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CONTENTS

C-20-P

NON-ISOTHERMAL KINETICS OF DEHYDRATION OF AG/PVA HYDROGEL NANOCOMPOSITE SYNTHESIZED BY Γ-IRRADIATION

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Abstract

In this study, the non-isothermal kinetics of dehydration of γ-radiolytically synthesized PVA and Ag/PVA nanocomposite hydrogels was investigated by thermogravimetric analysis (TGA). Kinetic analysis was performed by applying different model fitting and model-free kinetic analysis to estimate kinetic parameters, the activation energy (E_a) and pre-exponential factor (A). The analysis showed that incorporation of silver nanoparticles (Ag NPs) into PVA hydrogel matrix has influence on kinetic parameters of dehydration process.

Introduction

Metal NPs embedded in crosslinked polymer matrices, i.e. hydrogels, are the novel class of materials, which have attracted great attention due to applications in catalysis, photonics, optics, pharmaceutics and biomedicine. Incorporation of small amount of metal NPs as nanofiller into polymer matrix leads to improvement of their thermal conductivity, mechanical toughness, optical and catalytic activities [1]. The properties of nanocomposites are strongly dependent on the method of preparation and experimental conditions. Radiolytic method has proved as excellent tool for *in situ* synthesis of Ag/PVA hydrogel nanocomposite. The growth and aggregation processes of Ag NPs are well controlled by polymer molecules, and the interactions between polymer molecules and NPs is responsible for the stability of nanocomposite systems [2].

TGA is a common experimental method used to study variety of chemical and physical processes (thermal degradation, crosslinking, crystallization, dehydration, glass transition, etc.) in polymer systems, induced by temperature changes. Kinetics of degradation can be determined by applying the computational analysis which allows estimating the parameters of the thermal degradation process with specific information about thermal stability of nanocomposites [1].

The aim of this study was to investigate non-isothermal kinetics of dehydration process of PVA and Ag/PVA nanocomposite hydrogels. Kinetic analysis was performed by applying model fitting (Coats-Redfern (CR), Van-Krevelen (VK) and Horowitz-Metzger (HM)) and isoconversional "model-free" methods (Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Tang (T)) to estimate kinetic parameters.

Experimental

The investigated hydrogels, PVA and Ag/PVA nanocomposite, were synthesized following procedure published elsewhere [3]. Non-isothermal thermogravimetric measurements were carried out using a SETSYS Evolution 1750 Thermogravimetric Analyzer. The measurements were conducted on equilibrium swollen PVA and Ag/PVA nanocomposite hydrogels, at heating rates (β) of 2.5; 5; 10 and 15 ^{o}C/min in a dynamic argon atmosphere (flow rate 25 cm^3/min), in the temperature range from 20 to 280 ^{o}C.

Results and Discussion

The TG and DTG curves (not presented) of the dehydration of equilibrated swollen PVA and Ag/PVA nanocomposite hydrogels, obtained at different heating rates, show a one step process. Characteristic temperatures of dehydration process (initial (T_i), at the maximum rate (T_m), final (T_f)) increase with increasing of heating rate, and their values are presented in Table 1.

Table 1. Characteristic temperatures of dehydration process of hydrogels.

	PVA			Ag/PVA		
β (°C/min)	T_i (^{o}C)	T_m (^{o}C)	T_f (^{o}C)	T_i (^{o}C)	T_m (^{o}C)	T_f (^{o}C)
2.5	34	98	129	33	90	124
5	42	105	133	41	110	162
10	50	120	162	46	134	206
15	53	99	173	44	147	230

Kinetic parameters (E_a and A) were estimated using different model fitting and model-free methods, assuming the first-order reaction model for investigated dehydration of equilibrated swollen hydrogels (Table 2) [4, 5].

Table 2. Kinetic parameters determined by different model fitting method.

		PVA			Ag/PVA		
Method	β (°C/min)	lnA	A (1/min)	E_a (kJ/mol)	lnA	A (1/min)	E_a (kJ/mol)
CR	2.5	11.98	$1.60\cdot10^5$	43.8	12.04	$1.69\cdot10^5$	43.3
	5	12.55	$2.82\cdot10^5$	44.2	9.81	$1.82\cdot10^4$	37.5
	10	11.39	$8.84\cdot10^4$	41.4	7.02	$0.11\cdot10^4$	29.6
	15	11.50	$9.87\cdot10^4$	38.9	6.82	$0.09\cdot10^4$	28.8
VK	2.5	13.80	$9.85\cdot10^5$	48.9	13.71	$9.00\cdot10^5$	47.9
	5	14.50	$1.98\cdot10^6$	49.7	11.55	$1.04\cdot10^5$	42.6
	10	12.95	$4.21\cdot10^5$	46.0	8.55	$0.52\cdot10^4$	34.1
	15	12.82	$3.70\cdot10^5$	42.6	8.38	$0.43\cdot10^4$	33.4
HM	2.5	15.34	$4.59\cdot10^6$	53.6	15.33	$4.55\cdot10^6$	52.8
	5	16.02	$9.07\cdot10^6$	54.4	13.09	$4.84\cdot10^5$	47.5
	10	14.69	$2.40\cdot10^6$	51.7	10.30	$2.97\cdot10^4$	40.0
	15	14.61	$2.21\cdot10^6$	48.2	10.14	$2.53\cdot10^4$	39.6

As can be seen from table 2, the highest values for E_a and A was obtained by using HM method, while CR and VK methods give lower values. Independently of the applied method, increase of the β leads to decrease of kinetic parameters.

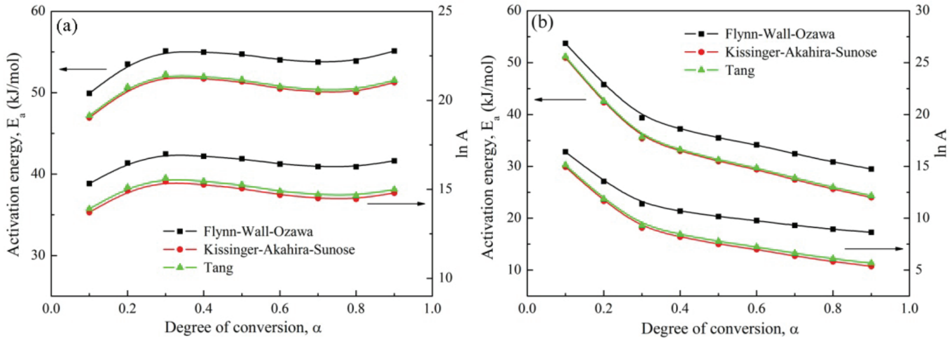

Figure 1. Kinetic parameters E_a and *lnA* as a function of degree of conversion for PVA (a) and 16 mM Ag/PVA nanocomposite (b) hydrogels.

Fig. 1 shows the variation of E_a and *lnA* with the degree of conversion (α) obtained using isoconversion model-free kinetic methods.Values of kinetic parameters for PVA increase with increasing α in the range of 0.1-0.3, and after this range the values are almost the same. On the other hand, for Ag/PVA the values of E_a and *lnA* decrease on the whole range of α, indicating that incorporation of Ag NPs into PVA hydrogel has influence on dehydration process. The stabilization of Ag NPs occurs by interaction with OH groups [3], which probably affect the formation of hydrogen bond between molecules of water and hydrogel and thus changing the mechanism of dehydration.

Conclusion

Kinetic parameters of dehydration of PVA and Ag/PVA nanocomposite hydrogels were determinated by model-fitting and model free kinetic analysis. The obtained values of E_a and A are lower for Ag/PVA nanocomposite. The interactions of Ag NPs with OH groups probably affect the structural rearrangements, and thus induce changing of relaxation mechanism of hydrogel and dehydration process.

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