International Archive of Applied Sciences and Technology
Int. Arch. App. Sci. Technol; Vol 10 [1] March 2019 : 228-231
© 2019 Society of Education, India
[ISO9001: 2008 Certified Organization]
www.soeagra.com/iaast.html

IAAST
ONLINE ISSN 2277- 1565
PRINT ISSN 0976 - 4828

CODEN: IAASCA RESEARCH ARTICLE
DOI: .10.15515/iaast.0976-4828.10.1.228231

Differential Scanning Calorimetry of Polyvinyl Nitrate and Additives

S. C. Mishra
Department of Chemistry, M. B. Govt. P. G. College Haldwani, Nainital, Uttrakhand
Email: drsharadmishra96@gmail.com

ABSTRACT
DSC of fibrous PVN samples, differing in nitrogen content from 11.76% N to 15.71% N, has been carried out at 5^{0}C/min heating rate. Results indicate that thermal stability is maximum for PVN containing 11.71% N and decreases with increasing %N. Calorimetric value, however, is maximum (3445 J/g) for fibrous PVN containing 15.72% N. DSC of gelatinized PVN containing 15.71% N shows that its heat of decomposition is 3100 J/g, and this value is generally lowered by incorporating additives, namely, DPA, 2NDPA, carbamite and resorcinol, in 0.25%-1% weight concentration. Also, these additives do not significantly affect the onset temperature and the peak temperature.
Keywords: *Fibrous, Thermal Stability, calorimetric value, Gelatinized, Heat of decomposition, Additives, on set temperature, Peak temperature*

Received 13.12.2018 Revised 20.01.2019 Accepted 30.03.2019

CITATION OF THIS ARTICLE
S. C. Mishra. Differential Scanning Calorimetry of Polyvinyl Nitrate and Additives. Int. Arch. App. Sci. Technol; Vol 10 [1] March 2019 : 218-227

INTRODUCTION
The results on TGA and thermal decomposition kinetics of fibrous as well as gelatinized samples of polyvinyl nitrate (PVN) have been published [1]. To augment these studies, we are reporting, in this paper, the results of our work on differential scanning calorimetry (DSC) of the following samples of PVN:-

a) Fibrous PVN, containing 11.76% N, 13.34% N, 14.95% N and 15.71% N.
b) Gelatinized PVN, containing 15.71% N, without and with additives.

MATERIAL AND METHODS
Materials
Fibrous PVN, with mol. wt. about 100,000 and nitrogen content between 11.76% and 15.71%, was prepared by controlled nitration of polyvinyl alcohol [2]. PVN (15.71%N) was gelatinized with acetone, and during gelatinization, four different additives, namely diphenylamine (DPA), 2-nitrodiphenylamine (2NDPA), carbamite and resorcinol, were separately incorporated so as to obtain additive concentration of 0.25%, 0.5%, 0.75% and 1% by weight [2].

Method
DSC of the test samples was carried out using Dupont Instruments 910 DSC apparatus. 1-3 mg samples were used for the experiments. A heating rate of 5^{0}C/min and a constant flow rate of nitrogen gas (20ml/min) were maintained.

RESULTS AND DISCUSSION
DSC of Fibrous PVN (11.76%N-15.71%N)
DSC thermograms for the four samples of fibrous PVN, differing in %N, are shown together (to facilitate comparative assessment) in Diagram 1. The data on exothermic onset temperature, peak temperature and calorimetric value for the same PVN samples are presented in Table 1.

Table-1: DSC Results of Fibrous PVN samples Containing Different %N. (Heating Rate=5^{0}C/min. Sample size 1 of 3 mg)

Sample	Exothermic onset temperature 0^0C	Peak temperature 0^0C	Calorimetric Value J/g
PVN (11.76%N)	190.5	205.0	1533
PVN (13.34%N)	182.3	195.9	1991
PVN (14.95%N)	185.2	196.9	3070
PVN (15.71%N)	181.2	196.3	3445

DSC results confirm that the thermal properties of fibrous PVN are largely dependent upon %N in the samples. For the samples having 13.34% N, 14.95% N and 15.1%N, the exothermic onset temperature and the peak temperature are 183.3±2^{0}C and 196.4±0.5^{0}C, respectively, but these temperatures significantly increase to 190.5^{0}C and 205^{0}C, respectively, for the sample having 11.76%N. Hence, fibrous PVN with 11.76% N is thermally morestable than the others, probably because it has relatively less number of the weaker O-NO2, bond (bond energy 57 kcal/mol) in the polymer chain and is, therefore, less favourable to auto-analysed decomposition.

Calorimetric value of fibrous PVN increases considerably, that is, from 1533 J/g to 3445 J/g, with %N increasing from 11.76% to 15.71%. This happens because, with increasing degree of nitration, the oxygen balance also increases leading to higher reaction rate and grater exothermicity of decomposition.

DSC of gelatinized PVN (15.71%N) without and with Additives

DSC thermograms for gelatinized neat PVN (15.71%N) is shown diagram 2, whereas two DSC thermograms for gelatinized PVN (15.71%N), doped with 0.25% carbamite and with resorcinol, are shown together in diagram 3. The data on exothermic onset temperature, peak temperature and calorimetric value for gelatinized PVN (15.71%N), without and with additives, are presented in Table 2.

Table-2: DSC Results on Gelatinized PVN (15.71%N) without and with Additives. (Heating Rate=5^{0}C/min. Sample size 1 of 3 mg)

Sample Composition			Exothermic onset temperature 0^0C	Peak temperature 0^0C	Calorimetric Value J/g
PVN type	Additive	Conc. of additive %			
PVN (15.71%N), * Fibrous	NONE	0.00	181.6	196.3	3445
	NONE	0.00	185.8	196.1	3100
PVN (15.71%N), gelatinized	DPA	0.25	185.4	196.7	2746
		0.50	188.7	196.0	2783
		0.75	184.2	196.8	2818
		1.00	171.9	194.7	3034
	2NDPA	0.25	185.9	198.2	2700
		0.50	185.6	197.9	3113
		0.75	183.4	196.3	2835
		1.00	185.0	197.0	2798
	Carbamite	0.25	183.0	196.3	2873
		0.50	185.2	197.5	2861
		0.75	185.3	197.4	2773
		1.00	184.0	196.5	3052
	Resorcinol	0.25	185.1	196.8	2966
		0.50	184.8	197.1	2768
		0.75	185.9	194.5	2696
		1.00	186.8	196.3	3236

*Included for comparison only.

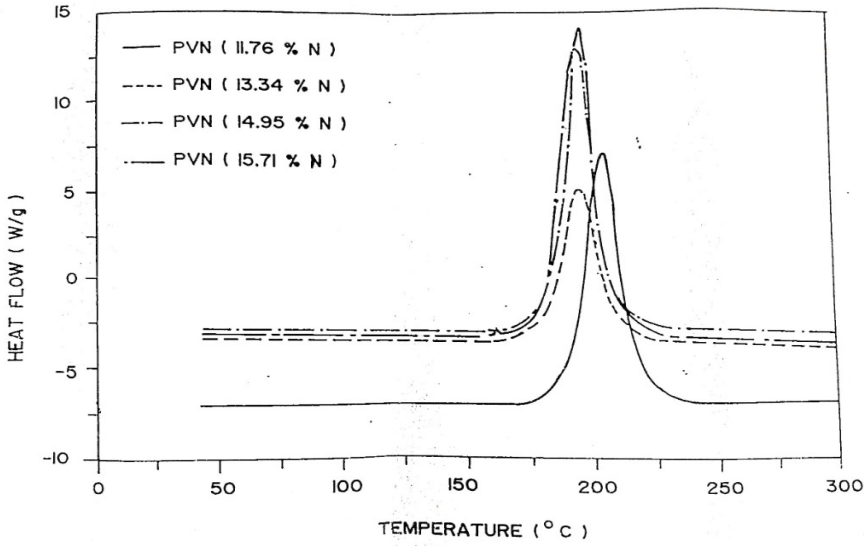

Diagram : 1 DSC CURVES FOR FOUR SAMPLES OF FIBROUS PVN (HEATING RATE 5 °C/min)

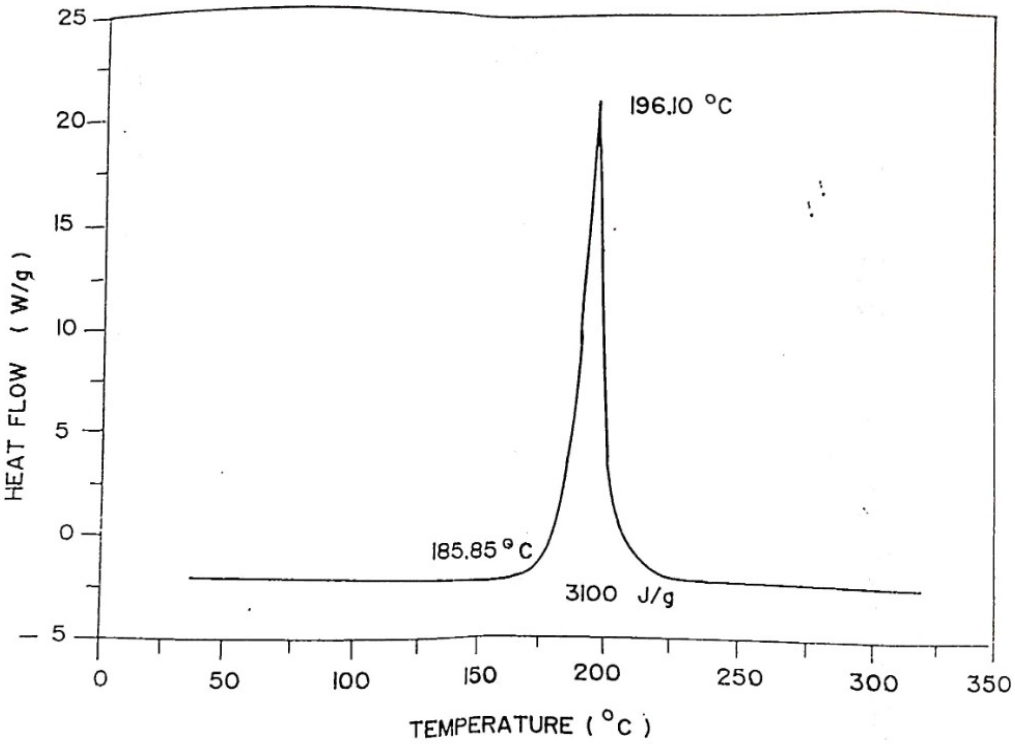

Diagram: 2 DSC THERMOGRAM FOR GELATINIZED PVN (15.71 % N) (HEATING RATE 5 °C/min)

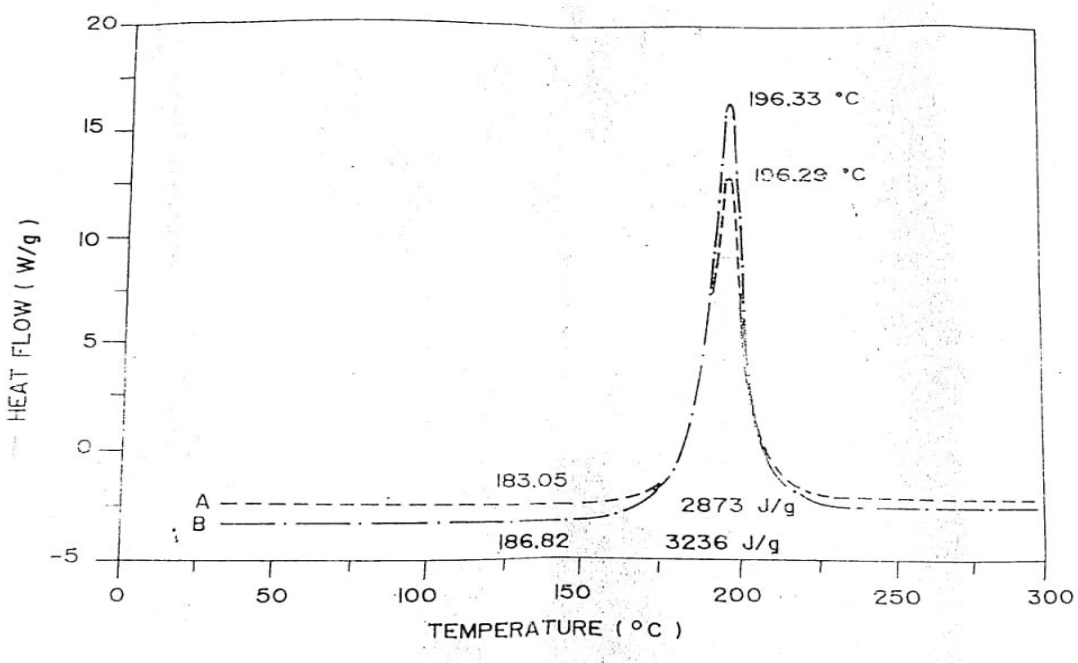

Diagram : 3 DSC THERMOGRAM FOR GELATINIZED PVN (15.7 %) DOPED WITH (A) 0.25 % CARBAMITE AND (B) 1.0 % RESORCINOL (HEATING RATE 5 °C/min)

It is observed from these data that the calorimetric value of fibrous PVN (15.71%N) decreases on gelatinization, from 3445 J/g to 3100 J/g. The calorimetric vale of gelatinized PVN (15.71%N) is usually further lowered by incorporation of the additives, namely, DPA, 2NDPA, carbamite and resorcinol, in 0.2% to 1% concentration, with very few exception. This may be due to the relatively nonenergetic nature of the additives. It is also observed that these additives do not significantly affect the onset temperature and the peak temperature values.

CONCLUSION

Thermal stability of fibrous PVN decreases with increasing %N. However, the heat of decomposition of fibrous PVN increases from 1533 J/g to 3445 J/g, corresponding to increase in %N from 11.76 to 15.71. Heat of decomposition of PVN (15.71% N) decreases, on gelatinization, to 3100 J/g, and usually decreases further on incorporating the additives DPA, 2NDPA, carbamite and resorcinol in 0.25%-1% concentration.

REFERENCES

1. Mishra S.C., Pant Jyotsna, Pant G. C., Dutta P. K. and Durgapal U.C. (1995). Studies on Thermal Decomposition Kinetics of Polyvinyl Nitrate, Propellants, Explosives, Pyrotechnics 20, 91-95.
2. Durgapal U.C., Dutta P. K., Mishra S.C. and Pant Jyotsna (1995). Investigations on Polyvinyl Nitrate as a High Energetic Material, Propellants, Explosives, Pyrotechnics 20, 64-69.