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Analysis of Poly(2-Hydroxyethyl Methacrylate)-co-Poly(4-Vinyl Pyridine) Copolymers [COP2,4] Irradiated: an EPR study

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Poly(2-hydroxyethyl methacrylate)-co-poly(4-vinyl pyridine) and poly(HEMA)-co-poly-(4-VP) copolymers were synthesized by free radical polymerization. $K_2S_2O_8$ was used as an initiator. Chain lengths of the copolymer was changed by varying the monomer/initiator ratio. These polymers have molarites of 2.6 and 2.1 respectively and are called COP2 and COP4. The samples were exposed to gamma rays at room temperature. After irradiation, the EPR spectra of COP2 and COP4 were recorded between 120 K and 450 K. From the temperature dependence of the line intensity, it was concluded that unpaired spin concentration in the irradiated samples has been changing with temperature. A theoretical study, presented in this report, was aimed to test success of the machine learning methods and to select the best learning method.

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1.Introduction

Polymer structures, especially copolymers, are attractive due to their mechanical [1], optical [2–4] and electrical [5, 6] properties. Hydrophilically modified polymers have been used in coatings, paints, cosmetics, drilling fluids, in food industry, for petroleum recovery and also in the drug release systems in medical industry [7–9].

The irradiation has important role in polymer chemistry [10]. Generally polymerization and modification of the multicomponent polymer structures have been performed by radiation, because the reactions do not require initiators or catalysts. Sometimes irradiation results in bond scission, degradation of polymer structures [11] and eventually trapped radicals may occur [12]. EPR is a powerful spectroscopic method for detecting radicals in the materials [13–15].

In this study the EPR technique was used for detection of produced radical and measurement of their half-life time. It was also investigated whether the radical concentrations depend on temperature. The copolymers used in the study were synthesized by Hasim Yilmaz at the department of chemistry at Gazi University. The polymer samples used in the study have some interesting properties, for instance, when the powder copolymer in solvent is exposed to electric field, the powder structure in the solvent changes into solid state, however in the absence of electric field, the solid structure again changes into viscous state.

2. Experimental

2.1. Materials

Purification of tetrahydrofuran (THF) (Aldrich, Germany) was performed in vacuum. HEMA (Aldrich, Germany) and 4-VP (Aldrich, Germany) were stored at temperatures below 273 K. The monomers were purified by vacuum distillation before the monomers were transferred into the reaction vessel by a drop funnel under dry N_2(g) atmosphere. Potassium persulfate ($K_2S_2O_8$) (Aldrich, Germany) was used as initiator. The initiator was dried in vacuum oven at 343 K for at least two days.

2.2. Polymerization

HEMA, 4-VP, and $K_2S_2O_8$ were dissolved in THF at different compositions by keeping the mole number of one of the monomer constants. 1.0% of $K_2S_2O_8$ initiator was used in the polymerization mixture. All the glassware and transfer needles were dried by storing in oven at 413 K for overnight before the experiment of polymerization.

$K_2S_2O_8$ (0.1 mol) was dissolved in 50 ml of anhydrous THF at 60 °C and then HEMA (six different amounts of 10, 10, 10, 15, 20 and 25 ml) was added to the solution by dropwise method. The reaction mixture was stirred at 60 °C for 2 h. Subsequently 4-VP (six different

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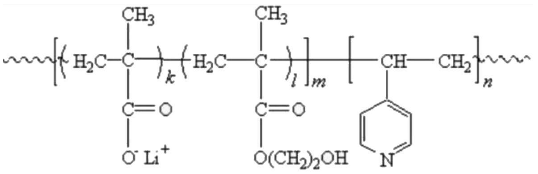
amounts of 15, 20, 25, 10, 10 and 10 ml) was added to the prepared homo poly(HEMA) solution. This reaction proceeded at 333 K for about 32 hours. Afterwards, each of the viscous copolymer solutions was poured in a beaker. Cooled n-hexane was slowly added to this viscous solution to precipitate the copolymers separately. Polymerization was carried out in three-necked flask. All reactions were carried out under dry N_2(g) atmosphere. Reaction mechanism of hydrolysis and formation of lithium salt of poly(HEMA)-co-poly(4-VP) copolymers is shown in Scheme 1, where m, k is the mole number of used monomers and m is identified by the following equation, $m = k + l$.



In addition, the preparation conditions of the copolymers (COP2, COP4) are shown in Table I.

TABLE I

Preparation conditions of the copolymers.

Copolymer	Monomer-1	Monomer-2	Volume-1 [ml]	Volume-2 [ml]	[1] + [2] [mol/l]
COP2	HEMA	4-VP	10	20	2.6
COP4	HEMA	4-VP	15	10	2.1

[1] + [2]/[$K_2S_2O_8$] = 100; $T = (60.0 \pm 1.0)$ °C; $t = 24$ h; solvent = THF; non-solvent = n-hexane.

The precipitates were washed with methanol several times to remove residues of homopolymers and unreacted monomers. The resulting copolymers were dried in vacuum oven at 323 K for two days.

According to the synthesis order, the copolymers were coded as shown in Table I.

The copolymers with different compositions were produced by changing molar ratio of comonomers. The polymers with different molecular weight were obtained by varying the comonomer/initiator ratio.

Homo poly(HEMA) was polymerized at the beginning and then the second monomer, 4-VP, was added to the homo poly(HEMA) solution.

2.3. EPR measurements

The copolymer samples, called COP2 and COP4, were exposed to gamma source with dose rate of 0.980 kGy/h at room temperature for two days at Saraykoy Laboratory of Turkish Atomic Energy Authority. The polycrystalline samples of 0.8 g were placed into cylindrical EPR quartz tubes, and then the EPR measurements were performed at different temperatures between 120 K and 450 K using Bruker EMX 081 Spectrometer (X-Band, Germany). The settings of experimental system were as follows, microwave power of 5 mW, modulation amplitude of 1 G, sweep width of 150 G.

3. Theoretical

3.1. Machine learning method

Machine learning is the common name of the computer algorithms that model a given problem according to the data from the environment of the problem. Machine learning is one of major branches of artificial intelligence which provides several indispensable tools for intelligent data analysis [16]. Artificial neural networks, decision trees, bayesian networks, support vector machines are examples of machine learning methods. Machine learning methods have been commonly used in many different areas for sampling and forecasting, and have high predictive accuracy. Recent successful applications of machine learning include stock market prediction [17], prediction of the future drainage chemistry [18], slump flow prediction [19], medical diagnosis [16] and face recognition [20] applications.

Machine learning algorithms consist of two phases; training phase and the testing phase. The dataset is divided into two parts for training and testing. Training set is used to train the system and a model is created in the first phase, then trained model generates estimates by using the test set.

4. Results and discussion

Formation of radicals in the copolymers (COP2 and COP4) irradiated with gamma rays was observed by EPR measurements. The measurements were performed in the range of 120–450 K. A single line was observed in the spectra of both copolymers. It was shown that the line intensity in the spectra was increasing in the range of 120–300 K, however above 300 K, the intensity values were decreasing. We have observed the disappearance of

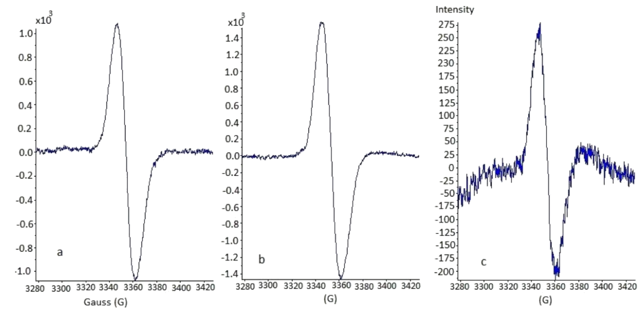


Fig. 1. EPR spectrum of radicals in COP4 at (a) 120 K, (b) 290 K and (c) 390 K.

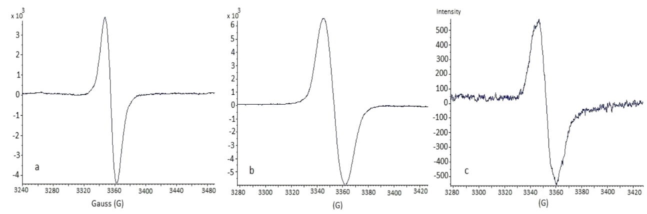


Fig. 2. EPR spectrum of radicals in COP2 at (a) 120 K, (b) 290 K and (c) 430 K.

the signals above 390 K for COP4 and above 430 K for COP2 (Figs. 1 and 2). From the line-shape and the linewidth in the spectra, it was concluded that the same radical structures were produced in the samples after gamma irradiation. Taking into account data from Table I and recorded spectra, it can be said that although COP2 has a smaller molarity than COP4, it has stronger bonds than COP4. in addition it was found that after irradiation, the color of COP2 had not changed, but the color of COP4 had.

Zainuddin et al. have studied gamma-irradiated poly(vinyl alcohol) [12]. They have observed four absorption lines in the recorded EPR spectra at 77 K and have assigned those to the presence of three radicals, an C_α-radical (a triplet), a superimposed neutral radical (a doublet), and an anion radical (a doublet). They have also found the absence of the doublet of neutral radicals and the occurrence of the triplet of the C_α-radical at increased temperature (290 K). Most polymers, exposed to gamma source, have changed mechanical properties from ductile to brittle. Suarez et al. have studied the correlation of mechanical and chemical changes in gamma-irradiated ultra-high-molecular-weight polyethylene [1]. Their experimental results have shown crosslinking and changing of molecular structure, degradation of the mechanical properties and changes in the fracture mechanism from ductile to brittle. The results of our experiments show that following irradiation, the COP4 polymer structure has changed the fracture mechanism from ductile to brittle, however no changes were observed in COP2. The measurements were performed at the same experimental conditions. It was determined from these results that the EPR spectra of the COP2 are similar to the spectra of the COP4, but the g parameters have different values, g-values are 2.0167 for COP4 and 2.0139 for COP2. From these it was concluded that magnetic environment of unpaired electrons in the copolymers (COP2 and COP4) is different. After EPR measurements, we put the samples in the EPR tubes and then the samples were kept in liquid nitrogen for five days. Afterwards, EPR measurements were carried out again and the spectra were recorded. Considering these spectra, it was understood that the materials had stable radicals. The EPR spectra for COP4 is shown in Fig. 3a and for COP2 in Fig. 3b.

TABLE II

Statistical values of the training phase with COP2 data.

Method	Correlation coefficient	Mean absolute error	Root mean squared error	Relative absolute error, [%]	Root relative squared error, [%]
LAZY IBk	0.9998	19.1031	36.0116	2.39	2.17
Bagging RepTREE	0.9989	46.6860	76.7145	5.85	4.62
REPTree	0.9982	58.3557	100.7975	7.31	6.07
M5P	0.9947	100.2402	173.7900	12.56	10.47
M5Rules	0.9930	113.2561	200.4699	14.00	12.00
Regression by discretization	0.9881	169.1283	255.1795	21.19	15.38

TABLE III

Statistical values of the training phase with COP4 data.

Method	Correlation coefficient	Mean absolute error	Root mean squared error	Relative absolute error, [%]	Root relative squared error, [%]
LAZY IBk	0.9996	8.0207	11.4151	4.24	2.92
Bagging RepTREE	0.9993	11.0247	14.9227	5.82	3.81
REPTree	0.9986	13.8677	20.4842	7.33	5.24
M5P	0.9954	23.9465	38.2856	12.65	9.79
M5Rules	0.9924	29.6261	49.4169	15.65	12.63
Regression by discretization	0.9883	41.0134	59.7557	21.67	15.28

At the implementation of the theoretical phase, studies were performed separately for COP2 and COP4. Unlike in our previous work [21], trainings were performed separately for the data sets and average statistical values were calculated. The basic steps of the theoretical study are as follows: firstly the current data was used for training for ten-fold cross validation in the Weka Explorer and it was tried to determine the methods having the least error values. Statistical results for the top six methods are shown in Tables II and III for COP2 and COP4, respectively.

TABLE IV

Average statistical values of the training and test phases for COP2 data.

	Mean absolute error		Root mean squared error		Relative absolute error, [%]		Root relative squared error, [%]	
	Training	Test	Training	Test	Training	Test	Training	Test
LAZY IBk	19.294	108.543	36.679	154.900	2.447	12.116	2.212	9.081
Bagging RepTREE	47.811	118.044	78.747	199.567	6.064	13.038	4.750	11.468
REPTree	59.072	127.778	102.475	214.179	7.492	14.141	6.180	12.353

TABLE V

Average statistical values of the training and test phases for COP4 data.

	Mean absolute error		Root mean squared error		Relative absolute error, [%]		Root relative squared error, [%]	
LAZY IBk	8.191	24.875	12.028	34.711	4.124	12.028	2.790	8.810
Bagging RepTREE	12.049	33.459	17.067	51.214	5.980	16.347	3.897	13.190
REPTree	15.366	34.228	24.722	52.197	7.593	16.699	5.537	13.424

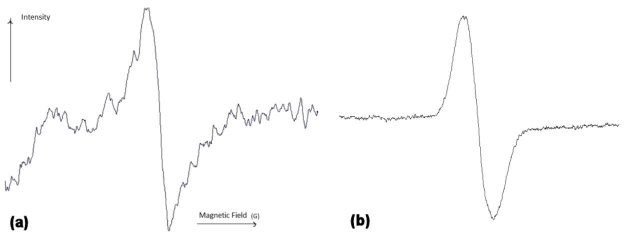


Fig. 3. Recorded EPR spectra of the COP4 (a) and COP2 (b).

The results obtained in this phase helped to determine the methods that will be used in subsequent training and testing phases. Secondly, training and test data sets were created for all temperatures, then training and testing phases were performed separately for the first three methods. The average statistical values of each data set, calculated in the training and test phases, are shown in Tables IV and V.

The results obtained in training and testing phases show that Lazy IBK gave the best results. Comparison of the predicted values, obtained by Lazy IBK, and actual values is shown in Figs. 4 and 5, for test phase.

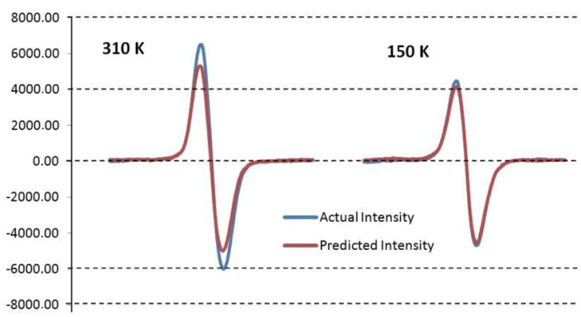


Fig. 4. Comparison of actual and predicted values for test phase of COP2 data (Lazy IBK method).

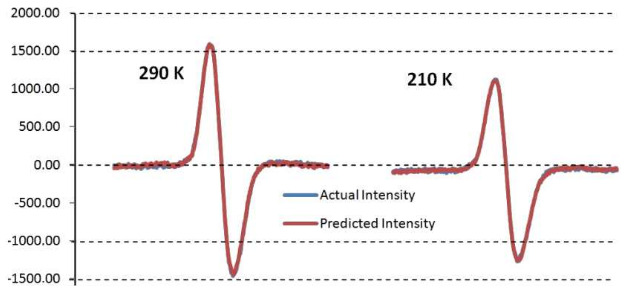


Fig. 5. Comparison of actual and predicted values for test phase of COP4 data (Lazy IBK method).

5. Conclusions

The results of our experiments have shown that after irradiation, fracture mechanism of the COP4 polymer was changed from ductile to brittle, however no change was observed in COP2. In addition, the color of COP4 polymer has changed and its color became claret, but the color of COP2 polymer did not change after the irradiation. The measurements were performed at the same experimental conditions. It was determined from these results that the EPR spectra of the COP2 are similar to the spectra of the COP4, but the g parameters have different values. It was concluded from these results that magnetic environment of unpaired electrons in the copolymers (COP2 and COP4) is different.

At implementation of the theoretical phase, studies were performed separately for COP2 and COP4. The results obtained in training and testing phases have shown that Lazy IBK gave the best results.

Acknowledgments

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