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An improved analytical method for determination of hydroxyl number of hydroxyl terminated polybutadiene (HTPB), 1, 4-butanediol (nBD) and trimethylol propane (TMP)

Chandra Shekhar Pant*, Rajendra S.Patil
Advanced Centre for Energetic Materials, Nasik -422 207, (INDIA)
E-mail : cspant79@gmail.com

ABSTRACT

Hydroxyl terminated polybutadiene (HTPB), 1, 4-butanediol (nBD) and trimethylol propane (TMP) are the key ingredients of binder system in composite propellant formulations. HTPB is a pre-polymer while nBD and TMP are used as chain-extender and cross-linker respectively. For these compounds determination of hydroxyl number is very essential, as depending upon the hydroxyl number the quantity of isocyanate curing agent is finalized to get the desired mechanical properties of the cured propellant.

This paper describes a method for determination of hydroxyl number of HTPB, nBD and TMP by a rapid and ambient temperature acetylation reaction. The results are obtained with remarkable repeatability.

KEYWORDS

HTPB;
nBD;
TMP;
Hydroxyl number.

INTRODUCTION

Hydroxyl number is the number of milligrams of KOH equivalent to the hydroxyl content in one gram of sample. Conventionally hydroxyl number is determined by acetylation of hydroxyl groups in the sample with acetic anhydride and pyridine[1-3]. The excess acetic anhydride is decomposed with water and the acetic acid which is formed is titrated with standard potassium or sodium hydroxide solution. This method requires couple of hours of reflux to complete the acetylation reaction and exposure to large amount of pyridine (catalyst cum solvent) which has serious health hazards as well as foul smell. Although various chemical and instrumental methods have been explored to determine the hydroxyl number of compounds[1,4-6] but acetylation method with pyridine and acetic anhydride is still the most widely used.

In the present study 4-(dimethylamino) pyridine was used as the catalyst for acetylation of HTPB, nBD and TMP for determination of their hydroxyl numbers. Due to the catalyst, acetylation reaction takes place at ambient temperature (25°C) at a very fast rate[7]. It is reported that 4-(dimethylamino) pyridine has a specific catalytic activity about 10^4 times greater than that of pyridine[8]. Further mechanistic studies on 4-(dimethylamino) pyridine catalysed acetylation of alcohol is reported by Shangjie Xu *et al.*[9]. Tetrahydrofuran was used as solvent for the acetylation reaction which facilitated the reaction content in homogenous state, contrary to the acetylation of HTPB in pyridine. Acetic acid, which is formed during the reaction as well as after hydrolysis of excess of acetic anhydride, was potentiometrically determined on autotitrator.

EXPERIMENTAL

Reagents

I. Acetylating solution: 5 mL acetic anhydride in 50 mL THF
II. Catalyst solution: 1 g 4-(dimethylamino) pyridine in 100 mL THF
III. Hydrolysis solution: 20 mL water in 80 mL THF.
IV. Tetrahydrofuran (THF)
V. Standard 1N ethanolic KOH solution.

Procedure

To a 50 mL titration flask around 1 g HTPB was accurately weighed and 10 mL THF was added. Contents were mixed with the help of magnetic stirrer. To this solution 10 mL catalyst solution was added followed by the addition of 5 mL acetylating solution. After 10 minutes of stirring at 25°C, 10 mL hydrolysis solution was added and the stirring continued for another 30 minutes. This solution was potentiometrically titrated with standard 1N ethanolic KOH solution in autotitrator using a glass electrode. Blank was determined in duplicate omitting the sample. All liquid additions were carried out with the help of pipette. Calculation of hydroxyl number was made according to the following formula.

$$OHN = \frac{(V2 - V1) * N * 56.11}{m} + AN$$

Where,
OHN = Hydroxyl number of sample in mg KOH/g
V1 = Volume of KOH solution needed for the sample (mL)
V2 = Volume of KOH solution needed for the blank (mL)
N = Normality of KOH solution
m = Weight of the sample in grams
AN = Acid number of the sample in mg KOH/g

For the hydroxyl number determination of nBD and TMP the sample size was reduced to 0.1 g. rest of the procedure was same as HTPB.

RESULTS AND DISCUSSION

Samples of two different grades of HTPB, nBD and TMP were analysed for their hydroxyl number. TABLE 1 shows the results of determination of hydroxyl number of HTPB, nBD and TMP using the standard

TABLE 1 : Hydroxyl number determination by standard and modified method

Sample	Hydroxyl number	
	Standard method [3,10]	Modified method
HTPB ($\overline{M}_n$: 2500 by VPO)	43.8	44.1
HTPB ($\overline{M}_n$: 3100 by VPO)	37.5	37.7
nBD	1242	1244
TMP	1254	1257

TABLE 2 : Statistical representation of replicate hydroxyl number determinations

Number of determination	Hydroxyl Number			
	HTPB ($\overline{M}_n$: 2500)	HTPB ($\overline{M}_n$: 3100)	nBD	TMP
1	43.8	37.9	1239	1259
2	43.9	37.4	1241	1255
3	44.1	37.9	1244	1256
4	44.3	37.7	1241	1258
5	44.4	37.6	1250	1261
6	44.3	37.3	1244	1258
7	44.2	37.8	1246	1251
Average	44.1	37.7	1244	1257
Standard deviation	0.22	0.23	3.69	3.24
Coefficient of variation (%)	0.50	0.61	0.30	0.26
Confidence Interval (95%)	44.1 ± 0.2	37.7 ± 0.2	1244 ± 2.7	1257 ± 2.4

method[3,10] and the modified procedure. Results obtained by both the methods were in close agreement.

In order to access the repeatability of the method, seven replicate determinations of hydroxyl number were performed. The results of their statistical evaluation are given in TABLE 2. As can be seen from the values of standard deviation and coefficient of variation, the test method gives an excellent degree of repeatability which is at par with the reported chemical methods used for determination of hydroxyl content. Test results were subjected to F-test to compare the precision of set of data obtained by modified method to that of the set of data obtained by standard method[11]. The test had shown that there was no significant difference between the precisions at 10 percent probability level. To establish the significance of variation of analysis results obtained by both the methods, paired t-test was conducted which again showed that there was no significant difference between the results at 10 percent probability level. The advantage of this method in comparison to the standard method is the ease of work and economy of time.

CONCLUSIONS

The method described in the paper gives a fast, convenient and repeatable mean for the determination of hydroxyl number of HTPB, nBD and TMP which are frequently used as components of binder system in composite rocket propellant formulations.

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