SYNTHESIS AND OPTICAL PROPERTIES ANALYSIS OF A NEW POLYMERIC OPTICAL FIBER FOR SIDE LIGHTING

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A new plastic optical fibre (POF) for lighting having good optical properties (transmission and diffusion) was developed. The plastic optical fibre was prepared using butylmethacrylate and acrylate monomers by bulk radical polymerisation. The possibility of increasing scattering loss which does not depend on the wavelength in an optical fibre for lighting application was described. A heterogeneous structure which increases the scattering light is generated during the reactive processing by the introduction of particles in the system. The strong contribution of the light scattering induced by the PMMA particles was described. The techniques used to determine the optical properties were light scattering and transmission. The present study illustrates the control of optical properties by the chemical composition of the POF.

INTRODUCTION

During the past 45 years, a new type of optical fibre has been researched, namely the plastic optical fibre. Polymer Optical Fibres (POF) used for optical communication are highly flexible waveguides composed of nearly transparent materials.

Specifically, the well-known plastic optical fibres with PMMA core were introduced in the 1960's, although the first glassy optical fibres were used as communication channel. In the last several decades, concurrent with the successive improvements in glass fibres, POFs have become increasingly popular, owing to their growing utility.[1] Due to their flexibility and high elasticity properties, POF are used in order to obtain interesting materials for optical devices.[2] In comparison with glass fibres, the POF curvature radius is 20 times the fibres diameter. This characteristic makes possible the use of POF with larger diameters than 500 μm.

Because of their properties, POFs varied applications have been developed and commercialised, from their use in simple light transmission guide (decorative and signage applications) to sensors[3] and telecommunication cables.

The main objective of this work is to achieve a prototype of plastic optical fibre with a good transmittance and where to be able to adjust the diffusion properties. The specifications to obey are the following: to increase the levels of luminance, to have an uniform lighting on the whole length of the fibre, to avoid the drifts of light colour and to get flexible fibres.

A large core plastic optical fibre (10 mm of core diameter) with an increased and well-controlled luminance was developed. The chemical synthesis process of this new fibre and its optical characterisation is shown in this paper. This light pipe is used for lateral illumination. This study has been made to provide inexpensive, flexible, and durable light guides.

The cross-section of POFs is circular and, generally, divisible into two layers called core and cladding. Most of the light propagates along the core, which is achieved by surrounding the core with a cladding of a lower refractive index.

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The essential of this study is based on the composition of the core material of the fibres, but it is however necessary to find a cladding allowing the achievement of some regular samples of fibre in their shape and interface flawless. The choice of usable material is limited due to the drifts of colour, so that it is necessary that the refractive index of the cladding is lower than that of the core. Some fluorinated materials are generally used for their weak refractive index (order of 1.35), chemical resistance and anti-adhesive properties. For a good transmission, a thermally retractable cladding and a copolymer of tetrafluoroethylene/hexafluoropropylene (TFE/HFP) was used. In this case, during the polymerisation a regular interface between the core and the cladding was achieved.

EXPERIMENTAL PART

The polymer generally used as core material is the poly(methyl methacrylate) (PMMA) because of its excellent transmission properties in the visible. But this polymer has a poor heat resistance leading to a major limitation. The maximum temperature where PMMA can be used is around 90°C. Above 90°C, its microstructure is modified with mechanical properties loss. A method used to improve the heat resistance of polymer light pipe is the modification of the polymer core structures by inserting a multifunctional monomer.

Basically, large diameter polymer light pipes are prepared by bulk radical polymerisation of butylmethacrylate. Ethyleneglycoldimethacrylate, the multifunctional monomer, is used to provide a cross-linked structure and therefore to enhance the heat resistance. Simultaneously, monomers with a long alkyl chain (ethyltriglycolmethacrylate (MET) or butylacrylate (BA)) were polymerised to improve polymer light pipes flexibility. Therefore, adjustment of the compositions of different compounds produces a polymer light pipe with good heat resistance, flexibility and optical transmission properties.

Materials

Butylmethacrylate (BMA), Butylacrylate (BA), Ethyleneglycoldimethacrylate (EGDMA), Azobisisobutyronitrile (AIBN), Ethyltriglycolmethacrylate (MET), PMMA were supplied by Aldrich Company. Monomers were dried over calcium hydride (CaH_2) and distilled, in order to remove the stabiliser, and degassed before use. Butylmethacrylate was carefully distilled under reduced pressure after treatment with sodium hydroxyl solution (5% wt in water). The copolymer hexafluoropropylen-tetrafluoroethylene (FEP) used as a tube with the outer diameter of 12.7 mm and the width wall of around 0.4 mm, exhibits the refractive index n = 1.34 (Adtech).

Polymerization

The solution including the monomers, the cross-linking agent and the initiator is filtered on fritted disc with 10 μm pore diameter and degassed by nitrogen. The polymerisation reaction is performed under a nitrogen pressure of 2 bars, at 85°C, and 6 h with a rate of heating of 1°C/min.

Characterisation

The fibre samples of different compositions were characterised by spectrometric measures.

Transmission of short fibres (11-15 cm) was measured with a UV-Visible spectrophotometer JASCO 7800.

The attenuation of light of the produced POF was measured by a classical spectroscopic method for wavelengths from 350 to 800 nm. The light source is a halogen lamp coupled to a grating monochromator. The outer intensity is measured with a silicon-photodiode (Fig. 1). The light diffusion was measured via the previous system.

The devices used in lighting to determine a luminance, with an integrating sphere, were provided by PHILIPS, Fig. 2.

The Differential Scanning Calorimeter (DSC) analysis was performed under flowing nitrogen using a Setaram DSC 92 equipment. The samples were sealed in DSC pans and run at 10°C/min under nitrogen atmosphere.
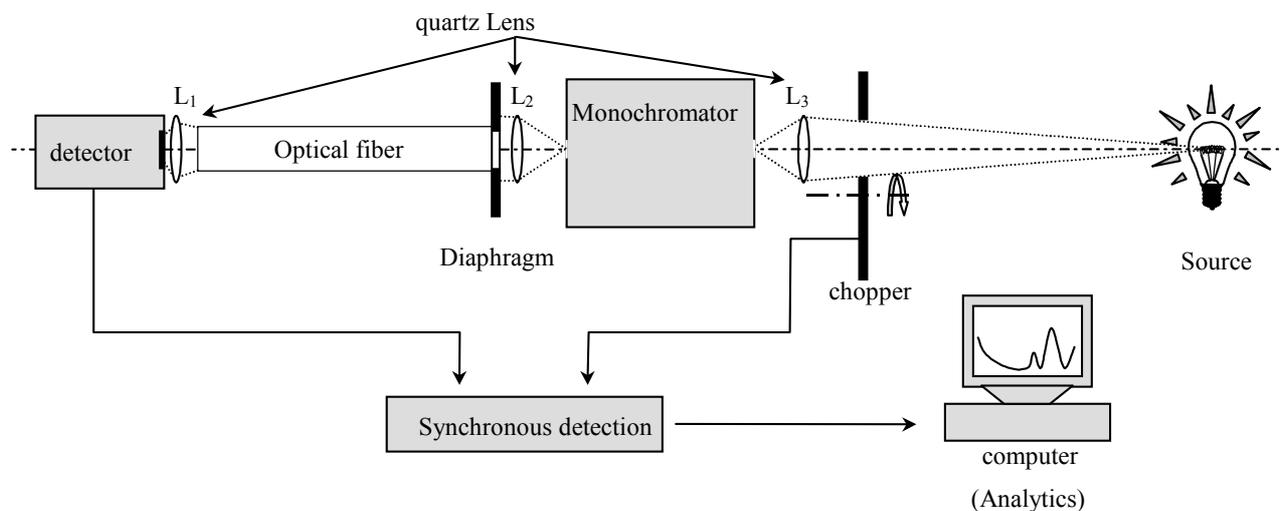

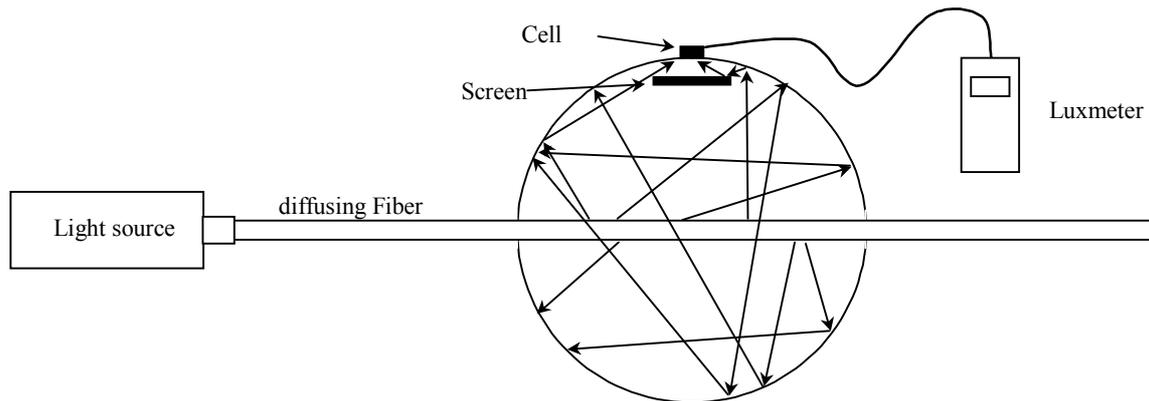Fig. 1 – Spectroscopic method to determine light attenuation.

Fig. 2 – Illumination measurements performed with an integrating sphere.

RESULTS AND DISCUSSION

The absorption loss of core material POF principally occurred in near infrared region is mainly due to the molecular vibration absorption caused by the overtone vibration of chemical bonds. Overtone bands appear because molecular vibrations are not perfectly harmonics. In near infrared region C-D and C-F overtones are few orders of magnitude lower in intensity than C-H overtones. Reduction of amorphous polymer loss is achieved by substituting the hydrogen atoms with fluorine.[4-5] The calculations show that the theoretical lower absorption loss limit for fully fluorinated polymers is reduced at less than 10^{-3}dB/km. In an ideal situation, it is necessary to choose some materials having a minimum of C-H links. But today, the fluorinated products, even taking into account their availability, are very expensive and therefore they are not used in a core material for lighting application.

To minimise the electronic absorption, it is necessary to limit the compounds with a double bond or aromatic groups. Monomer and additives choice was made according to this parameter.

The basic attenuation mechanisms in a POF can be classified into two main categories: intrinsic and extrinsic.[6-7] The absorption of the constituent material and the Rayleigh scattering are counted among the intrinsic losses. Both contributions depend on the composition of the optical fibre and, therefore, they cannot be eliminated. They are the ultimate transmission loss limit. Basically, they are caused by the molecular vibration absorption of the CH, NH, and OH groups, by the absorption due to electronic transitions between different energy levels within molecular bonds and by the scattering arising from composition, orientation and density fluctuations. The vibrations of the molecular bonds are the most important source of intrinsic losses. This fact occurs because the fibre is made up of polymer.

This behaviour suggests a way to improve the POF transparency by replacing the atoms of hydrogen with heavier elements. The vibrations shift toward longer wavelengths, so the influence of the vibration absorption in the visible and the infrared frequencies for which Rayleigh dispersion is also lower becomes negligible. Taking this fact into account, some PMMA POFs have been deuterated (PMMA-d8). However, the price of deuterium reagent is prohibitive.

Humidity also increases the attenuation significantly as a result of the strong vibration absorption of the OH groups, especially in the near infrared region. The Rayleigh scattering phenomenon gives rise to an absorption coefficient α_r inversely proportional to the fourth power of the wavelength.

On the other hand, polymers absorb light in the ultraviolet spectrum region. The mechanism for this absorption depends on the electronic transitions between energy levels in the molecular bonds of the material. The absorption of a photon causes a transition toward higher energy levels. The light absorbed induced a π - $\pi*$ transition of the double bond carbon-carbon C=C and the n - $\pi*$ transitions of the carbonyl groups C=O. Generally, the electronic transition absorption peaks appear at wavelengths in the ultraviolet region, and their absorption tails exhibit an influence on the POF transmission loss.

Contributions to the attenuation due to the absorption caused by molecular vibrations, electronic transitions, and Rayleigh scattering, facilitate the obtaining of the ultimate transmission loss limit.

Regarding the group of extrinsic losses, this is composed of those losses that would not appear in an ideal fibre. There also exists an extrinsic absorption caused by impurities in the core of the POF, fundamentally originated by the presence of organic pollutants, dust particles, micro fractures, bubbles and the hydroxyl group OH,[8] although the most significant extrinsic losses are, generally, those arising from the dispersion due to structural imperfections in the POF, generated during the manufacturing process (radiation losses, originated by both microscopic and macroscopic perturbations in the fibre geometry).

Some short fibres have been synthesised in order to determine the optimal conditions of synthesis as well as the evolution of the optical properties by an UV-Visible spectrophotometer. This first study was leaded on samples having the composition: BMA, EGDMA (0.7% in mole) and AIBN (0.1% in mole). Temperature and time of polymerisation are both variable parameters. After the synthesis, samples are polished and characterised by spectrophotometer between 250 and 800 nm, Fig. 3.
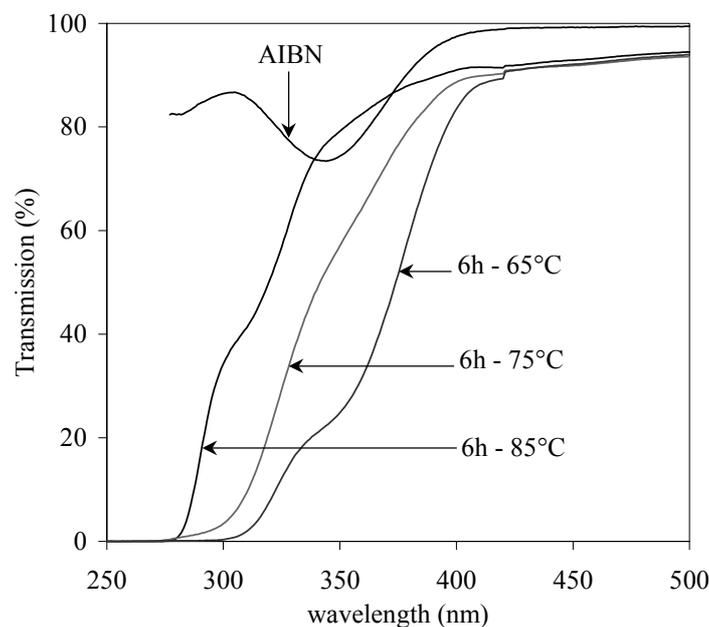

Fig. 3 – Optical properties of three polymers.

It is necessary to obtain a high conversion of monomer in order to manufacture low-loss fibres. In Fig. 3 there are presented the spectra of three samples having polymerised during 6 hours at three different temperatures: when the temperature decreases (65°C and 75°C), the polymerisation becomes incomplete and the presence of monomer and AIBN induce a deterioration of the optical properties.

Indeed, the absorption at 340 nm is due to the transitions [9] n - π^* notably present in the AIBN. At the temperature of 85°C, a weaker absorption shows there is a small part of unreacted monomer and AIBN initiator.

Fig. 4 – shows two distinct phenomena that appear in two different wavelength domains:

Between 280 nm and 320 nm, we can observe an absorption domain. This absorption comes from the monomer. The double bond is conjugated with the carbonyl group and the latter presents a strong absorption around 240-280 nm, due to the transition $\pi \rightarrow \pi^*$ and toward 300-320 nm, due to the transition n $\rightarrow \pi^*$.

Between 340 nm and 420 nm: When the polymerisation temperature increases, we can observe a reduction of the optic losses. Indeed, the UV spectra of the AIBN show a strong absorption in this domain. The absorption peak in this domain of wavelengths is provoked by the n $\rightarrow \pi^*$ electronic transitions. For too weak polymerisation temperatures, the decomposition speed of the initiator is therefore slower and after 6 hours of reaction, all didn't react.

The loss measurements show that an improvement in POF optical properties can be achieved only by a very high conversion of monomer in the core polymer. POF prepared by radical polymerisation at 85°C possess greater optical properties in comparison with other fibres. We also studied the influence of the polymerisation time on the optical properties.

Fig. 4 – Influence of polymerization conditions on the optical properties.

Polymerization at 75°C

6h   1h   2h
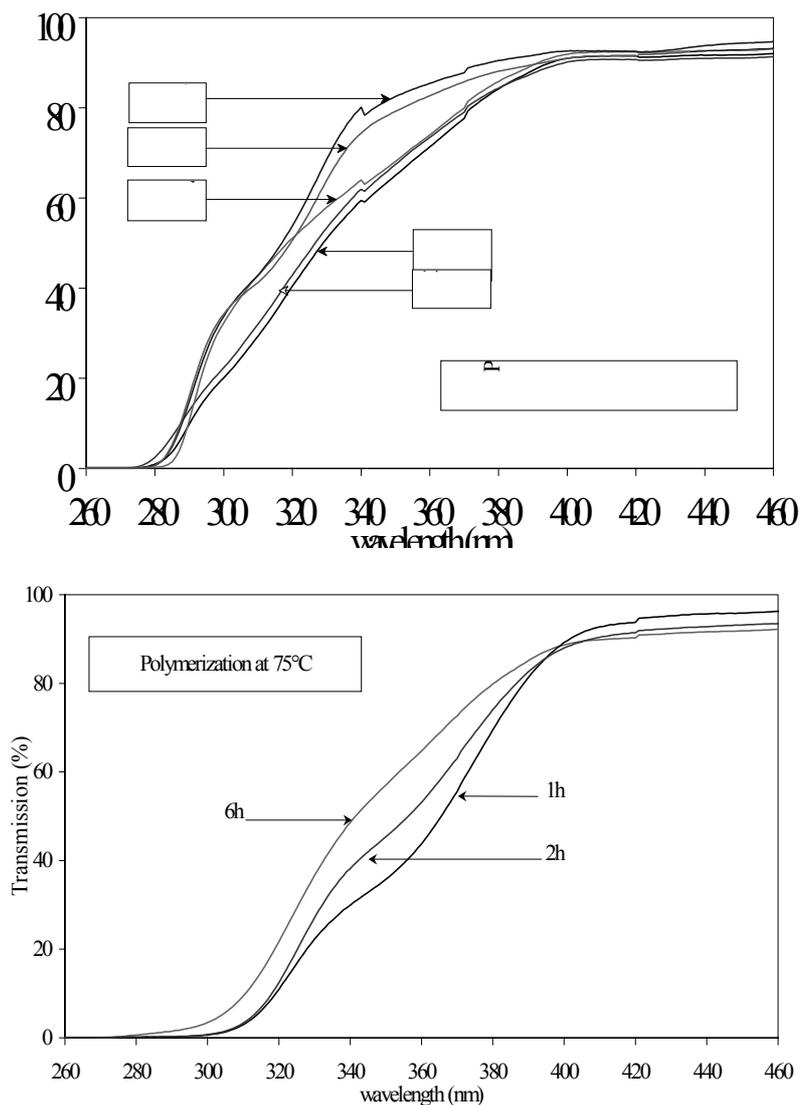
The evolutions according to the synthesis time are also different: between 1 and 6 hours to 75°C, the improvement of the transmission to 350 nm corresponds to the decomposition of the initiator. We have a better transmission in the domain of wavelength 280-380 nm at 85°C, because the residual quantities of monomer are weaker. Indeed, for 6 hours at 75°C, the transmission is close to 60% at 340 nm, while it is close to 80 % at 85°C.

A sample has also been polymerised during 24 hours to 85°C and no sensitive evolution of the optical properties has been observed.

Therefore, we decided to apply a 6 hours polymerisation time at 85°C.

In these conditions, the residual monomer and initiator can be eliminated by a thermal post treatment as shown in Fig. 5.

The flexibility of the core material[10] is an important parameter for the distributing optic fibres to large core, it is necessary to be able to

manipulate them and to bend them without damaging. To be able to apply to a 12 mm fibre a ray of 20 cm curvature, the glass transition temperature (Tg) must be sufficiently low in order to have a good flexibility for a manipulation without damaging the fibre. Indeed, a high value of Tg gives a brittle material.

In this case we decided to add to the BMA an acrylic co monomer. Indeed, it's better to use a co-monomer and not free small molecules which could lead to chemical diffusion phenomena during time. Two types of co-monomers were used: MET and BA. The choice of co-monomers depends of different parameters: principally a low glass transition and no aromatic compounds.

BMA:BA and BMA:MET mixtures bring a sufficient flexibility; the copolymer synthesised with latter mixture has a glass transition value equal to 5°C (Table 1).
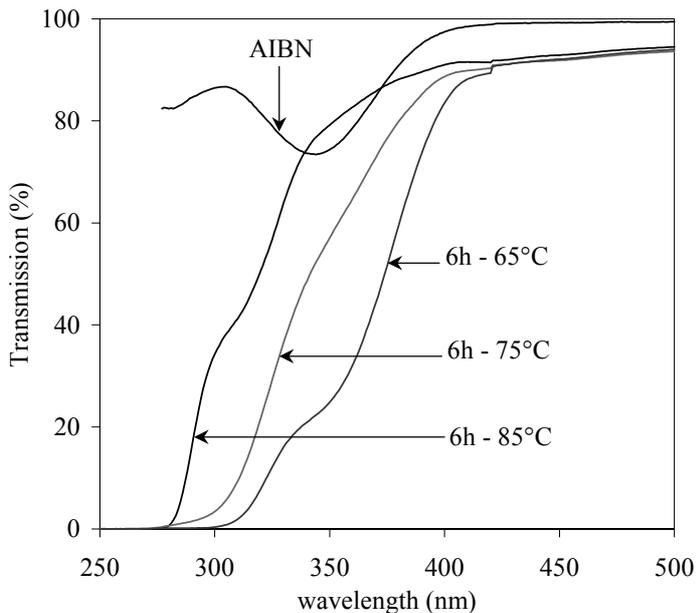
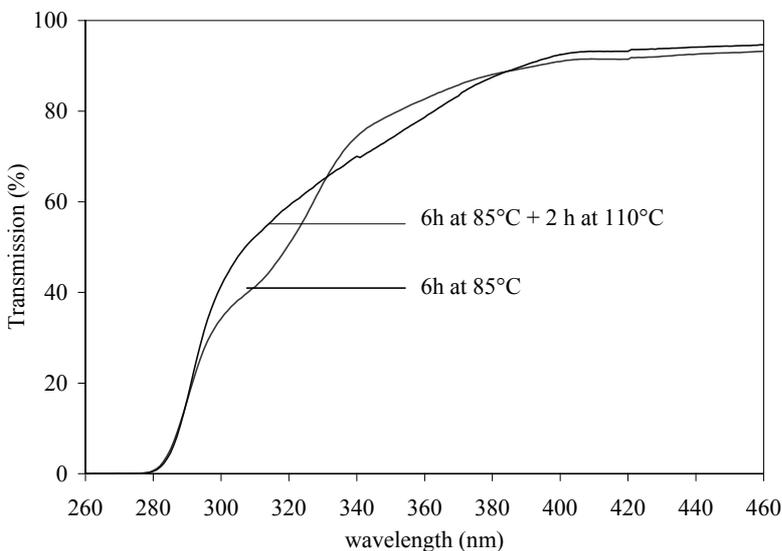Fig. 5 – Post-treatment evolution of transmission light.

Table 1

Glass transition temperature

Copolymer composition (molar ratios)	Glass transition temp., °C
BMA/ ETM (90/10)	5 °C
BMA/BA (90/10)	10 °C

The evolution of the optical properties during the time (after few years) is bound, of course, to the ageing phenomenon,[11-13] that we are not going to analyse in this work.

Optical properties of transported light powers are imposed by materials choice. The condition required in conducting the light is a refractive index difference between the core (n_1) and the optical cladding (n_2). The refractive index difference enables the medium to guide the light.

The refractive index of the core, where the light travels, must be higher than the refractive index of the surrounding material (optical cladding). The refractive index difference also controls the number of propagation modes and is linked to the numerical aperture.

In Fig. 6 we show that our samples present a weak attenuation that makes some good wave guide. The addition of different co-monomer quantity doesn't damage the optical properties.
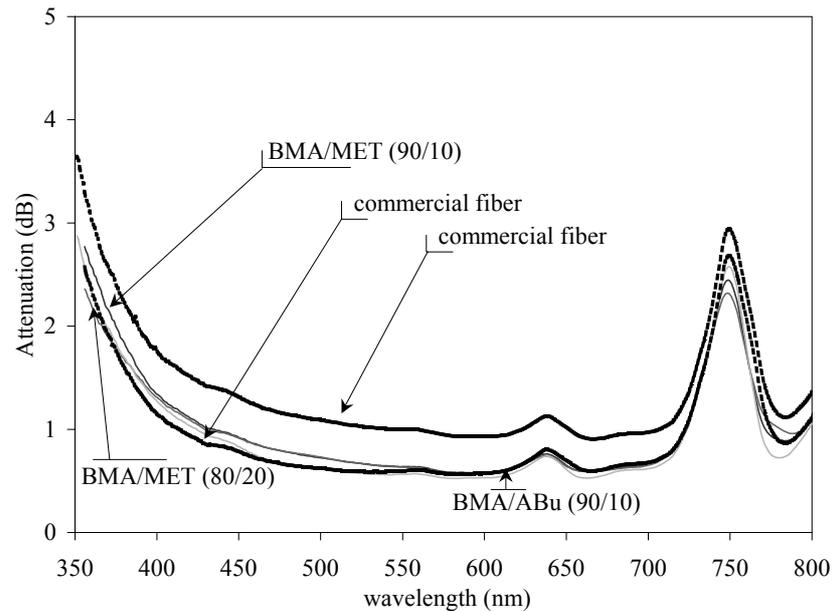
Fig. 6 – Transmission optical properties for various fibers.

In the range 0-20% of added co-monomer, the fibre flexibility can be adjusted without optical properties modification. Therefore, the optimal composition is: BMA:MET of 90:10 (mole/mole) and 0.7% mole of cross-linking EGDMA (with respect to the total molar ratio of BMA and MET).

In the last part, we worked on light diffusion [14-17] improvement in order to obtain a fibre with high and homogenous lateral illumination. Diffusion and transmission being two opposite phenomena, it has been necessary to find a compromise between such an excellent transmission along 10 m and, in the same time, to have sufficient lateral illumination. After having experimented different techniques, we had decided that the technique of the incorporation of spherical particles permit the control of the lateral diffusion. The scattering improvement was achieved with spherical particles of cross-linked PMMA (copolymer MMA-EGDMA). The average diameter of these particles is 8 μm (Fig. 7).
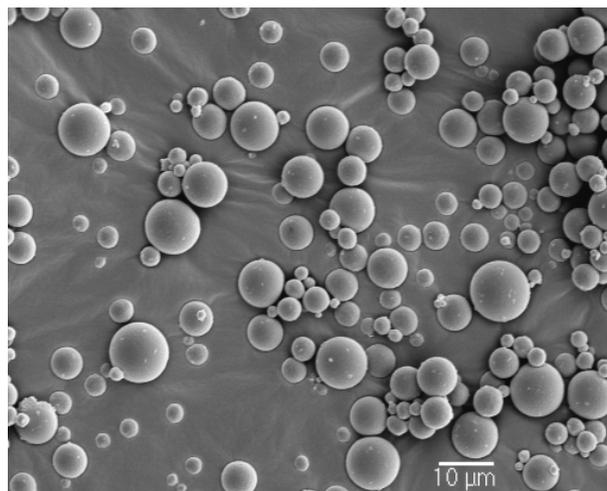

Fig. 7 – TEM microphotographs of PMMA particles.

We also studied the influence of the particles quantity on the optical properties of diffusion. The transmission properties of the plastic optical fibre are acceptable, but lateral scattering are too poor. So it's important to improve these properties of scattering while preserving a good light transmission. The scattering properties [18] are bonded to the size of the diffusing centres

(scattering $\alpha_r = \dfrac{1}{\lambda^r}$; r depends on the particles size). The idea is to introduce into the formulation significantly high size particles to have only a scattering independent from the wavelength to avoid the colour drift. Scattering due to different refractive index is obtained by using particles or a polymer blend which conduct to a phase separation. There were realised studies by incorporating glass particles to obtain polymers with good scattering optical properties. For the quantities lower than 0.1% in weight introduced, it was demonstrated that the scattering light increase.

Various samples of short fibre were realised from monomer mixture:

$$BMA / MET\ 90/10 + 0.7\%\ EGDMA + 0.1\%\ AIBN$$

Spherical particles addition in the monomers mixture, which is polymerised by radical method, creates a decantation phenomenon of the particles, which leads to a heterogeneous structure. To avoid this phenomenon, 10% (in wt) of PBMA is added to the mixture (Molecular weight: Mn = 208000 g.mole^{-1}). Various samples were synthesised using the ratios given in Table 2.

The attenuation curves increase with the introduced particles quantity (Fig. 8).
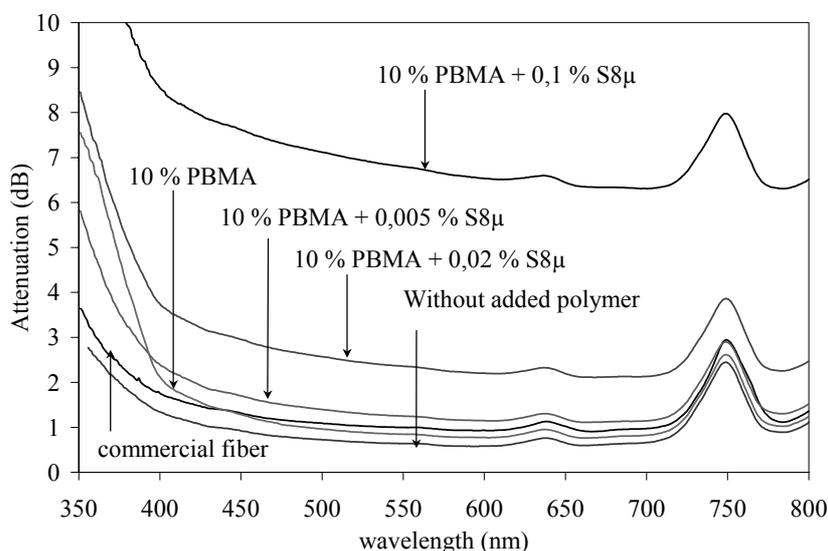
Table 2

Formulation of different fibres

BMA*	MET*	EGDMA**	AIBN**	PBMA***	MMA particles***
90%	10%	0.7%	0.1%	10%	0.005%
90%	10%	0.7%	0.1%	10%	0.02%
90%	10%	0.7%	0.1%	10%	0.1%
90%	10%	0.7%	0.1%	10%	0
90%	10%	0.7%	0.1%	0	0

* Molar ratios
** Molar % with regard to the total molar ratios of BMA and MET
*** Wt % with regard to the total weight ratios of BMA and MET

S8µ: spherical particle with a diameter of 8 µm

Fig. 8 – Attenuation modification according to the quantity of particles.

Lateral diffusion measurement shows an increase of scattering phenomenon. With 0.02% of particles, the increase of the attenuation is important and always independent from the wavelength. Indeed, we observe no modification in the shape of the curve, but merely an increase of the attenuation, independent of the value of the wave length. On the other hand, the diffused intensity has only a little improvement comparing with the sample containing 0.005% of particles. With 0.1% this increase is even more marked. These results show that the light scattering can be improved and adjusted by adding particles of sizes defined in the mixture of the reagent. From these

observations we synthesised two fibres of several meters with the following compositions:

Length: 3.5 m BMA/ MET: 90/10 (molar ratios), EGDMA: 0.7 (molar % with regard to the total molar ratios of BMA and MET) + 10% PBMA (wt % with regard to the total weight ratios of BMA and MET) + 0.005% balls (wt % with regard to the total weight ratios of BMA and MET),

Length: 10 m BMA/ MET 90/10 (molar ratios), EGDMA: 0.7 (molar % with regard to the total molar ratios of BMA and MET) + 10% PBMA (wt % with regard to the total weight ratios of BMA and MET) + 0.01% balls (wt % with regard to the total weight ratios of BMA and MET).

The total amount of scattered light can be measured with an integrating sphere**.** The integrating sphere principle supposes that the fibre is passed through a sphere whose inside is painted in white. It is the purpose of the integrating sphere to collect all the light, regardless at the projection fibre angle, and to observe the light density in the sphere

at one point on its inner surface with a light detector. The illumination registered is a measure of the total amount of light projected from the fibre (Fig. 2).

At one point on the surface of the sphere, the illumination is proportional to the irradiance source. The detector used to make the measurement of irradiance in lux is a luxo-meter set at a point on the sphere.

For the measurements realised, the diffusing fibre gets through a 20 cm sphere. The measurement realised along the fibres axis are only qualitative, they are linked to the light source and they allow making comparisons with those obtained for various other fibres. The results (Fig. 9) show, in presence of 0.005% of sphere, that the scattered light is 3 to 4 times greater than that of the fibre containing only BMA / MET, EGDMA and about twice more than the commercial fibre. This shows that we can increase and adjust the scattering by modifying the composition.
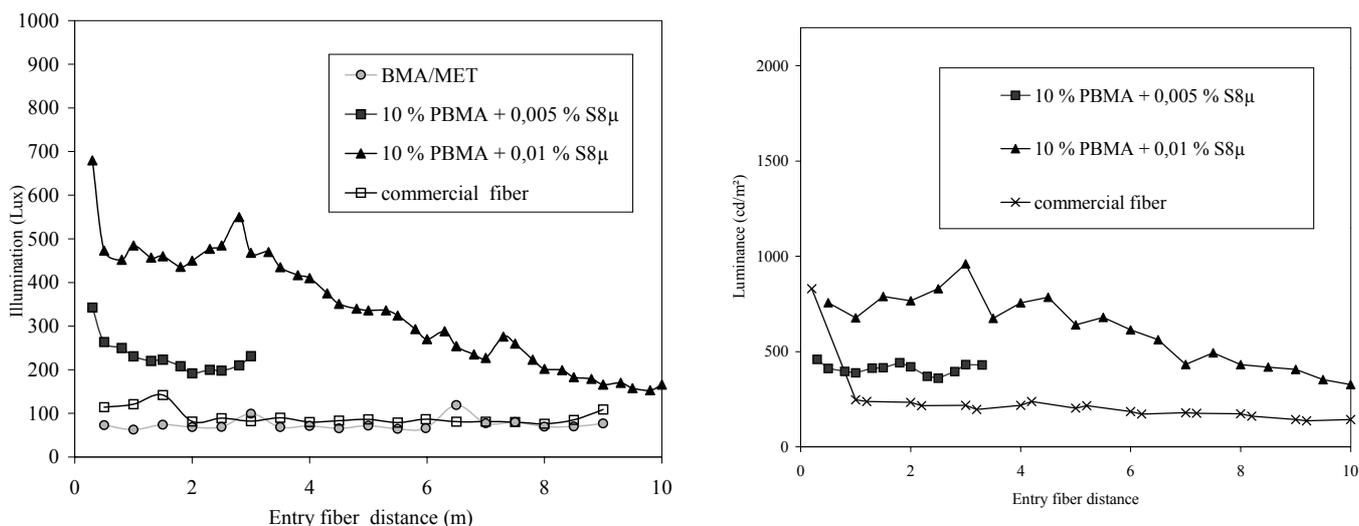

Fig. 9 – Curves of illumination and luminance obtained on various materials.

CONCLUSIONS

By a process of radical polymerisation we were able to finalise a plastic optical fibre with interesting optical properties. We showed that we can adapt the intensity of the light diffused by a notable modification of the mixture formulation by incorporating polymer particles. On the one hand, we demonstrated that it was possible to synthesise a fibre with excellent transmission properties of big length and, on the other hand, to improve the lateral diffusion while keeping an excellent

transmission. The sphere incorporation permits the control of the lateral diffusion intensity without creating colour drift within the fibre. In the field of the lighting it allows to adapt the intensity diffused according to the applications anticipated.

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