Proceedings of the 4th World Congress on Mechanical, Chemical, and Material Engineering (MCM'18)
Madrid, Spain – August 16 – 18, 2018
Paper No. ICCPE 111
DOI: 10.11159/iccpe18.111

Synthesis, Charecterization of a New 16 A, S, C-HBPAE-b-PCL Copolymers and the Mechanical Properties of the Copolymer-Cement Composites

S. Savaşkan Yılmaz[1*], E. Tütüncü[1], Y. Mısırlıoglu[1], A. Küçük[1], H. Cuvalcı[2], M. Aslan[2]
[1]Department of Chemistry, Karadeniz Technical University
61080, Trabzon, Turkey
[2]Metallurgical and Materials Engineering, Karadeniz Technical University
61080, Trabzon, Turkey

Abstract - The new 16-Arms, Star, Coil-HBPAE- b-PCL(16 A, S, C-HBPAE-b-PCL) copolymers was synthesized hyperbranched poly amide-ester (HBPAE) as the macroinitiator and epsilon caprolactone (ε-CL) monomer by using Ring Opening(ROP). Characterisation of the polymers was achieved by FTIR, ^{1}H NMR GPC, MS, SEM, AFM, TGA, DSC, techniques and MTS Criterion brand 45 model mechanical testing. The new 16 A, S, C-HBPAE-b-PCL-OPC composites containing 16 A, S, C-HBPAE-b-PCL additive were prepared for the purpose of improve of Ordinary Portland Cement(OPC) properties. The compressive strength and the bending resistance tests of the composites were investigated.The cement mortar samples prepared for the experiments were produced in the laboratories of Karadeniz Technical University in accordance with TS EN 196-1, TS EN ISO 15630-1 and TS EN ISO 7500-1 "Cement test methods" standard.

Keywords: Epsilon Caprolactone (ε-CL) Copolymer, Ring Opening(ROP), Polymer-Cement Composites, Impact Resistance, Mechanical Strength.

1. Introduction

The new 16 A, S, C-HBPAE-b-PCL copolymers was synthesized HBPAE as the macroinitiator[1, 2, 3, 4, 5] and ε-CL monomer by using ROP. PPCC (Polymer portland cement concrete); coatings, cobble stones, combined water structures, decorative surface coatings, abrasion-resistant lining, repair materials and bridging materials. The most widely used is latex modified concrete (LMC), and concrete is the concrete in which polymer emulsions called latex are used instead of part of the mixture water. Polymer-impregnated concrete is concrete produced by impregnating a hardened Portland cement concrete with a monomer and then polymerizing it [6, 7]. In a study by Okada and Ohama, the mortars modified with polymers with the trade names SBR-EVA and PAE. It has been reported to be used in a variety of applications such as coating, waterproofing, adhesive decorative coatings, surface finishing materials, abrasion resistant deck coatings [8].

2. Experimental

2.1. Synthesis of AB2 Monomer

AB2 monomer was synthesized by using maleic anhydride (MA) and Diethanolamine (DEA) solution in 100 ml distilled chloroform at 25 ° C. The reaction mixture in the Schlenk system was submerged in oil bath at 60 ° C. The final chloroform was evaporated. The product was dried in vacuum. Yield: 15 g (74%). The structure of the AB2 monomer was investigated using FT-IR, ^{1} H-NMR, ^{13} C-NMR, TGA and mass spectroscopy.

2.2. Synthesis of Highly Branched PoliAmino-Ester (HBPAE) Macroinitiator

HBPAE macroinitiator was synthesized by AB2 monomer, pentaerythrol and polythiosulfonic acid (p-TSA). Yield: 68 g (71.7%). 3360 cm^{-1} (-OH), 2945 cm^{-1} (Aliphatic-CH), 1718 cm^{-1} (C = O), 1172 cm^{-1} (C-O) in the FT-IR spectrum of the synthesized macroinitiator. ^{1}H-NMR (DMSO-d_6, ppm) of HBPAE macroinitiator:2.68 (s, 2H, CH_2), 2.84 (s, 2H, CH_2), 2.94 (t, 4H, 2CH_2-N), 3.31(s, 2H, CH_2 + H_2O), 3.47 (d, 2H, OH, *j*=10 MHz), 3.60 (t, 4H, 2CH_2-OH), 6.00 (s, 1H, CH_2), 6.35(m, 1H, CH), 6.42 (s, 1H, CH), 6,64 (m, 1H, CH).^{13}C NMR (DMSO-d_6), δ:ppm) of HBPAE macroinitiator: 31.29 (-C-), 36.32 (2CH_2-N), 49.56 (2CH_2-N), 57.07 (2CH_2-OH), 62.64 (2CH_2-O), 74.67 (CH_2), 126.00 (2CH), 128.66 (CH), 135.70 (2CH), 136.66 (CH), 162.89 (3C=O), 167.63 (2C=O) , 168.95 (C=O).

2.3. Synthesis of 16-Arm, Star Coil-HBPAE-b-PCL(16 A, S, C-HBPAE-b-PCL) Copolymer with ROP

16 A, S, C-HBPAE-b-PCL Copolymer was synthesized by HBPAE macroinitiator and ε-caprolactone as tin (II) octoate catalyzer under argon gas at 120 ° C. Yield: 98 g (88.5%). 3417 cm^{-1} (-OH), 2938 cm^{-1} (Aliphatic CH), 1726 cm^{-1} (C=.O), 1159 cm cm^{-1} CO) in the FT-IR spectrum of 16 A, S, C-HBPAE-b-PCL copolymer.

^{1}H-NMR (DMSO-d_6, ppm) of of 16 A, S, C-HBPAE-b-PCL Copolymer: 1.25(1.25(t, 8H, 4CH_2), 1.45-1.52 (m, 16H, 8CH_2), 2.23(m, 8H, 4CH_2-C=O), 2.45-2.47 (m, 8H, 4CH_2), 2.48 (s, 2H, CH_2-C=O), 3.32-3.35 (m, 2H, CH_2), 3.70 (2H, 2OH) , 3.94 (t, 8H, 4CH2), 4.10 (s, 2H, CH_2). 5.72(s, 1H, CH), 5.97(s, 1H, CH), 6.65(s, 1H, CH), 6.71 (s, 1H, CH).

^{13}C NMR (DMSO-d_6, ppm) of 16 A, S, C-HBPAE-b-PCL Copolymer: 24.47(4CH_2), 24.94(CH_2), 25.42(4CH_2), 25.46(2CH_2), 28.14(4CH_2), 32.68(C), 33.88(4CH_2),34.09(CH_2), 34.80(CH_2), 58.80(CH_2), 61.05(CH_2), 62.80(CH_2), 64.02(2CH_2), 65.44(CH_2), 124.15(2CH), 133.33(2CH), 173.18(C=O), 173.32(2C=O), 173.44(C=O), 174.35(C=O), 176.36(C=O).

The Mn, Mw and Mz values obtained by GPC of the 16 A, S, C-HBPAE-b-PCL copolymer are 3370, 4151, 5501 $gmol^{-1}$. The heterogeneity index (HI) was calculated as 1.23.

The glass transition temperature (Tg) at -52 °C was determined from the DSC thermogram of the 16 A, S, C-HBPAE-b-PCL copolymer. Homo-PCL literature has a glass transition temperature of -60 °C. The Tg value of the copolymer is greater than the homo-PCL value. An endothermic melting peak was observed at 110 °C in the DSC thermogram. It was observed that it started to degrade at 358°C. The TGA thermogram was also observed to degrade at 417 °C.

2.4. Preparation of Cement Block

The cement blocks prepared for the experiments were produced in the laboratories of Karadeniz Technical University in accordance with TS EN 196-1, TS EN ISO 15630-1 and TS EN ISO 7500-1 "Cement test methods" standard. The first set, the second set, the third set consist of 120 mm × 25 mm × 15 mm, of 80 mm × 15 mm × 5 mm, of 60 mm × 15 mm × 5 mm with 6 blocks, respectively. Three different weight ratios (1%, 3%, 5%) of 16 A, S, C-HBPAE-b-PCL copolymer were added to the mortar samples as included in the test program. The polymer addition was carried out immediately after the addition of the aggregate, and stirring at high speed was continued so that the mixture could be in a completely homogeneous form. Apart from these, blind samples were made.

2.5. Mechanic Tests

The compressive strength and the bending resistance tests of the composites were investigated.The cement mortar samples prepared for the experiments were produced in the laboratories of Karadeniz Technical University in accordance with TS EN 196-1, TS EN ISO 15630-1 and TS EN ISO 7500-1 "Cement test methods" standard.The flexural strength R_f is calculated in N/mm^2 by using MTS Criterion marka 45 model mechanic test. After bending strength, the two halves of the fractured specimen are subjected to separate compressive strength. Thus, six different values are obtained from a mortar sample poured into three molds at a time.

3. Results and Discussion

It was used for improving the mechanic properties of OPC that the new 16 A, S, C-HBPAE-b-PCL copolymers synthesized from HBPAE as the macroinitiator[1, 2, 3, 4, 5] and ε-CLmonomer with ROP method. Also, HBPAE was a new macrinitiator synthesized by us in Ring Opening(ROP) of ε-CLmonomer. Proton signals of the 16 A, S, C-HBPAE macroinitiator were observed. 2.47 (s, 2H, CH_2-C-O) ppm of the 16 A, S, C-HBPAE- b-PCL copolymer belongs to the repeating unit of the observed PCLs (-$OCH_2CH_2CH_2CH_2CH_2$-). The methylene-OH at the end of the polymer chain is 3.60 (bs, 2H, 2OH) ppm. The disappearance of the -OH signal at 3.47 (d, 2H, OH) ppm of the HBPEA macroinitiator is evidence of the formation of the copolymer. In the ^{13}C NMR spectrum of the HBPAE macroinitiator, the peak of the OH-CH_2 carbon at the end was 57.07 ppm, while the 57 C ppm of the ^{13}C NMR spectrum of the 16 A, S, C-HBPAE-b-PCL copolymer was not observed. The observation of the carbon signal at 62.64 ppm of the O - (- C = O -) - group formed by the removal of the H atom at the end of the HBPAE macroinitiator during the polymerization with ε-caprolactone is evidence of ring opening.

The percentage of 16 A, S, C-HBPAE-b-PCL copolymer incorporated in the cement increases compressive strength and bending resistance. According to the blind sample, it was observed that the pressure and impact strength increased as the amount 16 A, S, C-HBPAE-b-PCL copolymer increased. It was determined that the bending strength of the cement increased as the amount of 16 A, S, C-HBPAE-b-PCL copolymer added to the cement increased. MTS Criterion brand 45 model mechanical testing. The new 16 A, S, C-HBPAE-b-PCL-OPC composites containing 16 A, S, C-HBPAE-b-PCL additive were prepared for the purpose of improve of Ordinary Portland Cement(OPC) properties. The percentage of 16 A, S, C-HBPAE-b-PCL copolymer incorporated in the cement increases residual pressure and impact resistance. According to the blind sample, it was observed that the pressure and impact strength increased as the amount 16 A, S, C-HBPAE-b-PCL copolymer increased. It was determined that the bending strength of the cement increased as the amount of 16 A, S, C-HBPAE-b-PCL copolymer added to the cement increased. The compressive strength and bending resistance of the composite with 16 A, S, C-HBPAE-b-PCL copolymer (weight, 1%) is 10.245 N. The compressive strength and bending resistance test of the composite with 1%, 16 A, S, C-HBPAE-b-PCL copolymer is higher than the blind sample (2.901 N). The compressive strength and bending resistance of the composite 16 A, S, C-HBPAE-b-PCL copolymer (weight, 3%) is 60.423 N. The pressure and impact strength test of the composite with % 3, 16 Arms, Star, Flake-HBPAE-b-PCL copolymer is higher than blind sample.

The compressive strength and bending resistance of the composite with, 16 A, S, C-HBPAE-b-PCL copolymer(weight, 5%) is 66.357 N. The pressure and impact strength test of the composite with 5%, 16 A, S, C-HBPAE-b-PCL copolymer is higher than the blind sample.

The percentage of 16 A, S, C-HBPAE-b-PCL copolymer incorporated into the cement increases residual pressure and impact strength. According to the blind sample, as the amount of 16-arm, star, flake-HBPAE-b-PCL copolymer increases, pressure and impact resistance increase. It is observed that the strength of the 16 A, S, C-HBPAE-b-PCL copolymer added composite material increases as the amount of polymer increases.

References

[1] A. A. Ibrahim, A. E. S. Abdel-Megied, M. S. Selim, H. H. Darweesh, and M. M. Ayoub, “New Polymeric Admixture for Cement Based on Hyperbranched Poly Amide-Ester with Pentaerythritol Core,” Hindawi Publishing Corporation ISRN Materials Science, pp. 1-7, 2013.

[2] D. Kul, L. M. Van Renterghem, M. A. R. Meier, S. Strandman, H. Tenhu, S. S. Yılmaz, “Encapsulation and release by star-shaped block copolymers as unimolecular nanocontainers,” Schubert U.S., Du Prez F.E., *Journal of Polymer Science: Part A: Polymer Chemistry,* vol. 46, pp. 650–660, 2008.

[3] M. Mısır, T. Öztürk, M. Emirik, S. Yılmaz Savaşkan, “Synthesis of novel tetrahydrofuran-epichlorohydrin [Poly(THF-b-ECH)] macromonomeric peroxy initiators by cationic copolymerization and the quantum chemically investigation of initiation system effects,” *Journal of Polymer Science: Part A: Polymer Chemistry*, vol. 48, pp. 2896–2909, 2010.

[4] T. Öztürk, S. Savaşkan Yılmaz**,** B. Hazer, Y. Menceloğlu, “ATRP of Methyl Methacrylate Initiated with A Bifunctional Initiator Bearing Bromomethyl Functional Groups and Synthesis of The Block and Graft Copolymer,” *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 48, p. 1364, 2010.

[5] T. Öztürk, S. Savaşkan Yılmaz, B. Hazer, “Synthesis of a New Macroperoxy Initiator with Methyl Methacrylate and t-Butyl Peroxy Ester by Atom Transfer Radical Polymerization and Copolymerization with Conventional Vinyl Monomers,” *Journal of Macromolecular Science, Part A*, vol. 45, pp. 1-10, 2008.

[6] S. Ramachandran and S. Krishnamoorthy, *Indian J. Tech*., 1984.

[7] R. Sidney and J. R. Young, *Concrete*. Prentice Hall Inc, Englewood Cliffs, p. 671, New Jersey, 1981.

[8] K. Okada and Y. Ohama, “Recent Research and Application of Concrete-Polymer Composites in Japan,” 1987.