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Synthesis of Polymer Composites with Luminescent Properties [†]

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Abstract: This paper presents the synthesis and characterization of new polymeric materials in form of composites with luminescent filler using the photopolymerization methodology. In the synthesis of composites as a main monomer a bisphenol A glycerolate (1 glycerol/phenol) diacrylate was used, whereas methyl methacrylate, N-vinyl-2-pyrrolidone and 2-hydroxyethyl methacrylate were applied as a reactive diluents. In role of photoluminescent dopant a previously synthesized photoluminescent copolymer N-vinyl-2-pyrrolidone witch 2,7-(2-hydroxy-3-methacryloyl oxypropoxy)naphthalene was used. The compositions were prepared with an increasing amount of filler: 0, 0.5, 1,2, 5, 10% *w*/*w*. As a result of the performed syntheses, 18 new compositions were obtained, which generating of green-yellow light after excitations by UV radiation. The influence of the increasing luminescent filler content on the selected properties of the composites was evaluated. The thermal and mechanical behaviors of composites were determined by means of differential scanning calorimetry (DSC), and Shore D hardness. Moreover, the chemical structures of polymeric materials were confirmed by the attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FT-IR) method. These results shown that the incorporation of the photoluminescent copolymer into polymeric composition can be method of obtaining functional materials for production of special polymeric coatings or production of optical fiber sensors.

Keywords: UV-polymerization; polymer composites; photoluminescence

1. Introduction

Numerous substances and materials with luminescence property are found in chemistry. Their amount increases due to the demand for more specific, effective and resistant polymeric materials. The group of luminescent polymer materials includes, among others coordination polymers (CPs). They are an important group of materials owing to their diverse crystal structures and extensive application such as gas adsorption/separation, heterogeneous catalysis, luminescent probe, drug delivery, magnetism, guest/ion-exchange and catalysis [1–6]. Trivalent rare earth elements (lanthanides) similarity to other selected metals and their metal organic frameworks (MOFs) are characterized by good photoactive properties, e.g., a broad emission region or a color intensity. These features of MOF's contribute to a great variety to be applied inlighting or optical devices (displays, lasers, optical fibers) and biomedical equipment (medical diagnosis) [7,8]. Unfortunately, these materials are quite expensive due to the poor accessibility to rare earth elements.

Nowadays stimuli-responsive organic luminescent materials are attract more and more attention of science and providing new possibilities of their application. Exposed to different stimuli, these materials exhibit fluorescent properties [9–12]. Volatile organic compounds are one of the causes of air pollution issues, which promoted the studies on metal organic frameworks which can be used for sensing environmental pollutants based on colours change [13–16]. Photochromic substances based on organic compounds attract much attention owing to their optical properties application for example in displays, security inks, optical recording or sensors [17,18]. Photochromic CPs are constructed using, among others, naphthalene diimides (NDIs) which possess luminescent properties and are chemically robust [19,20]. Easily processable fluorescent polymers based on naphthalene due to their intense fluorescence, and good thermo-chemical stabilities can be used for production of polymer light-emitting diodes, laser dyes and fiber optic sensors [21–23].

The aim of this study was to obtain new resistant polymeric composites with photoluminescent properties using the photopolymerization method and their detailed characterization.

2. Materials and Methods

2.1. Materials

N-vinyl-2-pyrrolidone (NVP) (Fluka), methyl methacrylate (MMA) (Sigma Aldrich) and 2-hydroxyethyl methacrylate (HEMA) (Fluka) were used as active solvents and bisphenol A glycerolate (1 glycerol/ phenol) diacrylate (Bis.GDA) (Sigma Aldrich) was used as a main monomer in the synthesis of composites. 2,2-dimetoxy-2-phenylacetophenone (Irqacure® 651) (Fluka) was added to these mixtures as a photoinitiator of UV-polymerization. As a photoluminescent filler there was applied the powdered copolymer of N-vinyl-2-pyrrolidone with 2,7-(hydroxy-3-methacryloyloxypropoxy)naphthalene form, whose synthesis is detailed elsewhere [24].

2.2. Methods

The ATR-FT/IR spectra were obtained with a Bruker TENSOR 27 FTIR spectrophotometer (Germany). They were recorded from 4000 to 600 cm^{-1} averaging 32 scans with a resolution of 4 cm^{-1} in the transmittance mode. The DSC thermograms were obtained with the use of Netzsch 204 calorimeter (Germany). The 10.0 ± 0.05 mg samples were placed in the aluminum pans with pierced lids whereas an empty aluminum crucible with a pierced lid was a reference. Dynamic scans were performed in the temperature range from 25 to 600 °C in the nitrogen atmosphere with a flow rate of 10 mL/min. Hardness of the analyzed samples was measured using by a Shore D method using a Zwick 7206/H04 hardness apparatus (Germany) at 25 °C. Three measurements were made for all composites and the average values were calculated.

2.3. Composites Preparation

The method of composites synthesis was based on radical polymerization. The process of samples preparation proceeded in several stages. Bisphenol A glycerolate (1 glycerol/phenol) diacrylate (Bis.GDA) was heated in a laboratory dryer to 60 °C and then its appropriate amount was weighed and placed in a glass vessel. Next the calculated amount of MMA was transferred to Bis.GDA and mixed thoroughly mixed. The ratio of Bis.GDA and the to active solvent was 7:3 in all samples. The weighed amount of the photoluminescent filler was put into the mixture in small portions (still mixing). Next the 1% wt. of UV-initiator (2,2-dimethoxy-2-phenylacetophenone) was added. Finally, the whole content was moved into a special glass form and irradiated with UV light for 30 minutes [25]. As a result, a composite (8 × 12 cm) was obtained. The same procedure was repeated for the samples with NVP and HEMA as solvents. Finally, in this way there were synthesized 18 samples, whose thickness was 4 mm (± 0.1 mm). The experimental parameters of the synthesis were collected in Table 1. The chemical structures of monomers and composites are presented in Figure 1.

Table 1. Composition of the polymeric composites containing 2,7-NAF.DM-NVP.

Type of Sample	Amount of Bis.GDA (g)	Amount of Active Solvent	Amount of Irgaqure®651	Amount of 2,7-NAF.DM-NVP
0% wt. 2,7-NAF.DM-NVP	10 g	4.28 g	0.14 g	0 g
0.5% wt. 2,7-NAF.DM-NVP	10 g	4.28 g	0.14 g	0.07 g
1% wt. 2,7-NAF.DM-NVP	10 g	4.28 g	0.14 g	0.14 g
2% wt. 2,7-NAF.DM-NVP	10 g	4.28 g	0.14 g	0.29 g
5% wt. 2,7-NAF.DM-NVP	10 g	4.28 g	0.14 g	0.76 g
10% wt. 2,7-NAF.DM-NVP	10 g	4.28 g	0.14 g	1.60 g

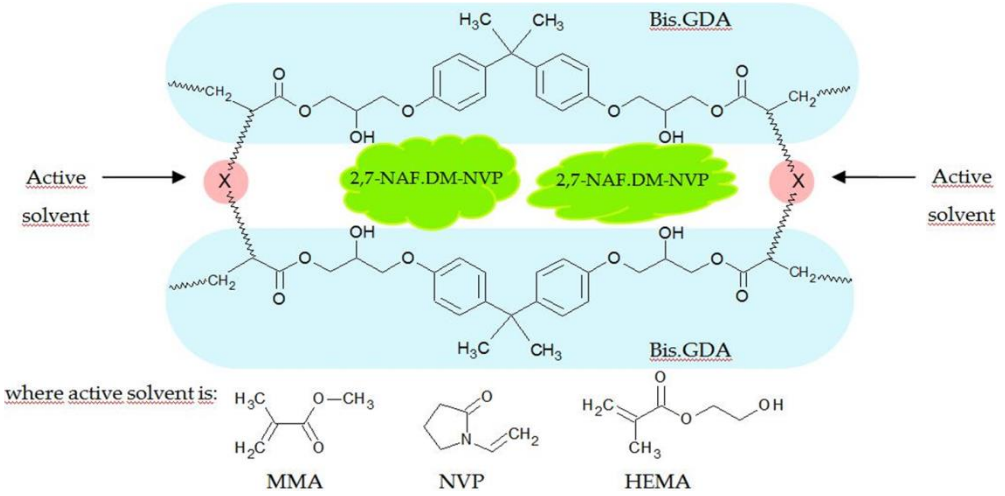
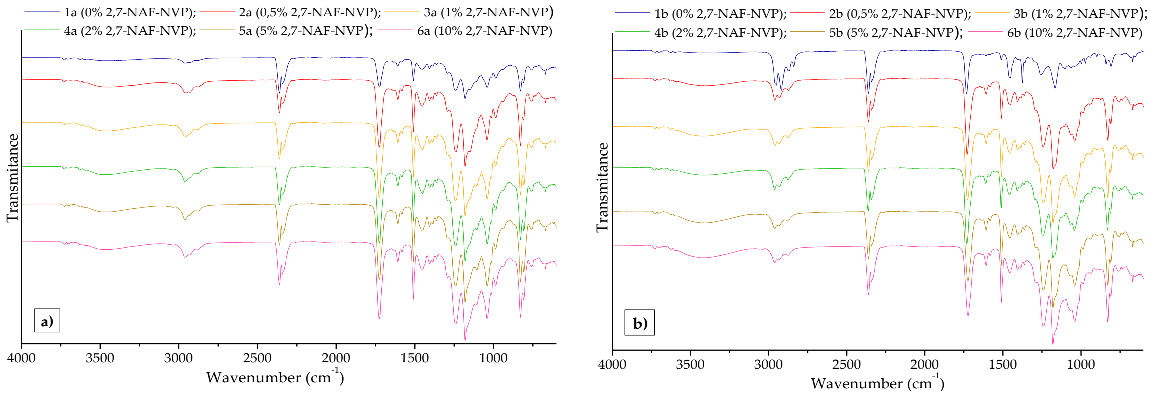


Figure 1. Simplified structure of polymer composite with the derivative photoluminescent filler of naphthalene-2,7-diol.

3. Results

3.1. *Attenuated Total Reflectance—Fourier Transform Infrared Spectroscopy (ATR-FTIR)*

Characteristic bands of the functional groups are visible on the FT-IR/ATR spectra (Figure 2). The courses of the spectra were similar due to the fact that main components of these materials are Bis.GDA and NVP which is evidenced by the presence of characteristic bands of appropriate functional groups. FT-IR (cm^{-1}) of the photoluminescent composites: 2964–2950 and 2875–2874 (asymmetric and symmetric C–H stretching of CH_2 and CH_3, respectively); 1725–1722 cm^{-1} (stretching vibrations of C=O groups which is characteristic of acrylates); 1610 and 1509 cm^{-1} (aromatic C=C symmetric and asymmetric stretching vibrations); 1450–1425 cm^{-1} (deformation vibrations of methyl and methylene groups); 1242–1241 and 1040–1039 cm^{-1} (stretching vibrations of C-O bonds in alkyl-aryl and aromatic and respectively); 1181–1180 cm^{-1} (stretching vibrations of ester group C-O-C); 828–826 cm^{-1} (deformation vibrations of Ar and Ar-H).



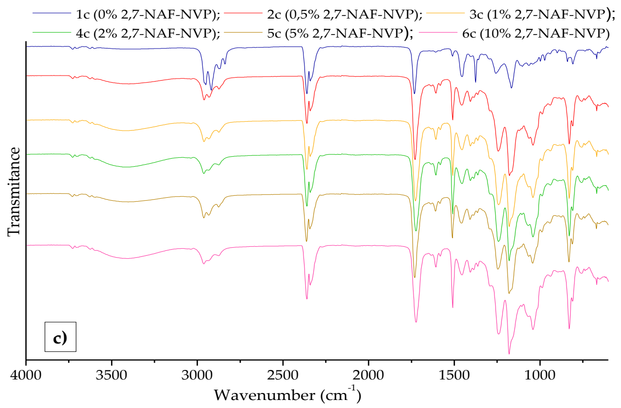


Figure 2. ATR/FT-IR spectra of the composites: (**a**) samples with MMA; (**b**) with NVP; (**c**) with HEMA.

3.2. Differential Scanning Calorimetry (DSC)

The DSC analyses show some similarities in thermal behaviour of the obtained materials. It can be seen that for six chosen composites change of filler content in the sample has no significant effect on the shape of DSC curves (Figure 3). Table 1 contains numerical data determined from the DSC curves after the heating cycles. Comparing the obtained results, a clear endothermic effect connected with the maximum degradation of the samples is visible. The values of **T_{max}** temperatures are in the range 390.1–413.1 °C. Besides, on all curves one see a small endothermic peak (**T_1**) at a temperature between 60.4 and 81.2 °C. This effects probably a result of evaporation of small amounts of unreacted monomers. For the studied samples no exothermic effects occur during heating.

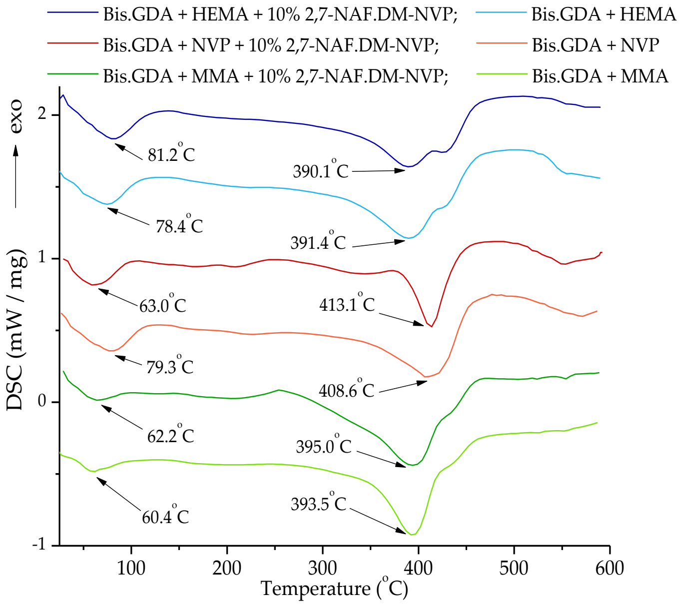


Figure 3. DSC curves of six selected samples.

Table 2. DSC curves of six selected composite samples.

Type of Sample	**T_1**	**T_{max}**
1a (Bis.GDA + MMA)	60.4	393.5
6a (Bis.GDA + MMA + 10% 2,7-NAF.DM-NVP)	62.2	395.0
1b (Bis.GDA + NVP)	79.3	408.6
6b (Bis.GDA + NVP + 10% 2,7-NAF-NVP.DM-NVP)	63.0	413.1
1c (Bis.GDA + HEMA)	78.4	391.4
6c (Bis.GDA + HEMA + 10% 2,7-NAF.DM-NVP)	81.2	391.5

3.3. Hardness Measurements

The values of hardness were expressed in the D scale and presented in Figure 4. The hardness of the samples was in the range from 64.3 to 73.3 units.

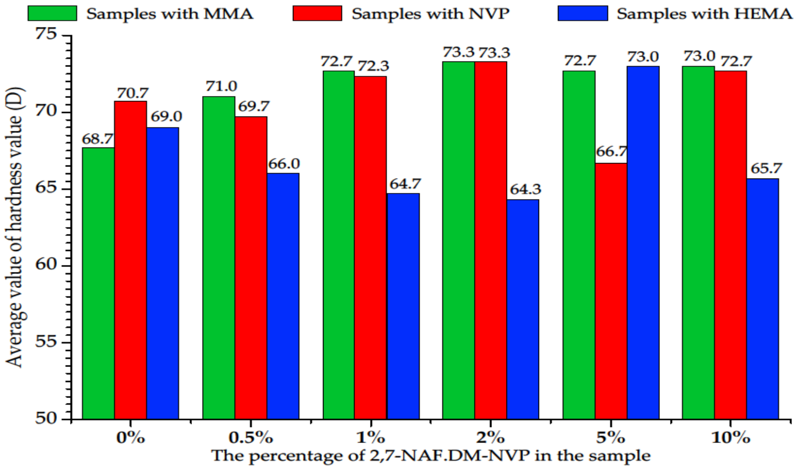


Figure 4. Hardness diagram of the obtained composites.

The above results show that the amount of luminescent dopant in the NVP and MMA samples increases hardness of the synthesized materials slightly. This parameter is comparable for individual series of composites. The hardness values show slight changes with the type of used solvent. The results for the composites with NVP improved slightly compared to those with HEMA. The highest values of hardness were recorded for the materials with the MMA.

4. Conclusions

This paper discusses the synthesis of new polymeric composites with luminescent. The photoluminescent copolymer derivative of naphtaleno-2,7-diol. Was used as a filler three different solvents: MMA, NVP, HEMA as well as different amounts of a filler (0, 0.5, 1, 2, 5 and 10%*w*/*w*.) were synthesized through UV polymerization. The ATR/FT-IR analysis confirms the proper course of the polymerization process. The spectra show the peaks derived from the characteristic fragments like: methyl and methylene groups, aromatic rings, ether and carbonyl groups. The data obtained during the DSC analysis confirm that the amount of dopant does not affect thermal properties of the samples. The materials were characterized by similar parameters of thermal stability. Based on the hardness tests it can be concluded, that the type of solvent results in different values of hardness (the samples with MMA are statistically the hardest).

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