8	0.2	346.3	410.5	443.3	M	1.4401
0.7	0.3	336.7	405.0	439.9	M	1.4380
0.6	0.4	327.2	369.1	443.5	M	1.4358
0.5	0.5	314.0	350.9	447.5	M	1.4334
0.4	0.6	311.5		446.0	C	1.4310
0.0	1.0	245.0		448.1	C	1.4200

Abbreviations: see footnotes to *Tables 1* and *2*

Table 8 Characteristics of MAT 33/PVDF blends

MAT 33 (MF)	PVDF (X8N) (MF)	T_g (K)	T_c (K)	T_m (K)	Physical state	n_D
1.0	0.0	379.4			A	1.4679
0.9	0.1	370.5			A	1.4643
0.8	0.2	358.6			A	1.4605
0.7	0.3	348.0			A	1.4565
0.6	0.4	334.9	421.7	440.0	M	1.4523
0.5	0.5	319.3	398.0	438.4	M	1.4477
0.4	0.6	326.6	369.2	442.2	M	1.4429
0.2	0.8	325.1		445.9	C	1.4323
0.0	1.0	245.0		448.1	C	1.4200

Abbreviations: see footnotes to *Tables 1* and *2*

Table 9 Characteristics of MAT 33/VDF–HFP (9/1) copolymer blends

MAT 33 (MF)	VDF–HFP (9/1) (MF)	T_g (K)	T_c (K)	T_m (K)	Physical state	n_D
1.0	0.0	379.4			A	1.4679
0.9	0.1	370.2			A	1.4643
0.8	0.2	359.6			A	1.4605
0.7	0.3	349.3			A	1.4565
0.6	0.4	336.4			A	1.4523
0.5	0.5	323.0			A	1.4477
0.4	0.6	311.0	396.0	427.4	M	1.4429
0.3	0.7	294.7	334.4	429.5	M	1.4378
0.2	0.8	nd		433.5	C	1.4323
0.0	1.0	250.8		434.7	C	1.4200

Abbreviations: see footnotes to *Tables 1* and *2*

Table 10 Characteristics of MAT 66/VDF–HFP (9/1) copolymer blends

MAT 66 (MF)	VDF–HFP (9/1) (MF)	T_g (K)	T_c (K)	T_m (K)	Physical state	n_D
1.0	0.0	370.0			A	1.4440
0.9	0.1	359.1			A	1.4422
0.8	0.2	347.5			A	1.4401
0.7	0.3	338.8			A	1.4380
0.6	0.4	326.8			A	1.4358
0.5	0.5	314.2	370.0	429.6	M	1.4334
0.4	0.6	290.9	338.1	431.9	M	1.4310
0.3	0.7	nd		432.1	C	1.4230
0.1	0.9	nd		433.3	C	1.4230
0.0	1.0	250.8		434.7	C	1.4200

Abbreviations: see footnotes to *Tables 1* and *2*

Table 11 Characteristics of MAT 33/VDF–HFP (4/1) copolymer blends

MAT 33 (MF)	VDF–HFP (4/1) (MF)	T_g (K)	T_c (K)	T_m (K)	Physical state	n_D
1.0	0.0	379.4			A	1.4679
0.9	0.1	370.2			A	1.4643
0.8	0.2	361.2			A	1.4605
0.7	0.3	351.5			A	1.4565
0.6	0.4	339.3			A	1.4523
0.5	0.5	326.5			A	1.4477
0.4	0.6	313.6			A	1.4429
0.3	0.7	300.9	367.5	397.2	M	1.4378
0.2	0.8		333.8	402.8	M	1.4323
0.1	0.9			406.3	C	1.4264
0.0	1.0	259.5		408.9	C	1.4200

Abbreviations: see footnotes to *Tables 1* and *2*

Table 12 Characteristics of MAT 66/VDF–HFP (4/1) copolymer blends

MAT 66 (MF)	VDF–HFP (4/1) (MF)	T_g (K)	T_c (K)	T_m (K)	Physical state	n_D
1.0	0.0	370.0			A	1.4440
0.9	0.1	359.1			A	1.4422
0.8	0.2	350.4			A	1.4401
0.7	0.3	339.5			A	1.4380
0.6	0.4	328.2			A	1.4358
0.5	0.5	315.0			A	1.4310
0.4	0.6	294.0	360.0	399.3	M	1.4310
0.3	0.7	283.4	338.1	402.5	M	1.4285
0.1	0.9	nd		406.8	C	1.4230
0.0	1.0	259.5		408.9	C	1.4200

Abbreviations: see footnotes to *Tables 1* and *2*

fluorine containing equivalents, as a consequence of the electron withdrawing in fluorine–carbon bonds.

Following these considerations, the total intermolecular interaction enthalpy in blends will thus be lowered as a consequence of strong internal intramolecular interactions from the fluorine containing acylic ester units either with themselves or with vicinal carbonyl containing structural units.

Trifluoroethyl methacrylate copolymers/PVDF and VDF/HFP copolymer systems. In order to obtain amorphous homogeneous materials, we have substituted fluorinated methacrylate homopolymers by some MMA-based copolymers. Two copolymer compositions (MAT 33 and MAT 66 according to *Table 1*) have been synthesized and used in blends with vinylic fluorinated polymers.

Thermal analysis results presented in *Tables 7–12* give evidence for the existence of large miscibility domains in these blends: in all non-crystalline blends, we have observed only one glass transition temperature, the value of which is strongly correlated with blends composition.

Whatever the methacrylic copolymer we have used, the blends offering the largest miscibility domains were observed with VDF–HFP (4/1) copolymer, as noted above with PMMA itself. Introduction of MATRIFE units in methacrylic polymer also leads to a decrease of the glass transition temperature, and the miscibility domain widths are reduced.

Again, intermolecular interactions intensity has been estimated through Kwei and Jenckel–Heusch relations; *q* and *b* parameters calculated to fit best with experimental results are presented in *Table 5* for the studied blends; *Figures 3* and *4* show their variations *versus* the MATRIFE unit content in methacrylic copolymers.

It is clear from these results that intermolecular interaction intensities rapidly decrease with increasing MATRIFE contents in the methacrylate copolymers. Although copolymerization of VDF with 10 and 20%

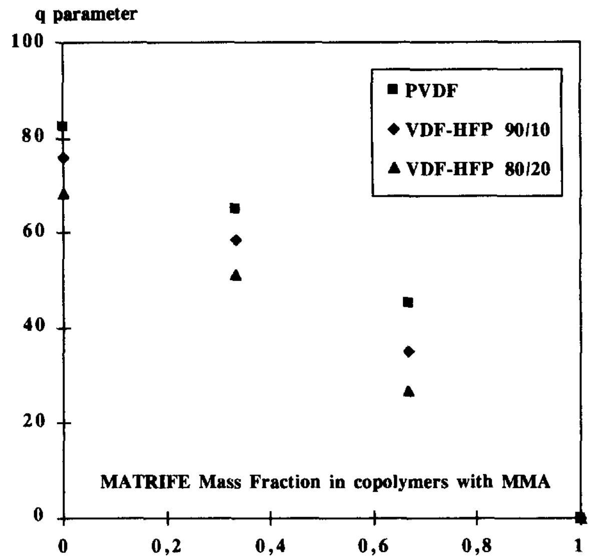

Figure 3 Kwei parameter *versus* MATRIFE mass fraction in fluorinated methacrylate/VDF–copolymer blends

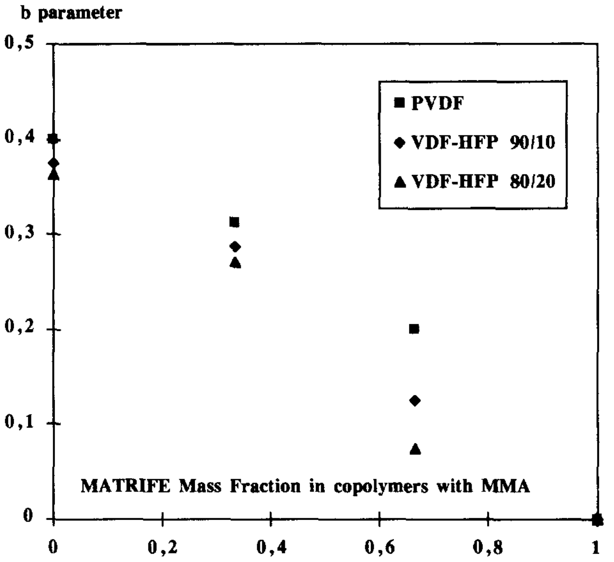

Figure 4 Jenckel–Heusch parameter (*b*) *versus* MATRIFE mass fraction in fluorinated copolymers/VDF–HFP copolymer blends

HFP has a positive influence on the 'width' of the miscibility domains—correlated with crystallinity loss in the copolymers—it has a negative influence on the interactions intensity as measured through q as well as b parameters. This result may be understood in taking account of the loss of H-bonding sites on PVDF as more VDF units are replaced by HFP units.

Our results are thus consistent with both Kwei and Jenckel–Heusch correlation and inconsistent with the Gordon–Taylor relation[22]. An approximately linear decrease of q and b parameters can be observed in relation to a MATRIFE content increase in the methacrylic copolymers. A more detailed investigation should be useful to obtain more information.

We can conclude that an increase of the HFP unit content of PVDF chains or an increase in MATRIFE unit content of methacrylic copolymers contribute in the same way to a decrease in q and b parameters and thus to the lowering of the hydrogen bond interaction intensity between polymers. It can be explained by steric hindrance increase and creation of unfavourable interactions induced by the introduction of such comonomers in the blends.

PMMA/VDF–TrFE copolymers system. As for HFP monomers, bulky comonomers such as TrFE units introduce defaults in the PVDF chain; the presence of a more strongly positive hydrogen atom in TrFR units can also contribute to hydrogen bond formation. However, TrFE–VDF copolymerization with reactivity parameters near 0.5 and 0.7[29] leads to partially crystalline polymers with high melting temperatures. It can be explained by the fact than TrFE units are able to crystallize; PTrFE polymer itself is a crystalline polymer ($T_m = 473$ K) as well as PVDF.

Nevertheless, calorimetric study of these copolymers by Yagi *et al.*[30] shows that it is possible to obtain materials with melting points lower than the PVDF melting temperature. We can also see on thermograms the presence of a second endothermic peak, only for copolymers with more than 50% TrFE units, which corresponds to the Curie temperature T_C. When enough VDF units are present in the copolymer, crystallite melting occurs before the conformation change happens ($T_m > T_C$).

Another advantage for TrFE monomer use is a lower PTrFE refractive index than that for PVDF (1.3890

Table 13 Characteristics of PMMA/VDF–TrFE (3/1) copolymer blends

PMMA (MF)	VDF–TrFE (3/1) (MF)	PMMA (VF)	VDF–TrFE (3/1) (VF)	Physical state	T_g (K)	T_C (K)	T_m (K)	n_D
1.0	0.0	1.000	0.000	A	391.0			1.4920
0.9	0.1	0.931	0.069	A	379.2			1.4865
0.8	0.2	0.857	0.143	A	368.1			1.4806
0.7	0.3	0.778	0.222	A	357.8			1.4744
0.6	0.4	0.692	0.308	A	346.9			1.4675
0.5	0.5	0.600	0.400	A	334.5			1.4602
0.4	0.6	0.500	0.500	A	321.0			1.4523
0.3	0.7	0.391	0.609	A	311.7			1.4436
0.2	0.8	0.273	0.727	C	322.0	403.5	413.9	1.4342
0.0	1.0	0.000	1.000	C	nd	411.0	424.0	1.4125

Abbreviations: see footnotes to *Tables 1* and *2*

against 1.4200). Addition of TrFE units to the PVDF chain could then contribute to lower the refractive indices in such copolymers.

Two VDF–TrFE copolymers have been used: VDF–TrFE 3/1 and VDF–TrFE 1/1. Blends with PMMA have been prepared as described above and studied by d.s.c. Results presented in *Tables 13* and *14* show that T_m and T_C have disappeared; a single T_g is observed for less than 70 wt% of VDF–TrFE copolymer in PMMA/VDF–TrFE 3/1 blend and less than 60 wt% of VDF–TrFE copolymer in PMMA/VDF–TrFE 1/1 blend. We can conclude that the polymers used are compatible. However, the T_gs of PMMA/VDF–TrFE 3/1 copolymer are lower than the T_gs of PMMA/VDF–TrFE 1/1 copolymer.

For higher contents, materials become partially crystalline; we can note on the thermograms a second peak characteristic of the Curie transition corresponding to ferromagnetic properties of the (VDF–TrFE) crystalline phase, despite the addition of PMMA. A simultaneous lowering of T_m and T_c is, however, observed.

We can also notice that the PMMA/(VDF–TrFE) system miscibility domain slightly narrows for a higher TrFE unit content of the PVDF chain. Because of substitution of VDF monomer units by TrFE units in the fluorinated polymer, the number of hydrogen atoms in

Table 14 Characteristics of PMMA/VDF–TrFE (1/1) copolymer blends

PMMA (MF)	VDF–TrFE (1/1) (MF)	PMMA (VF)	VDF–TrFE (1/1) (VF)	Physical state	T_g (K)	T_c (K)	T_C (K)	T_m (K)	n_D
1.0	0.0	1.000	0.000	A	391.0				1.4920
0.9	0.1	0.931	0.069	A	383.1				1.4860
0.8	0.2	0.857	0.143	A	371.5				1.4795
0.7	0.3	0.778	0.222	A	362.2				1.4727
0.6	0.4	0.692	0.308	A	352.5				1.4652
0.5	0.5	0.600	0.400	A	343.9				1.4572
0.4	0.6	0.500	0.500	A	333.0				1.4485
0.3	0.7	0.391	0.609	M	324.6	398.1		418.7	1.4390
0.2	0.8	0.273	0.727	C	nd		332.5	421.2	1.4287
0.0	1.0	0.000	1.000	C	nd		339.0	428.0	1.4050

Abbreviations: see footnotes to *Tables 1* and *2*

Table 15 Characteristics of MAT 33/VDF–TrFE (3/1) copolymer blends

MAT 33 (MF)	VDF–TrFE (3/1) (MF)	MAT 33 (VF)	VDF–TrFE (3/1) (VF)	T_g (K)	T_C (K)	T_m (K)	Physical state	n_D
1	0	1.000	0.000	379.4			A	1.4679
0.9	0.1	0.925	0.075	371.9			A	1.4638
0.8	0.2	0.846	0.154	361.3			A	1.4594
0.7	0.3	0.763	0.237	352.1			A	1.4547
0.6	0.4	0.674	0.326	341.0			A	1.4498
0.5	0.5	0.579	0.421	329.7			A	1.4446
0.4	0.6	0.479	0.521	318.0			A	1.4390
0.2	0.8	0.256	0.744	330.3	407.3	416.0	C	1.4267
0	1	0.000	1.000	nd	411.0	424.0	C	1.4125

Abbreviations: see footnotes to *Tables 1* and *2*

Table 16 Characteristics of MAT 33/VDF–TrFE (1/1) copolymer blends

MAT 33 (MF)	VDF–TrFE (1/1) (MF)	MAT 33 (VF)	VDF–TrFE (1/1) (VF)	T_g (K)	T_c (K)	T_C (K)	T_m (K)	Physical state	n_D
1	0	1.000	0.000	379.4				A	1.4679
0.9	0.1	0.925	0.075	373.6				A	1.4632
0.8	0.2	0.846	0.154	365.8				A	1.4582
0.7	0.3	0.763	0.237	357.8				A	1.4530
0.6	0.4	0.674	0.326	347.4				A	1.4474
0.5	0.5	0.579	0.421	337.6				A	1.4414
0.4	0.6	0.479	0.521	328.0	396.3		421.7	M	1.4351
0	1	0.000	1.000	nd		339.0	428.0	C	1.4050

Abbreviations: see footnotes to *Tables 1* and *2*

Table 17 Characteristics of MAT 66/VDF–TrFE (3/1) copolymer blends

MAT 66 (MF)	VDF–TrFE (3/1) (MF)	MAT 66 (VF)	VDF–TrFE (3/1) (VF)	T_g (K)	T_{c1} (K)	T_{c2} (k)	T_C (k)	T_m (k)	Physical state	n_D
1	0	1.000	0.000	370.0					A	1.4440
0.9	0.1	0.920	0.080	358.1					A	1.4416
0.8	0.2	0.836	0.164	350.8					A	1.4388
0.7	0.3	0.748	0.252	339.3					A	1.4361
0.6	0.4	0.656	0.344	330.1					A	1.4332
0.5	0.5	0.560	0.440	318.3					A	1.4301
0.4	0.6	0.459	0.541	306.7	347.1	393.0	385.8	414.0	M	1.4270
0.2	0.8	0.242	0.758	326.9			406.8	417.2	C	1.4201
0	1	0.000	1.000	nd			411.0	424.0	C	1.4125

Abbreviations: see footnotes to *Tables 1* and *2*

Table 18 Characteristics of MAT 66/VDF–TrFE (1/1) copolymer blends

MAT 66 (MF)	VDF–TrFE (1/1) (MF)	MAT 66 (VF)	VDF–TrFE (1/1) (VF)	T_g (K)	T_c (K)	T_C (K)	T_m (K)	Physical state	n_D
1	0	1.000	0.000	370.0				A	1.4440
0.9	0.1	0.920	0.080	361.8				A	1.4410
0.8	0.2	0.836	0.164	354.4				A	1.4376
0.7	0.3	0.748	0.252	345.5				A	1.4342
0.6	0.4	0.656	0.344	334.1				A	1.4306
0.5	0.5	0.560	0.440	325.7	375.3		415.3	M	1.4268
0.4	0.6	0.459	0.541	316.0	351.8		417.8	M	1.4229
0.2	0.8	0.242	0.758	nd		341.5	425.8	C	1.4144
0	1	0.000	1.000	nd		339.0	428.0	C	1.4050

Abbreviations: see footnotes to *Tables 1* and *2*

the copolymer is lowered and consequently the creation of hydrogen bond interactions with PMMA carbonyl groups is reduced.

Blending of VDF–HFP 4/1, VDF–TrFE 3/1 and VDF–TrFE 1/1 copolymers with PMMA has been studied. The higher glass transition temperature is obtained for PMMA/(VDF–TrFE 1/1) system.

MATRIFE–MMA copolymer/VDF–TrFE copolymer systems. To improve blend characteristics for POF applications, fluorinated methacrylic copolymers of lower refractive indices have been substituted for PMMA. Blends of VDF–TrFE copolymers with MATRIFE–MMA (1/2) and MATRIFE–MMA (2/1) copolymers have been prepared and studied by thermal analysis.

The results reported in *Tables 15–18* show that all the MATRIFE–MMA/VDF–TrFE copolymer blends are more or less compatible. Amorphous materials are obtained in some range of compositions. We can, however, notice a narrowing of the miscibility domains when there is an increase in the number of MATRIFE units in methacrylic copolymer or TrFE units in VDF–TrFE increases. Correlations of T_g *versus* the VDF content through the various relations was not attained for these blends as the VDF–TrFE copolymers are too different from PVDF homopolymers to use the same *k* value.

Optical material application in POF

Technical background. As indicated in the Introduction, POFs are obtained preferably through simultaneous coextrusion of both core and cladding materials. When PMMA ($n_1 = 1.4920$, $T_g = 115$°C) is chosen as core material, cladding materials need to have a sufficiently high T_g so that its thermal behaviour is similar to that of PMMA. In practice, a T_g above 60°C (333 K) is required for room temperature applications.

POF optical properties are strongly dependent on the physical and chemical purity of the core material. The best process to fit these requirements is achieved through continuous mass polymerization of specially purified MMA, followed by degassing extrusion and coextrusion with the cladding material. The later needs also to be free of any solid particles or anistropy in the interface vicinity. So it seems that at first semi-crystalline polymers could not be used for such a purpose.

The second strong requirement is that the cladding material refractive index (n_2) must be as low as possible in contrast to the core material index (n_1). Usually for PMMA-core POF, n_2 must be lower than 1.44, thus allowing N.A. values larger than 0.40, sufficient for normal uses in e.g. local networks or transportation vehicles.

Blends selection. From the preceding tables, it is clear that many amorphous blends might be used as POF cladding materials. A summary of the available compositions appears in *Table 19* (only tested limits are indicated).

Table 19 Blend compositions available as POF cladding materials

A (acrylic polymer)	V (vinylic polymer)	A/V blend composition	Calculated n_D	T_g (K) (solution blending)
MAT 66	PVDF–HFP (4/1)	From 7/3 to 4/1	1.4380–1.4401	339–350
MAT 66	PVDF–TrFE (3/1)	From 7/3 to 4/1	1.4361–1.4388	343–350
MAT 66	PVDF–TrFE (1/1)	From 3/2 to 4/1	1.4306–1.4376	334–354

Table 20 Characteristics of fluorinated methacrylic copolymers/VDF–HFP and VDF–TrFE copolymer blends

A (acrylic polymer)	V (vinylic polymer)	A/V Blend composition	Experimental n_D	Calculated n_D	T_g (K) (Bulk melt blending)	T_g (K) (solution blending)
MAT 66	PVDF	9/1	1.4401	1.4422	359	361
		4/1	1.4359	1.4401	349	346
MAT 74	PVDF	9/1	1.4348	1.4372	356	
		4/1	1.4319	1.4356	349	
MAT 66	VDF–HFP (4/1)	7/3	1.4303	1.4380	341	339
MAT 74	VDF–HFP (4/1)	4/1	1.4322	1.4356	349	
MAT 81	VDF–HFP (4/1)	9/1	1.4304	1.4324	351	
MAT 66	VDF–Trfe (3/1)	7/3	1.4302	1.4361	338	339
MAT 74	VDF–TrFE (3/1)	4/1	1.4303	1.4345	347	
MAT 66	VDF–TrFE (1/1)	7/3	1.4253	1.4342	346	345
MAT 74	VDF–TrFE (1/1)	4/1	1.4289	1.4333	352	
MAT 81	VDF–TrFE (1/1)	9/1	1.4285	1.4314	354	
		4/1	1.4248	1.4285	348	

Results for bulk-mixed blends. As shown in the preceding section, MAT 66 is an interesting material for optical materials prepared through blending with VDF copolymers. It is also clear that high MATRIFE contents induce higher T_gs as well as lower refractive indices.

Some methacrylic copolymers, slightly different in composition, were then prepared for large scale testing: namely, MAT 74 (74% MATRIFE–26% MMA) and MAT 81 (81% MATRIFE–19% MMA). These copolymers were examined as well as MAT 66 itself, through bulk melt blending with the selected fluorinated vinyl polymers: PVDF homopolymer, VDF–HFP 4/1, VDF–TrFE 3/1 and VDF–TrFE 1/1 copolymers. The main results are reported in *Table 20* and show that blending efficiency is quite good in the melt process as it appears from the nearly identical glass transition temperatures observed in both blending procedures.

However, systematic differences are noted between the measured and the estimated blends' refractive indices. The measured value is always lower than the calculated one. These results may be understood by taking into account that no density correction was introduced in the n_D calculations: the reference refractive indices for pure vinylic polymers were measured (or given) for semi-crystalline materials, whereas the examined blends were totally amorphous. It would, therefore, have been useful to correct the value by using the crystallinity ratio in the starting vinylic polymers and copolymers. These data are somehow difficult to estimate for some copolymers we have used and we have preferred to underestimate the usefulness in the screening of blends described in the former parts of this paper.

POFs with semi-crystalline cladding material. An important result from the above study is the quite large miscibility domain in blends of PMMA (homopolymer) with the less crystalline VDF–HFP or VDF–TrFE copolymers. As the core material of POF is pure PMMA, a co-extrusion process including such a VDF copolymer will create an interfacial contact zone between the molten PMMA and VDF copolymer. It could be reasonably supposed that interdiffusion between the two polymers could be sufficient to create very interesting characteristics in the so-obtained POF:

- High adhesion between core and cladding materials as a result of strong intermolecular interactions.
- Progressive refractive index transition in the interface.
- Formation of an amorphous intermediate layer thick enough to avoid light penetration in the semi-crystalline cladding material through coextrusion of VDF-copolymer cladding on continuously free-radical polymerized high purity PMMA.

The last point seems nearly obvious in the case of the

VDF copolymers in which PMMA contents as low as 20–30% are often sufficient to suppress crystallization.

Pilot experiments conducted by the late Gilbert Clouet[31] and his co-workers at the Institut Charles Sadron (Strasbourg, France) have largely confirmed this assumption, yielding POFs of high mechanical and optical performances. An industrial procedure for POF production has been developed using both bulk continuous MMA free-radical polymerization and VDF copolymer cladding through coextrusion.

CONCLUSION

Various types of substitution have been used in blends similar to the well known PMMA–PVDF system. In VDF–HFP and VDF–TrFE copolymers, the crystallinity loss induced by the comonomer units is associated with an enlargement of the miscibility domains in blends with PMMA as well as MMA copolymers containing fluorinated alkyl ester groups

However, the increasing substitution of methyl ester groups in PMMA by trifluoroethyl induces more intramolecular interactions which take place *in* and/or *between* the methacrylic polymer structural units. As a result of this kind of competition the intensity of intermolecular interactions is lowered and miscibility with PVDF or VDF copolymers appears only for lower vinylic polymer concentrations. This effect is well documented through the influence of each copolymer composition on the q and b parameter values appearing, respectively, in Kwei and Jenckel–Heutsch correlations.

Other methods—including infra-red spectroscopy—will be employed in the near future to improve our knowledge on these blends.

This study on binary blends has allowed us to obtain amorphous blends useful as optical cladding in POF preparation as well as to make more clear the use of semi-crystalline VDF copolymers in the same application.

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