INVESTIGATION OF THE EFFECT OF BROMINE-CONTAINING FLAME RETARDANTS ON THE THERMAL STABILITY OF POLYVINYL CHLORIDE

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Abstract. Polyvinyl chloride (PVC) compositions modified with a bromine-containing flame retardant - **3-bromo-2,3-diiodopropen-2-ol-1** were developed. The thermal characteristics of the PVC compositions, including mass loss, thermal decomposition rate, and the amount of energy consumed during polymer degradation, were investigated using the derivatographic method. It was established that an increase in the content of **3-bromo-2,3-diiodopropen-2-ol-1** leads to a decrease in the thermal stability of PVC compositions. The thermal decomposition rate of PVC compositions was determined, and it was revealed that an increase in the content of **3-bromo-2,3-diiodopropen-2-ol-1** results in an increase in the decomposition rate. In addition, the amount of energy consumed during the decomposition of PVC compositions was evaluated. The results indicate that a higher flame-retardant content leads to increased energy consumption during thermal degradation, which may be attributed to enhanced intermolecular interactions between PVC macromolecules and flame-retardant molecules.

Keywords: 3-bromo-2,3-diiodopropen-2-ol-1, bromine, iodine, temperature, mass loss, decomposition rate, energy consumption during decomposition, polyvinyl chloride, flame retardant, fire resistance.

Аннотация. Разработаны композиции поливинилхлорида (ПВХ) с бромсодержащим антипиреном - 3-бром, 2,3-дийод пропен-2-ол-1. Исследованы их термические характеристики композиций поливинилхлорида, таких как потеря массы, скорость термического разложения и количество израсходованной энергии для разложения полимеров дериватографическим методом. Установлено, что с увеличением содержания 3-бром, 2,3-дийод пропен-2-ол-1 термостабильность композиций ПВХ снижается. Определена скорость термического разложения композиций ПВХ. Выявлено, что с увеличением содержания 3-бром,2,3-дийод пропен-2-ол-1 возрастает скорость разложения композиций ПВХ. Также определено количество израсходованной энергии для разложения композиций ПВХ. Установлено, что с увеличением содержания 3-бром, 2,3-дийод пропен-2-ол-1 возрастает количество израсходованной энергии композиций ПВХ. Это может быть связана усилением межмолекулярного взаимодействия между макромолекулами ПВХ и молекулами антипирена.

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Ключевые слова: 3-бром, 2,3-дийод пропен-2-ол-1, бром, йод, температура, потеря массы, скорость разложения, израсходованной энергии разложения, поливинилхлорид, антипирен, огнестойкость.

Annotatsiya. Brom tutgan antipiren — **3-brom, 2,3-diyod propen-2-ol-1** bilan modifikatsiyalangan polivinilxlorid (PVX) kompozitsiyalari ishlab chiqildi. Polivinilxlorid kompozitsiyalarining massa yo‘qotilishi, termik parchalanish tezligi hamda polimerlarning parchalanishi uchun sarflanadigan energiya miqdori kabi termik xususiyatlari derivatografik usul yordamida tadqiq etildi. **3-brom, 2,3-diyod propen-2-ol-1** miqdorining ortishi bilan PVX kompozitsiyalarining termik barqarorligi pasayishi aniqlandi. PVX kompozitsiyalarining termik parchalanish tezligi aniqlanib, **3-brom, 2,3-diyod propen-2-ol-1** miqdori oshishi bilan parchalanish tezligi ortishi kuzatildi. Shuningdek, PVX kompozitsiyalarining parchalanishi uchun sarflanadigan energiya miqdori ham aniqlanib, antipiren miqdorining ko‘payishi bilan ushbu ko‘rsatkichning oshishi qayd etildi. Bu holat PVX makromolekulalari bilan antipiren molekulalari o‘rtasidagi molekulalararo o‘zaro ta’sirning kuchayishi bilan bog‘liq bo‘lishi mumkin.

Kalit so‘zlar: 3-brom, 2,3-diyod propen-2-ol-1, brom, yod, harorat, massa yo‘qotilishi, parchalanish tezligi, parchalanish uchun sarflangan energiya, polivinilxlorid, antipiren, olovbardoshlik.

Introduction

Among synthetic polymers, polyvinyl chloride (PVC) occupies a prominent position due to its extensive industrial application. According to global production statistics for 2022, PVC ranks fourth worldwide, with an annual output of approximately 47.5 million tons [1-5]. This widespread use is attributed to a combination of advantageous properties, including high dielectric performance, versatility, cost-effectiveness, hygienic safety, environmental compatibility, weather resistance, and inherent flame retardancy.

Despite these advantages, PVC exhibits certain technological limitations, the most significant of which is its limited processability. This drawback arises from the narrow temperature interval between its melting and thermal degradation. To overcome this limitation, PVC is commonly modified with various additives such as thermal stabilizers, plasticizers, fillers, pigments, bleaching agents, and other functional modifiers. These components significantly influence the physicomechanical, dielectric, and flammability characteristics of the resulting compositions.

Although unmodified PVC is classified as a self-extinguishing polymer with a relatively high oxygen index, the incorporation of conventional modifiers often reduces its flame-retardant performance. Consequently, additional flame retardants particularly halogen-, phosphorus-, and nitrogen-containing compounds are

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introduced to enhance fire resistance. In this context, the present study focuses on evaluating the effect of a bromine-containing flame retardant on the thermal stability of PVC composites.

Therefore, this paper presents the results of a study on the thermal stability of fire-resistant PVC compositions using the derivatographic method.

Research Objects and Methods. The research object was PVC obtained by aqueous suspension polymerization of vinyl chloride in the presence of a heterogeneous mercuric chloride catalyst impregnated with activated carbon, synthesized at Navoiazot JSC.

Bromine-containing fire retardant - 3-bromine, 2,3-diiodo propene-2-ol-1 was synthesized according to the method [6].

The compositions were prepared as follows: the required amount of 3-bromo, 2,3-diiodo propene-2-ol-1 was dissolved in acetone and mixed with the required amount of PVC powder, after which the solvent was removed in a vacuum drying oven until constant weight.

Derivatographic analysis of the samples was carried out using a DTG -60 differential thermal analyzer . Shimadzu " in the temperature range of 30-700 ° C with a heating rate of 5 degrees/min.

RESULTS AND DISCUSSION

The thermal characteristics of a polyvinyl chloride composite with 3-bromo, 2,3-diiodopropene-2-ol-1 were studied using the derivatographic method. The results are presented in Fig. 1, Fig. 2, and Table 1.

Table 1

Results of the analysis of DTGA curves of a composition of polyvinyl chloride with a brominated flame retardant

	Temperature , ° C	Weight loss, %				
		5.0 mass %	10.0 mass %	15.0 mass %	20.0 mass %	30.0 mass %
1	50	0.665	0.715	0.814	0.914	0.978
2	100	1,585	1,685	1,765	1,865	1,952
3	150	7 , 3 1 6	7,916	8,11 6	9 ,21 6	9,985
4	200	9,035	9,935	10.05	11.25	12.35
5	250	11.85	11.97	12.07	13.17	14.27
6	300	19.49	19.55	19,88	20.1 8	21.2 8
7	350	28,22	29 , 57	29 , 89	30 , 54	31 , 74
8	400	47,15	48,19	48,58	49,18	50.45
9	450	57 , 09	58 , 11	59 , 14	60 , 44	61 , 48
10	500	68,11	68.44	69.12	70.22	71.45

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11	600	77,27	79,63	80,98	81,11	82,15

Analysis of the results of the study of the DTA curves in Fig. 1 and Table 1 shows that the curve consists mainly of two sigmoids, the process of which occurs in two stages.

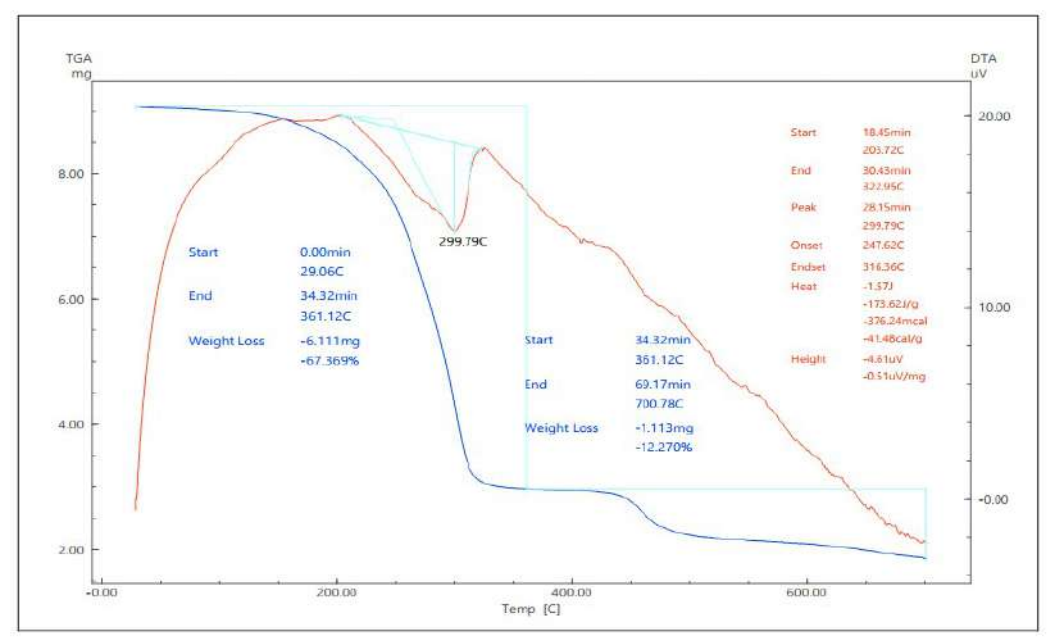


Fig. 1. Derivatogram of polyvinyl chloride compositions with 10.0 % 3-bromo, 2,3-diiodo propene-2-ol-1:(1-DTGA curve; 2-DSC curve)

The first stage occurs in the temperature range from 70 ˚C to 325 ˚C, with a mass loss of 24.45% by weight. The second stage occurs in the temperature range from 325 ˚C to 500 ˚C, with a mass loss of 68.44% by weight.

Decomposition begins at 50 ^{0}C for the original PVC, where the mass loss is 0.289 wt.%. With increasing temperature, the rate of decomposition of the original polymer increases. Intensive decomposition of the polymer mainly occurs after 300 ^{0}C and reaches a maximum at 350 ^{0}C, while the mass loss is 31.22 wt . % and 48.08 wt. %, respectively. Comparison of the study results in Table 1 show that when a brominated flame retardant is introduced into the PVC composition, the thermal stability of the composition decreases. For example, in polyvinyl chloride compositions containing 5.0; 10.0; 20.0 and 30.0 wt . % bromine -containing fire retardant the thermal stability of the composition with increasing content of the latter at 400 ^{0}C is 47.15 ; 48.19 ; 48.58 ; 49.18 and 50.45 mass %, respectively. This is apparently due to the fact that with an increase in the content of bromine-containing fire retardant, leading to a decrease in the thermal stability of the composition, associated with the intensifying action of bromine, which is an active electrophilic reagent that can attack double bonds and enter into an addition reaction with polyenes. The resulting structures can accelerate the elimination of hydrogen halides with the formation of polyenes , which accelerate the thermal decomposition of polyvinyl chloride [7].

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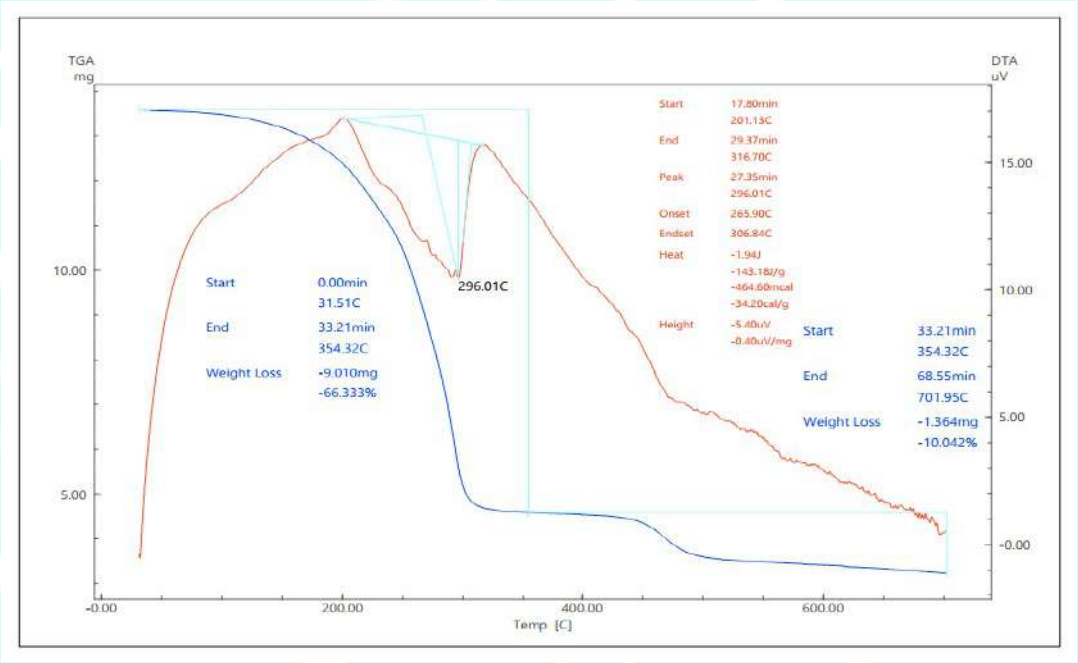


Fig. 2. Derivatogram of polyvinyl chloride compositions with 20.0 wt.% 3-bromo, 2,3-diiodo propene-2-ol-1: (1-DTGA curve; 2-DSC curve)

One of the criteria for assessing the thermal stability of polymeric materials is determining the rate of thermal decomposition of the PVC composition. Therefore, the DTGA curves were used to determine the dependence of the rate of mass change on time, the results of which are presented in Table 2.

Analysis of the decomposition rate of the PVC-based composition (Table 2) shows that the decomposition rate occurs in the temperature range from 50 ˚C to 600 ˚C at a rate of 0.138–3.467 mg/min. Analysis of the study results shows that the decomposition rate generally occurs at a high rate in the range from 250 ˚C to 500 ˚C.

Table 2

Results of the analysis of the decomposition rate of polyvinyl chloride with a brominated flame retardant using DTGA curves

No.	Temperature , ºC	Decomposition rate, mg/min				
		5.0 mass %	10.0 mass %	15.0 mass %	20.0 mass %	30.0 mass %
1	50	0.138	0.145	0.224	0.254	0.289
2	100	0.465	0.472	0.481	0.501	0.525
3	150	0.585	0.587	0.651	0.701	0.732
4	200	1,125	1,178	1,356	1,587	1,588
5	250	2,149	2,178	2,478	2,574	2,895
6	300	2,255	2,455	2,655	2,741	2,765
7	400	3,199	3,299	3,312	3,344	3,356
8	500	2,425	2,325	3,425	3,454	3,464

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9	600	1,265	1,325	1,465	1,574	1,687

Another method for assessing the thermal stability of polymer and polymer composite materials is to determine the amount of energy expended (μV·s/mg) for the decomposition of polymers along the DSC curves. We have determined the amount of energy expended for the decomposition of polymers along the DSC curves, the results of which are presented in Table 3.

Analysis of research results (Table 3) shows that for PVC and PVC-based composites, the amount of energy expended in polymer decomposition increases. For example, for a polyvinyl chloride composite containing 5.0; 10.0; 20.0 and 30.0 mass % b rom-containing fire retardant , the amount of energy expended for the decomposition of polymer compositions at 400 0 C is 3.199; 3.299; 3.312; 3.344 and 3.356 μ V·s / mg , respectively. This may be due to increased intermolecular interactions between polymer macromolecules and flame-retardant molecules.

From the comparison of the energy expended in the decomposition of polymers, it is evident that the amount of energy expended is greater mainly in the temperature range of 250-500 ^{0}C. The greatest amount of energy expended is spent at 400 ^{0}C. For example, at 250 ^{0}C; 300 ^{0}C ; 400 ^{0}C and 500 ^{0}C the amount of energy expended is 2.178; 2.455; 3.299 and 2.325 μ V·s/mg , respectively. This may be due to the staged decomposition of polyvinyl chloride itself.

Table 3

Results of the analysis of the DSC curves of the PVC composition with a brominated fire retardant

No.	Temperature , ^{o}C	Amount spent energy (μ V • s / mg)				
		5.0 mass %	10.0 mass %	15.0 mass %	20.0 mass %	30.0 mass %
1	50	1, 54	1, 59	1, 78	1, 88	1, 95
2	100	2, 62	2, 72	2, 78	2, 83	2, 92
3	150	2.42	2.55	2.58	2.63	2.74
4	200	2, 65	2, 74	2, 82	2, 88	2, 94
5	250	3, 21	3, 31	3, 33	3, 55	3, 75
6	300	2, 65	2, 74	2, 82	2, 91	2, 99
7	400	1.29	1.39	1.42	1.60	1.79
8	500	1, 11	1, 22	1, 35	1, 41	1, 58
9	600	1, 09	1, 16	1, 27	1, 38	1, 49

Also for comparative evaluation of thermal stability The data on the temperature of the onset of decomposition, 10; 20 and 50% mass loss of the polyvinyl chloride composition are presented, the results of which are given in Table 4.

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Analysis of the study results (Table 4) shows that with an increase in the content of brominated flame retardant, the onset temperature of decomposition of polyvinyl chloride decreases. For example, the onset temperature of decomposition of compositions containing 5.0; 10.0; 15.0; 20.0 and 30.0 wt.% is 111; 109; 105; 100 and 97 ^{0}C, respectively.

Table 4

Comparative results of dynamic thermogravimetric analysis curves

Sample	Decomposition temperature, ^{o}C				Mass loss temperature, %	
	T_0	T_{10}	T_{20}	T_{50}	B_{400}	B_{600}
5.0 wt .%	1 11	209	316	325	47,15	77,27
10.0 wt.%	109	207	311	327	48,19	79,63
15.0 wt.%	1 05	200	308	329	48,98	80,98
20.0 wt.%	1 00	195	300	331	49,18	81,11
3 0 ,0 mass%	97	1 87	294	334	50.45	82,15

Comparison of the research results (Table 4) the corresponding temperatures at 10.0 and 20.0 wt . % loss are observed as the temperatures of the onset of decomposition, which means that with an increase in the content of brominated flame retardant , the thermal stability of polyvinyl chloride decreases. In contrast to T_0, T_{10} and T_{20} at 50.0 % mass loss increases corresponding to the temperature, i.e. the thermal stability of PVC. For example, 5.0 ; 10.0; 15.0; 20.0 and 30.0 wt . % The decomposition temperature is 325; 327; 329; 331 and 334 ^{0}C, respectively.

The weight loss at temperatures of 400 and 600 ^{0}C was also determined. The results show that with an increase in the content of the bromine- containing flame retardant , thermal stability decreases. For example, with a content of bromine - containing flame retardant of 5.0; 10.0; 15.0; 20.0 and 30.0 wt . %, the weight loss at a temperature of 400 ^{0}C is 47.15; 48.19; 48.98; 49.18 and 50.45, respectively. This is due to the volatilization of the bromine-containing flame retardant itself.

CONCLUSION

In this study, the thermal behavior of polyvinyl chloride compositions modified with a bromine-containing flame retardant, 3-bromo-2,3-diiodopropen-2-ol-1, was investigated. Derivatographic analysis revealed that the thermal degradation of PVC compositions proceeds in two main stages. It was established that an increase in the flame retardant content leads to a decrease in the thermal stability of PVC, accompanied by higher mass loss and an increased decomposition rate. In addition, a rise in flame retardant concentration resulted in greater energy consumption during the thermal decomposition process. These effects are likely

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associated with enhanced intermolecular interactions between PVC macromolecules and flame retardant molecules.

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