플라스틱 광섬유 클래드용 MMA/fluoro-acrylate 공중합체의 합성과 특성 분석

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Preparation and properties of MMA/fluoro-acrylate copolymers for POF cladding application

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Introduction

Step index POFs(SIPOF) are composed of core polymers and cladding polymers. Poly(methyl methacrylate) (PMMA) and polystyrene (PS) are normally used as core materials. The refractive index of cladding materials should be less than 2-5 % that of the core material. PMMA and fluorinated polymers are used as cladding materials on PS and PMMA core, respectively[1].

Cladding materials which have lower refractive index than core materials reflect light at less than critical angle, which is transmitted down the core. Critical angle is a factor of the difference between core and cladding refractive index, so called numerical aperture (N.A)[2]. Small N.A causes a large fraction of light-leakage. Transparency of cladding materials is also a factor of light loss. Opaque materials do not reflect light but absorb it. This causes a reduction in resolution, contrast, and brightness in an image fiber which is consist of multifillament type fiber. Thus cladding of image guide requires low refractive index and high transparency.

Cladding materials are made by a few methods. Vinylidene-fluoride copolymers have a low refractive index and easy-processable than other fluoride polymers and have been widely used for cladding materials[3]. However translucent and somewhat bad adhesion with PMMA core due to high fluorine content make vinylidene-fluoride copolymers disadvantageous. Fluoro-acrylates have low refractive index, high transparency, and easy copolymerizable with MMA increasing adhesion[4]. This paper reports the difference properties of short side chain and long side chain fluoro-acrylate.

Experimental

Materials

MMA(LG chem, Korea), 2,2,2-trifluoroethyl methacrylate(TFEMA, World chemical, Korea), and fluoro-acrylate compound (Zonyl®, Dupont) were used as monomers. They were purified by filtration through an inhibitor-remover column (Aldrich) to remove hydroquinone inhibitor. V-601(Wako chemical, Japan) was recrystallized from methanol and used as initiator. 1-Butyl Mercaptane(Aldirich, USA) was used as chain transfer agent without further purification.

Copolymerization

PMMA, P(TFEMA), Poly(fluoro-acrylate compound), MMA-TFEMA, and MMA-fluoro acrylate compound copolymers with different comonomer composition were prepared by bulk polymerization method in test tube with nitrogen atmosphere at 60 ℃ for 24 h. Thus prepared polymers were post-polymerized at 100 ℃ *for 6 h for obtaining high conversion.*

Refractive index

Refractive indices were measured by Abbe refractometer. Samples were coated with bromo benzene(refractive index : 1.559) for optical contact.

Differential Scanning Calorimetry

The glass transition temperature (T_g) was obtained by DSC (TA Instruments 2910, USA). All the samples were scanned in a dried nitrogen atmosphere at a heating rate of 20 ℃/min. The inflection point method was adopted for deciding T_g from the second heat flow curve.

^{1}H NMR

The chemical structure of the samples was identified by ^{1}H NMR (Varian, 300MHz). The solvent for NMR experiment was deuterated chloroform (CDCl3, Aldrich) and aceton-d6 (Aldrich).

Result and Discussion

Copolymer characterization

The mole fraction of the comonomers in each copolymers was measured by ^{1}H NMR to calculate monomer reactive ratios and the x value of the copolymer. x is a parameter which indicates the randomness of the copolymer. x=0 and x=1 represent a block copolymer and a random copolymer, respectively. x=2 represents a alternating copolymer. The basic parameters of homopolymer and copolymers synthesized are listed in Table 1,2.

Using the values of f_{MMA} and F_{MMA}, the reactivity ratios of MMA, TFEMA, and fluoro-acrylate compounds can be estimated by the Fineman-Ross Method[5,6].

As mentioned previously, the x indicates the structural information of copolymers. The x values of 0,1, and 2 represent a block copolymer, random copolymer, and alternating copolymer. x values show nearly random copolymer in all polymer contents. Random copolymer is desirable for regulating refractive index and transmission. Many solid polymers including copolymers are optically heterogeneous. Heterogeniety may influences the refractive index and transmission varies from point to point within the material, which is the fatal disadvantages for SIPOF[7]. For example phase separation for blending and block copolymer or tacticity for copolymerization gives different refractive indices zones in a material, which may induce large light-leakage.

Refractive index

Table 1,2 shows refractive indices of homopolymers and copolymers. As fluorine content is increased, refractive index of copolymer is decreased. Refractive index depends on the molar refraction and the density[8]. It increases with increasing intrinsic refractive power of a material, as quantified by its molar refraction. If two polymers have identical V, the polymer with the larger intrinsic refractive power will have a larger refractive index. Refractive index increases with increasing amount of material per unit volume, as quantified by decreasing molar volume. The atoms act as obstacles to a beam of light traversing a material, and slow it down. If two polymers have identical molar refraction, then the polymer with the smaller V will present a larger number of such obstacles per unit length of the beam of light, and will therefore have a larger refractive index. Thus intrinsic refractivity of the structural units and the density are the key factors determining the refractive index.

Fluorinated polymers often have very high densities, but very low intrinsic refractivities, which brings about very low refractive indices. As expected, higher fluorine content of fluoro-acrylate compounds give lower refractive index with same amount of comonomer. As for MMA/TFEMA, and MMA/fluoro-acrylate compounds copolymer it is easy to anticipate refractive index because of linear decrease.

In POF, the difference of refractive index between core and clad is very important. If the difference is large, the light-gathering capacity is greater. The measure of light trapping in a fiber is the numerical aperature, NA[2]. A higher NA value means more light trapped in a fiber.

Thermal property

The DSC thermogram of MMA/TFEMA copolymers are shown in Figure 1. T_g decreases by increasing TFEMA content. Fluorinated side chain increases the free volume of the molecules. This increase of free volume decrease T_g. Fluorine decreases T_g due to its bulkiness. Sometimes T_g and refractive index meet conflict with POF clad materials. As fluorine content is increased, refractive index is decreased, but T_g is also decreased. Quite a longer fluorinated side chains are used to increase T_g[9]. These side chain induce molecular entanglement among side chains, therefore T_g is increased. Introducing long side chains is one of the solutions for low refractive index and high Tg. As for fluoro compound, long side chains induce crystallization. Figure 2 shows long side chains of fluoro compound inducing crystallization. Crystallization is a fatal disadvantage for POF cladding. Crystal may absorb light which are propagating by reflecting on the core-clad boundary. Crystallization also causes translucent region. Translucent region of cladding may not reflect light but absorb on the core-cladding boundary interface. However copolymerization with MMA reduces crystallization; transparent copolymer can be achieved. As MMA content is increased crystallization behavior disappears.

Table 1. The basic properties of MMA/TFEMA

MMA/TFEMA content	f_{MMA}^a	F_{MMA}^b	x^c	Refractive Index
100/0	1.0	1.0		1.492
85/15	0.905	0.913	0.984	1.483
70/30	0.795	0.806	0.969	1.472
50/50	0.625	0.627	0.955	1.454
30/70	0.417	0.423	0.953	1.442
15/85	0.228	0.228	0.966	1.427
0/100	0.0	0.0		1.410

a MMA mol fraction in the feed
b MMA mol fraction in the copolymer
c Randomness of copolymers
(× = 1, random copolymer; × = 2, alternating copolymer)

Table 2. The basic properties of MMA/fluoro-acrylate compound

MMA/Zonyl® content	f_{MMA}^a	F_{MMA}^b	x^c	Refractive Index
100/0	1.0	1.0		1.492
85/15	0.970	0.976	1.011	1.473
70/30	0.930	0.953	1.024	1.457
50/50	0.850	0.872	1.051	1.434
30/70	0.710	0.776	1.092	1.403
15/85	0.502	0.502	1.137	1.386
0/100	0.0	0.0		1.368

a MMA mol fraction in the feed
b MMA mol fraction in the copolymer
c Randomness of copolymers
(× = 1, random copolymer; × = 2, alternating copolymer)

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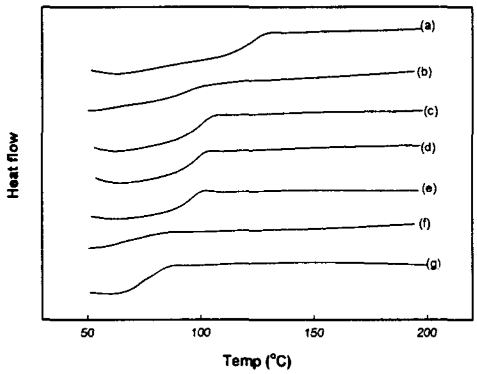

Figure 1. DSC thermograms of (a) PMMA, (b) MMA/TFEMA 85:15, (c) 70:30, (d) 50:50, (e) 30:70, (f) 15:85, (g) P(TFEMA) for 2nd heating scan.

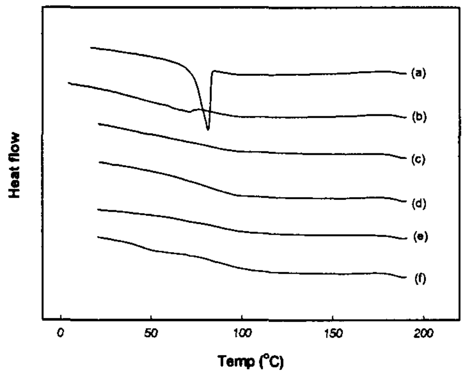

Figure 2. DSC thermograms of (a) Poly(fluoro-acrylate compound), (b) fluoro compound/MMA 85:15, (c) 70:30, (d) 50:50, (e) 30:70, (f) 15:85 for 2nd cooling scan.