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Kinetics Study on Thermal Degradation of Polystyrene and Sulfonated Polystyrene from Styrofoam Waste

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ABSTRACT. This research studied the kinetics of the thermal degradation of polystyrene (PS), and sulfonated polystyrene (sPS) which were synthesized from styrofoam waste. The thermal study was conducted by thermogravimetric analysis (TGA) at various heating rates of 10, 15, 20, and 25 dpm. The kinetics parameters were determined by Coats Redfern (CR), Friedman (FM), Kissinger-Akahira-Sunose (KAS), and Ozawa-Flynn-Wall (OFW) models. TGA results showed that PS has a range thermal stability of 274-415 °C, but sPS has range thermal stability of 175-582 °C. A kinetic study of PS shows that the activation energy increases by increasing fraction conversion for all kinetics parameters with a regression value close to 1. While in sPS, the CR method shows an increase in the activation energy value with an increasing fraction conversion. However, CR-FM-KAS and OFM methods obtained an increase in activation energy, then decreased at the fraction conversion above 0.6 and received negative activation energy. The kinetics model successfully explains the degradation of PS and sPS. Additionally, the high thermal stability of sPS from styrofoam waste shows that this material has good potential as a polymer electrolyte material.

Keywords: kinetics, polystyrene, styrofoam waste, sulfonated polystyrene, thermogravimetric analysis

INTRODUCTION

Polymer electrolytes have been widely used in various fields such as energy storage in the form of batteries, electrochemical equipment, ion sensor, electrochromic display (Tominaga, 2017), and as proton conductor (Hooshyari et al., 2021). In the polymer electrolyte should provide a high ionic conductivity and high thermal stability with conductivity of 0.1-1 S/cm with thermal stability up to 120 °C (Agrawal & Pandey, 2008; Esmaeili et al., 2019). Therefore, some research on polymer electrolyte aim to find a polymer with a good thermal stability represent by high degradation temperature, such as sulfonated poly(ether ether keton) (SPEEK) which has degradation temperature of 163.1 °C and up to 192.1 °C, and a final decomposition temperature of 617.1 °C (Awang et al., 2018). Polyacrilonitrile/cellulose acetate (PAN/CA) with Boehmite filler used for the lithium-ion battery has thermal stability up to 200 °C (Yang et al., 2021). A lithium battery separator using es-SP modified with LiTFSI created thermal stability of 408 - 463 °C (Hu et al., 2021). SPEEK with various fillers used to create PEM has a degradation temperature above 180 °C (Pokprasert et al., 2022). Poly (arylene ether nitrile) (PEN) porous membranes have degradation temperatures above 500 °C (Lin et al., 2021).

Polystyrene is a potential thermoplastic polymer for electrolyte because of its good mechanical properties and its high thermal stability (Andrade et al., 2019). Polystyrene is also a polymer for synthesizing styrofoam, a polymer with broad application in everyday living, such as fror food packaging, materials construction, electronic packaging and compact disks (Ho et al., 2018). Due to its wide application, styrofoam waste is now become a problem for the environment. Therefore, some effort to overcome this styrofoam waste is important, such as by extracting the polystyrene content within styrofoam and then using the PS for polymer electrolyte synthesis. Even though, PS has good mechanical and thermal properties, however it need modification to increase the ability to conduct protons. Lim et al., (2012) reported that Al₂O₃ modified polystyrene with an ionic conductivity of 9.78 x 10⁻⁵ S/cm. Meanwhile, polyacrylonitrilemodified polystyrene has an ionic conductivity of 3.83 x 10⁻³ S/cm (Tan et al., 2019), polystyrene-altered butadiene has proton conductivity of around 10⁻² S/cm (Idibie et al., 2009).

Polymer blend and composite of polystyrene have also been reported to have high thermal stability. A composite of sulfonated polysulfone with grafted poly(phosphonated polystyrene) to the polysulfone backbone has thermal stability up to 300 °C for fuel cell application (Yu et al., 2019). The Sulphonic acid polystyrene is also grafted with graphene oxide nanoplatelets (PSSA-g-GONP) grafting filler to increase the thermal stability of the poly(ethersulfonated ether ketone) (sPEEK) composite, with degradation temperatures of up to 315 °C (Shukla et al., 2020). These show that the thermal properties of the polystyrene blend and composite have been studied extensively. Meanwhile, from our literature review; there has been very little study on the polystyrene (PS) thermal of properties and sulfonated polystyrene (sPS) from styrofoam waste, so a comprehensive study on the material will be executed using thermogravimetric analysis with varying heating rate.

The mechanism of polymer degradation can be analyzed by Coats Redfern (CR), Ozawa-Flynn-Wall (OFW), Kissinger-Akahira-Sunose (KAS) and Friedman (FM) models. Analysis of polymer kinetics and degradation has been carried out on several polymers i.e The activation energy of polypropylene is analyzed by OFW method (Nisar et al., 2018). The degradation kinetics of PVC and its blends using ZnO when analyzed using the FWO, KAS, and FM methods (Altarawneh et al., 2022). The activation energy of PVDF was analyzed by the OFW method (de Jesus Silva et al., 2020).

In this work, polystyrene (PS) was extracted from styrofoam waste and have been synthesized to sulfonated polystyrene (sPS). Thermal degradation to the prepared-PS and sPS were performed at various heating rates of 10, 15, 20, and 25 degrees perminute (dpm) within the temperatures ranging 25 to 900 °C under air. The thermal stability and kinetics degradation of PS and sPS were determined using CR, OFW, KAS, and FM models. The results of each analytical model are also compared and discussed.

EXPERIMENTAL SECTION

Materials

The materials used in this study were styrofoam waste from food wrappers. CHCl₃, dichloromethane

(DCM), 2-propanol, and acetic anhydride purchase from Merck. H_2SO_4 (96-98%) obtained from Smart-Lab Indonesia. Commercial polystyrene (Mw: 350.000 g/mol) purchase from Sigma Aldrich. The instruments used in this study were Fourier Transform Infrared (FTIR) spectrometer (IRPrestige-21 Shimadzu) with a KBr plate in the range of 400–4000 cm⁻¹, and Thermogravimetic Analysis (TGA) (Linseis PT-1600) with various heating rates of 10, 15, 20, and 25 dpm.

Isolation of Polystyrene from Styrofoam Waste

The isolation of polystyrene (PS) from styrofoam waste was followed a previous work (Pramono et al., 2014). As much as 12 g of styrofoam waste was weighed and dissolved in 50 mL chloroform. The mixture was stirred until homogenous and isolated by dripping on hot aquadest. The isolate was dried in an oven at 60 $^{\circ}$ C for 24 h.

Synthesis of Sulfonated Polystyrene

As much as 5 g of isolated PS was dissolved using 40 mL of dichloromethane. After that, 20 mmol of acetyl sulphate was made by mixing acetic anhydride and sulphuric acid in dichloromethane solvent under ice condition. Acetyl sulphate was added to the mixture and refluxed at 40 °C for 1 h. The reaction was terminated using 10 mL of 2-propanol and isolated by slowly dripping the mixture into a hot aquadest. The product was dried in an oven at 60 °C for 24 h. After drying, the sample was characterized using FTIR to ensure the formation of sulfonated polystyrene (sPS) and determination of molecular mass using the viscometric method.

Determination of the Degradation Kinetics of Sulfonated Polystyrene from a Styrofoam Waste

Thermal degradation was carried out using Linseis STA 1600 thermogravimetric analysis, with variations of heating rate 10, 15, 20, and 25 degrees perminute (dpm) and range temperature from 25 to 900 °C using air atmosphere. The kinetics degradation and parameter were determined using CR, OFW, KAS, and FM equations in **Table 1**.

 Table 1. Variations of kinetics models used for kinetics studies of the degradation of PS and sPS from styrofoam waste (Nisar et al., 2021)

No.	Method	Equation	Reference		
1	CR	$ln\left[-ln\left[\frac{(1-\alpha)}{T^2}\right]\right] = -\frac{Ea}{RT} + ln\left(\frac{AR}{\beta Ea}\right)$	Coats et al., 1964		
2	OFW	$ln(\beta) = ln\left[\frac{AEa}{Rg(\alpha)}\right] - 5,331 - 1,052 \left(\frac{Ea}{RT}\right)$	Flynn & Wall, 1966; Ozawa, 1965; Popescu, 1996; Starink, 1996		
3	KAS	$ln\left(\frac{\beta}{T^2}\right) = ln\left[\frac{AR}{EaG(\alpha)}\right] - \frac{Ea}{RT}$	Akahira & Sunose, 1971; Kissinger, 1956,1957		
4	FM	$ln\left(\beta\frac{d\alpha}{dT}\right) = ln[f(\alpha)A_{\alpha}] - \frac{Ea}{RT}$	Fridman, 1969		

RESULTS AND DISCUSSION

Analysis of Functional Groups and Thermal Stability

The initial characterization of the commercial PS, PS and sPS identifted functional groups by FTIR analysis. The results are depicted in Figure 1. Meanwhile, thermal stability of commercial PS, PS and sPS was analyzed by TGA. The results are depicted in Figure 2. It can be seen in Figure 1 that polystyrene from styrofoam waste shows vibration at 3032 cm⁻¹ C-H aromatic vibration, which is identified as vibrations at 2932 and 2885 cm⁻¹ refer to aliphatic C-H. Meanwhile, peaks at 1494 and 1452 cm⁻¹ refer to aromatic C=C and at 763 and 702 cm^{-1} refer to the benzene monosubstitution of C-H. This is in line with commercial PS spectra which showed vibration at 2850-3081 cm⁻¹ indicating C-H aliphatic. Peak at 1450 and 1492 cm^{-1} indicates aromatic C=C vibrations. And absorption of 699 cm⁻¹ and 755 cm⁻¹ which shows the benzene mono substitution of C-H. After sulfonation, intensity peak of C-H and C-C in polystyrene decreases. Meanwhile, peaks at 3466 and 1169 cm^{-1} reveal indicate the presence of S=O and C-S vibrations in sulfonated polystyrene. A peak at 1032 cm⁻¹ also reveals indicating the presence of - SO_3H - group and a peak at 1005 cm⁻¹ refers to sulfonate substitution in phenyl ring, which confirm thesulfonated polystyrene to occurred (Tran et al., 2020). Determination of polymer molecular mass using viscometric method obtained molecular mass value of PS which is 6048.90 g/mol and sPS 9321.96 g/mol. The increase in polymer molecular mass is considered to be the presence of -SO₃H groups that enter the PS main chain (Ergun et al., 2012).

Figure 2 shows the thermogram and the degradation temperature ranges of PS and sPS. Thermal degradation of PS from styrofoam waste occurs in one step, between 274-415 °C. It shows the thermal degradation of the PS main chain. The degradation of PS from styrofoam waste has a degradation range that is guite similar to commercial PS at 292-422 °C. The difference in the degradation range between commercial PS and PS from styrofoam waste is due to differences in molecular weight. Commercial PS with a higher molecular weight than the isolated PS has a higher thermal stability. Meanwhile, in sPS appears in three stages of the degradation process. The first degradation is due to the evaporation of water in the room temperature up to 175 °C. The second stage due to the degradation of the sulfonate group and backbone PS chain in 175-407 °C and (Müller et al., 2012; Tran et al., 2020). At high temperature, the degradation produces polyaromatic compounds and cross-linked so that degradation occurs at higher temperatures 407-582 °C . Based on these data, PS has a range thermal stability of 274-415 °C, but sPS has range thermal stability of 175-582 °C. This indicates that sPS has better thermal stability than PS (Salim et al., 2021).

Effect of Heating Rate on the Kinetics of Thermal Degradation

According to the Kinetics Committee of ICTAC, it was stated that a minimum of three different heating speeds must obtain good kinetic results (Ali *et al.*, 2019). However, in this research, four heating speeds were used 10, 15, 20, and 25 °C/min.



Figure 1. FTIR spectra of commercial polystyrene (black), wasted polystyrene (red), and sulfonated polystyrene (blue)



Figure 2. Thermograms of commercial PS, PS, and sPS



Figure 3. Thermogram of PS from styrofoam waste



Figure 4. Thermogram of sPS from styrofoam waste

The effect of heating rate on the degradation temperature of PS from styrofoam waste are shown in Figure 3 and Table 2. The degradation of PS occurred in a single step with no change in the amount of water at the initial stage of degradation. The results showed that the degradation temperature became higher when the heating rate was increased. The degradation of polystyrene was observed in one step between 274 and 442 °C. Also, it can be seen that the heating rate enhancement also increase Tmax about 27 °C. Ali et al., (2019) used a heating rate of 5 to 20 °C/min and produced an increasing Tmax of 33.5 °C with a maximum temperature obtained at 403.26 to 436.76 °C. Nisar et al., (2019) reported that degradation of polystyrene with a heating rate of 5 to 20 °C/min resulted in Tmax of 387 to 438 °C, with an increase of 51 °C.

The degradation of sulfonated polystyrene occurs through several stages as shown in **Figure 4** and **Table 3**. The degradation temperature increased with an increasing heating rate. The first degradation occurred at room temperature and 236 °C. The degradation is related to the loss of water absorbed into the sulfonated polystyrene. The second degradation occurred at 175 and 424 °C. The second stage showed the degradation of the sulfonate groups attached to the polystyrene. The third degradation was observed at 407 and 699 °C. The third was the degradation of the polystyrene backbone (Pramono et al., 2014).

The thermograms of PS and sPS describe a shift as the heating rate increased due to the slow diffusion of heat. At a lower heating rate, the increasing temperature can reach equilibrium at any point. At a fast heating rate, equilibrium is reached slowly so that the curve moves toward a higher temperature (Nisar et al., 2019). The kinetics degradation was computed using CR, OFW, KAS, and FM methods; and some plots of kinetic parameters are presented in **Figure 5** and **Table 4**.

Heating rate (dpm)	Onset (°C)	Offset (°C)
10	274	415
15	287	422
20	294	432
25	298	442

 Table 2. Effect of heating rate on the degradation temperature of PS from styrofoam waste

Heating			Degradation Te	emperature (°C)		
Rate			l	l	l		
(dpm)	Onset	Offset	Onset	Offset	Onset	Offset	
10	30	175	175	407	407	582	
15	30	238	238	410	410	682	
20	30	233	233	416	416	641	
25	30	236	236	424	424	699	

Table 3. Effect of the heating rate on the degradation temperature of sPS from styrofoam waste

Table 4. Kinetic parameters using CR, OFW, KAS and FM methods for PS from styrofoam waste

	CR		OFW		KAS		FM	
α	Ea (kJ/mol)	R ²						
0.1	0.783	0.9999	73.02	0.9955	70.64	0.9911	60.30	0.9218
0.2	0.803	0.9999	80.68	0.9495	69.69	0.9647	69.99	0.8925
0.3	0.812	0.9999	91.88	0.9789	84.40	0.9603	126.38	0.9765
0.4	0.813	1	101.90	0.9473	97.30	0.9446	148.60	0.9438
0.5	0.810	1	120	0.9209	114.19	0.9454	196.28	0.9873
0.6	0.802	1	123.85	0.9808	121.95	0.9506	163.54	0.9857
0.7	0.791	1	148	0.9711	125.57	0.9521	146.07	0.9642
0.8	0.774	1	148	0.9711	128.38	0.9555	141.99	0.9469
0.9	0.746	1	119.99	0.9820	130.04	0.9401	139.46	0.8507



Figure 5. Kinetics plot of (a) CR, (b) OFW, (c) KAS and (d) FM methods for decomposition of PS from styrofoam waste.

Figures 5a-d show plots of CR, OFW, KAS and FM for polystyrene from styrofoam waste, with the activation energy as shown in Table 4. The activation energy value obtained on tests using CR plots increased with an increase in fraction convertion of up to 0.4 with an activation energy value of 0.813 kJ/mol. The activation energy decreased until the fraction convertion reached 0.9, which was 0.764 kJ/mol. The OFW plot increased activation energy following an increase of fraction from 0.1 to 0.8 i.e 73.02 kJ/mol to 148 kJ/mol, and decreased for 0.9 fraction, which was 119.99 kJ/mol. The KAS plot showed an increase in the activation energy value with an increase in the fraction value from 0.1 to 0.9 ranging from 69.69 kJ/mol to 130.04 kJ/mol, while the FM plot shows an increase in the activation energy value from the fraction convertion of 0.1 to 0.5, namely 60.30 kJ/mol to 196.28 kJ/mol. Then it decreased in the 0.6 to 0.9 fraction of 56.82 kJ/mol. In general, the regression coefficient generated in the calculation of PS activation energy has a good linearity, which ranges from 0.8507-1. Where, the best regression coefficient value is in the CR plot, which is around 0.999-1, with a low activation energy value. The activation energy which was calculated by CR method is smaller than the value in the literature. Nisar et al., (2019) found that activation energy values obtained ranged from 105.421 to 126.289 kJ/mol by the CR method. Meanwhile, in Ali et al., (2019) the activation energy values obtained from 105 to 148.48 kJ/mol.

Activation energies calculated by OFW, KAS and FM methods are closed to literatures. Nisar et al., (2021) used the OFW, KAS, and FM methods to determine the activation energy in the pyrolysis

process for making fuel oil. The activation energy was obtained of 76.02-124.23 kJ/mol, 72.24-121.30 kJ/mol and 79.98-130.69 kJ/mol, for OFW, KAS, and FM, respectively. Ali et al., (2019), in the process thermocatalytic decomposition using polystyrene waste under OFW, KAS and FM methods, the activation energy values produced were 99.41-140.52 kJ/mol, 103.67-149.15 kJ/mol, and 99.93-141.25 kJ/mol, respectively.

Figures 6a-d show the plots of CR, OFW, KAS and FM for sPS from styrofoam waste with the activation energy shown in **Table 5**. The activation energy value on tests using CR plots increased with an increase in fraction convertion up to 0,9 with an activation energy value of 0.888 kJ/mol. The OFW plot increased activation energy following an increase of fraction from 0.1 to 0.6, i.e at 9.30 kJ/mol to 341.73 kJ/mol and decreases for 0.7 up to 0.9 fraction with activation energy 60.10 kJ/mol. Fraction of 0.7 OFW method was found negative activation energy which is -64.75 kJ/mol. The KAS plot showed an increased in the activation energy value with an increase in the fraction value up to 0.6, with range of activation energy value is 3.12 to 347.46 kJ/mol, and decreases for 0.7 up to 0.9 fraction with activation energy 49.22 kJ/mol. Fraction of 0.7 KAS method was found negative activation energy i.e -79.78 kJ/mol. The FM plot increase activation energy followwing an increase in the fraction up to 0.5 and 0.6 with the activation energy values almost the same, i.e 429.58 kJ/mol and 429.28 kJ/mol and decreases for 0.7 up to 0.9 with a negative activation energy 18.42 kJ/mol. Where the best regression coefficient value is in the CR method with a regression coefficient value of 0.9995-1.



Figure 6. Kinetics plot of (a) CR, (b) OFW, (c) KAS and (d) FM methods for the decomposition of sPS from styrofoam waste

	CR		OFW		KAS		FM	
α	Ea	R^2	Ea	\mathbb{R}^2	Ea	\mathbb{R}^2	Ea	R ²
	(kJ/mol)		(kJ/mol)		(kJ/mol)		(kJ/mol)	
0.1	0.551	0.9995	9.30	0.6403	3.12	0.1502	1.28	0.0062
0.2	0.735	0.9998	23.61	0.5191	15.34	0.2914	29.45	0.5181
0.3	0.779	1	111.97	0.9029	107.5	0.8850	248.24	0.9586
0.4	0.787	1	155.74	0.9759	153.27	0.9726	216.01	0.9923
0.5	0.793	1	268.61	0.9828	271.74	0.9814	429.58	0.9875
0.6	0.793	1	341.73	0.9631	348.46	0.9607	429.28	0.9561
0.7	0.815	0.9999	-64.75	0.8708	-79.78	0.9023	-212.87	0.9563
0.8	0.884	1	44.31	0.0907	33.38	0.0486	-39.35	0.2630
0.9	0.888	0.9999	60.10	0.6687	49.22	0.5497	-18.42	0.5308

Table 5. Kinetic parameters using CR, OFW, KAS and FM methods for sPS from styrofoam waste

The activation energy of PS is increased with an increase in the fraction conversion, as in some methods. Similar results were also obtained for sPS, but a higher fraction conversion of sPS decreases the activation energy. The increase in activation energy value proportional to the fraction convertion indicates a gradual breakdown of bonds in the polymer (Nisar et al., 2021). Molecules with weak bonds will be broken first, followed by those with stronger bonds (Ali et al., 2019). Additionally, most solid-state reactions were not simple which were one-step reactions and the mechanism has many stages.

The thermal stability of PS is due to the type of carbocation produced due to branching in the basic structure. PS has a weak bond due to the presence of tertiary carbon at the beginning of the degradation reaction at each heating stage (Palmay et al., 2021). The mechanism of degradation PS and sPS follows a free radical mechanism. Which involves initiation, propagation and termination steps. Initiation process

show the initial activation energy was to be low which was attributed to the breakage of a few weak linkages and loss of volatile compounds. After reaching the optimum temperature, there were several secondary reactions in the form of dimerization and polymerization, which produced polyaromatic compounds that required higher energy for the degradation process (Nisar et al., 2019). The presence of an aromatic ring in polystyrene increases the activation energy at the heating rate. The degradation of the polystyrene chain began with a rapid random splitting. This degradation involves breaking the bonds between individual atoms that make up the polymer chain and requires a higher activation energy, and degradation occurs above 400 °C at low heating rates, where heat diffusion is slower, degradation can easily occur initiated due to more thermally bonded attached to the polymer chain (Das & Tiwari, 2017; Palmay et al., 2021). However, there was an increase in activation energy in sPs because the presence of intra



Figure 7. Comparison graph between the activation energy values using CR, OFW, KAS, and FM methods on α (a) PS and (b) sPS

and intermolecular interaction hydrogen bonds in the sulfonate group causes an increase thermal stability (Luo et al., 2009). Thus, more energy is needed to break the strong bonds in the backbone chain. The activation energy value increased due to the breaking of several covalent bonds (Heydari et al., 2015; Nisar et al., 2019)

Additionally, there was also a negative activation energy value of sPS fraction conversion above 0.6. This phenomenon is caused by the relationship between the effective activation energy and the activation energy and the enthalpy for each step of the reaction (Vyazovkin, 2016). As in the previous explanation, that the second stage of degradation in PS can form polyaromatic compounds, while in sPS, it is possible to form new species of sulfonate segments that form cross-linked during heating, so that in fractions above 0.6, negative enthalpy is obtained.

Kinetic Studies Comparison

The activation energy of the conversion fraction using CR, OFW, KAS and FM methods on polystyrene and sulfonated polystyrene is shown in Figure 7. The CR model shows a lower and slightly increase in activation energy in both samples. The FM model shows the highest activation energy value, while OFW and KAS models show the activation energy values that similar. The comparisons produced in this test had the same results as those in the study by Nisar et al., (2019). Inconsistent activation energies over a certain conversion range can be caused by a series of complex and non-isoconventional reactions that are formed in the solid state (Dhaundiyal et al., 2019). The inconsistency of activation energy is also influenced by differences in the kinetic methods. CR method is highly inaccurate and highly incoherent (Dhaundiyal et al., 2019) where the reaction model changes with the extent of the reaction, cannot be analyzed with CR method (Ebrahimi-Kahrizsangi & Abbasi, 2008). The activation energies of OFW and KAS methods shown

similar result cause both of this method assuming a constant activation energy. This assumption can lead to some systematic errors in estimating the value of activation energy with variations in the conversion rate. Meanwhile, the FM method activation energy is independent of the range of heating rates. (Wu et al., 2013).

CONCLUSIONS

The thermal stability and kinetics of degradation of PS and sPS from styrofoam waste have been analysed by thermogravimetric under various heating rates of 10, 15, 20, and 25 dpm. The degradation of PS occurred in one step degradation, meanwhile the degradation of sPS occurred in three steps degradation that showed evaporation of water absorbed on sulfonated polystyrene, sulfonate groups, and PS backbone. The thermal degradation of the polymer increased when the heating rate was increased. The activation energy of the PS CR model i.e 0.813 kJ/mol with fraction value 0.4, OFW model i.e 148 kJ/mol with fraction value 0.8, the KAS model i.e 130.04 kJ/mol with fraction value 0.9 and the FM model i.e 196.28 kJ/mol with fraction value 0.5. Meanwhile, the activation energy of the sPS CR model i.e 0.888 kJ/mol with fraction value 0.9, the OFW model i.e 341.73 kJ/mol with fraction value 0.6, the KAS model i.e 348.46 kJ/mol with fraction value 0.6 and the FM model i.e 429.58 kJ/mol with fraction value 0.5. The best regression coefficient for determining the activation energy using four kinetic models on PS and sPS samples is the CR model with a regression coefficient value of 0.9995-1 with a lower and constant activation energy value compared to other models.

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