Trade Science Inc.

April 2008 Volume 7 Issue 6

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ 7(6) 2008 [337-341]

Development of a new method for quantitative estimation of liquid ingredients used in composite propellant using refractometry technique

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Received: 25th March, 2008 ; Accepted: 30th March, 2008

ABSTRACT

Composite propellants are the most important class of solid rocket propellants and basically contain ammonium perchlorate as an oxidizer, aluminium powder as a fuel and hydroxy terminated polybutadiene as a binder. It also contains certain process aids such as dioctyl adipate as plasticizing agent and a mixture of n-butyl alcohol and trimethylol propane as an adduct to achieve desired elongation and tensile strength, respectively, after curing with bi-functional isocyanates. The solid ingredients are dispersed in a binder matrix, which is also referred as 'Prepolymer' a terniary mixture of HTPB, DOA and adduct which is responsible for processibility of the composition and mechanical strength of the cured propellant grains. A systematic study has been carried out to quantify the exact percentage of liquid ingredients used in prepolymer before addition of solid ingredients using refractometry technique at different ratio and temperatures. The data obtained by analyzing refractive indices of individual ingredients as well as their mixture at different ratio and temperatures reveal that on comparing with standard refractive index of liquid ingredients and prepolymer to that of unknown mixture of prepolymer at a given temperature, the percentage of liquid ingredients can be quantified successfully even if there is a change in refractive index at fourth place.

KEYWORDS

Refractive index;
HTPB;
DOA;
Adduct;
Quantification.

INTRODUCTION

Of late, composite propellants are being used in various missile applications and basically contain ammonium perchlorate (AP) 65-70% as an oxidizer, a metallic fuel like aluminium powder (15-20%) and a liquid binder such as hydroxy terminated polybutadiene (HTPB,10-15%) [1]. It also contains certain process aids such as dioctyl adipate (DOA) as plasticizer and an adduct which is a mixture of n-butyl alcohol and trimethylol propane for structural elongation and tensile strength, respectively, after curing with bi-functional isocyanates like toluene diisocyanate(TDI)/isophorone diisocyanate(IPDI), hexamethylene diisocyanate (HMDI), diphenylmethane diisocyanate(MDI) and 4,4-dicyclohexylmethane diisocyanate(H_{12}MDI)[2,3]. In addition to this, certain bonding agents such as MAT-O-Bond are also added to get the increased rigidity required for the free standing type grains. During the processing of propellant compositions, initially the solid ingredients are dispersed in a binder matrix. The binder matrix also referred as prepolymer, is a ternary mixture

of HTPB, DOA and Adduct which is responsible for processibility of the composition and to impart mechanical strength of cured propellant grains. Further, mechanical properties of the propellant grains can be tailored by changing the percentage of HTPB, DOA or adduct in the prepolymer.

In view of the importance of the prepolymer for deciding the processibility of propellant slurry as well as mechanical properties, an exhaustive literature survey has been carried out to find out the reported methods to quantify the exact percentage of the liquid ingredients of prepolymer. The literature reveals that conventional analytical methods based on titrimetry as well as advanced instrumental analyses such as GC and HPLC can be employed to quantify the liquid ingredients of propellant. However, conventional methods are not simple and are time consuming, whereas instrumental techniques always require pure reference sample. On the other hand, refractometry technique does not require any reference sample and it is very fast, accurate, simple though temperature sensitive reported by other researchers[4-6]. Thus, by using refractometry technique, the purity level of the liquid ingredients and percentage of a mixture containing different liquid ingredients can be quantified even if there is a change in RI value at fourth place of decimal point.

In view of the vast importance of refractometry technique in quantification of liquid ingredients, a systematic study has been carried out to quantify the exact percentage of liquid ingredients used in the preparation of prepolymer mixture using this technique.

In the following section, we report the method of determination of the RI of different liquid ingredients used in the preparation of prepolymer and based on the value of RI a method has been established to quantify the exact percentage of liquid ingredients present in prepolymer.

EXPERIMENTAL

Material

Hydroxy terminated polybutadiene (HTPB), manufactured by the free radical solution polymerization[7], having number average molecular weight (M_n)2300-2900 with hydroxyl value of 42 mg KOH/g and viscosity in the range of 4500-6500 cP at 30^{0}C, was procured from M/s Anabond Limited, Chennai (India) and used as such, Dioctyl adipate (DOA),having saponification value 303±3 mg KOH/g and viscosity value in the range of is 13-15 cP at 30^{0}C, was also procured from Indo-Nippon Company Ltd., Vadodara. Trimethyl olpropane and n-butyl alcohol used to prepare adduct were also procured from M/s Bayer, Germany, and M/s BASF, USA, respectively, and used as such without further purification.

Instrument employed

The instrument used for refractometry study was Digital Automated Refractometry, Model ATAGO, Japan, having a facility to determine refractive index of liquid ingredients from +5^{0}C to +70^{0}C upto 4th place of decimal point.

Procedure

During the determination of refractive index, first of all the refractive index of liquid ingredients was determined individually by putting 2-3 drops of sample on the prism of the instrument at 20^{0}C being standard temperature for reporting RI as well as at different temperatures from 10^{0}C to 50^{0}C also. After this, samples containing HTPB, DOA and adduct in different ratio, prepared earlier, were also used for determination of RI at 20^{0}C.

RESULTS AND DISCUSSION

It is well known that refractive index (RI) of pure liquid ingredients is constant at a given temperature and the value of RI indicates the level of purity of the liquid ingredient. Conventionally, the standard temperature for the determination of RI is 20^{0}C using D-line of sodium at 593 nm wavelength[8,9]. The standard form of reporting of RI is as follows

$$\mathbf{R\ I = \eta_D^{20}}$$

Where, η = Refractive index of the liquid ingredient; D = Sodium line wavelength, generally 593.5 nm; 20 = is the standard temperature.

During the processing of composite propellant, liquid ingredients used are HTPB, DOA and Adduct alongwith di-functional curing agents such as TDI, IPDI and H_{12} MDI etc. RI is an important physical parameter of these ingredients which will give an idea about the purity of the substance. Hence, RI is determined to

qualify the ingredients. The RI of each liquid ingredient is specified at 20^0C and based on the specified value; liquid ingredients are used for the processing of composite propellants.

In view of the importance of RI in composite propellant processing, a new method has been developed to determine RI of binder matrix or prepolymer, which is a mixture of three main liquid ingredients viz. HTPB, DOA and Adduct i.e. ternary in nature. The binder matrix is mainly responsible for mechanical properties of the grain after curing with bi-functional di-isocyanates like TDI/IPDI. Further, slight errors in the weighing or charging into the mixer, percentage of HTPB/ DOA or Adduct during its use as prepolymer, affects the mechanical properties of the grains. Therefore, it is essential to quantify the exact percentage of liquid ingredients of prepolymer before their use in propellant processing. Accordingly, a simple reliable and fast method was conceived and developed to determine exact percentage of liquid ingredients using RI technique.

Refractive index of liquid ingredients at different temperatures

During this study, first of all the RI of liquid ingredients (HTPB, DOA and Adduct) was determined individually at different temperatures (10^0C-50^0C) and data obtained are presented in TABLE 1. It is clear from the TABLE that on increasing the temperature of the liquid ingredients RI value decreases. It is also clear from the TABLE that decrease in RI value at higher temperature is corresponding to 0.0004/^{0}C in case of HTPB and DOA while the decrease in RI value for adduct at higher temperature is about 0.0003 per degree centigrade . The slight variation in RI value for adduct does not change the prepolymer value as the percentage of adduct in binder matrix is not more than 0.12%. Furthermore, the value of RI also varies as molecular weight of HTPB decreases or increases based on different sources or change in parameters during its manufacture. The change in RI at 4th place of decimal was observed. However, the change in RI is nullified as during the processing of propellant only one source is used at that time and if different source of HTPB is to be used accordingly the value of RI is determined further.

Refractive index of prepolymers in different ratio

TABLE 1 : Data on refractive index of liquid ingredients at different temperatures

Sr. no.	Temperature /RI	HTPB	DOA	Adduct
1	10^0C	1.5202	1.4511	1.4604
2	15^0C	1.5183	1.4491	1.4588
3	20^0C	1.5164	1.4470	1.4573
4	25^0C	1.5145	1.4450	1.4558
5	30^0C	1.5126	1.4433	1.4545
6	35^0C	1.5107	1.4413	1.4529
7	40^0C	1.5089	1.4393	1.4514
8	45^0C	1.5070	1.4372	1.4499
9	50^0C	1.5052	1.4352	1.4483

TABLE 2 : Data on refractive index of prepolymers at standard temperature

Sr. no.	HTPB, %	DOA,%	ADDUCT, %	R.I., 20^0C
1.	-	90	10	1.4510
2.	10	80	10	1.4550
3.	20	70	10	1.4614
4.	30	60	10	1.4692
5.	40	50	10	1.4766
6.	50	40	10	1.4829
7.	60	30	10	1.4915
8.	70	20	10	1.4993
9.	80	10	10	1.5067
10.	90	-	10	1.5116

In continuation to this work further, the RI of HTPB, DOA and Adduct was determined by varying the ratio of HTPB and DOA while keeping the adduct percentage constant at 10% level at standard temperature and data obtained are presented in TABLE 2. The data of binder matrix reveal that on increasing the percentage of HTPB from 10-90%, the value of RI increases while on increasing the percentage of DOA from bottom to top, a decreasing trend in RI was observed. The increase in RI value on increasing the HTPB content is due to increase in viscous liquid resin as well as presence of intermolecular forces such as Van der Waals etc. while increase in DOA content reduces the intermolecular forces which leads to increase in intersegmental mobility, thus reduces the value of RI.

Effect of temperatures on refractive index of prepolymers at different ratio

The effect of temperatures on RI of prepolymers having different percentage of HTPB andDOA while adduct content was kept constant on 10% level, was also studied by varying the temperatures from 10^0C to 50^0C and data obtained are presented in TABLE 3. It is clear from the TABLE that on increasing the percentage of HTPB in prepolymer the value of RI increases further reveals the entanglement of polymeric chains as

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TABLE 3 : Data on refractive index of prepolymers at different temperatures

Sr. no.	Prepolymer/RI	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C	50°C
1	HTPB/DOA/Adduct (50/40/10)	1.4859	1.4850	1.4829	1.4806	1.4786	1.4765	1.4752	1.4732	1.4710
2	HTPB/DOA/Adduct (40/50/10)	1.4801	1.4782	1.4766	1.4745	1.4727	1.4715	1.4700	1.4672	1.4655
3	HTPB/DOA/Adduct (30/60/10)	1.4746	1.4725	1.4692	1.4677	1.4656	1.4637	1.4616	1.4604.	1,4581
4	HTPB/DOA/Adduct (20/70/10)	1.4650	1.4628	1.4614	1.4597	1.4577	1.4557	1.4536	1.4520	1.4497
5	HTPB/DOA/Adduct (10/80/10)	1.4592	1.4566	1.4550	1.4531	1.4512	1.4492	1.4472	1.4453	1.4438

TABLE 4 : Data on refractive index of prepolymers without DOA at 20°C

Sr. no.	HTPB,%	ADDUCT,%	R.I.
1	100	-	1.5164
2	99	1	1.5159
3	98	2	1.5154
4	97	3	1.5150
5	96	4	1.5145
6	95	5	1.5140
7	94	6	1.5135
8	93	7	1.5130
9	92	8	1.5126
10	91	9	1.5121
11	90	10	1.5116

TABLE 5 : Data on refractive index of liquid mixture without HTPB at 20°C

Sr. no.	DOA, %	ADDUCT,%	R.I.
1	90	10	1.4510
2	91	9	1.4506
3	92	8	1.4502
4	93	7	1.4498
5	94	6	1.4494
6	95	5	1.4490
7	96	4	1.4486
8	97	3	1.4482
9	98	2	1.4478
10	99	1	1.4474
11	100	-	1.4470

well as enhancement of intermolecular forces. The data on DOA content of RI also reveal the plasticizing effect of resin which is responsible for reducing the intermolecular forces and thus enhance the intersegmental mobility of HTPB chains by penetrating in between segments of the resin, being a small molecule. Thus, overall effect of temperature on RI also supports the same finding that on increasing the temperature RI decreases. This is due to better movement of segments and reduction in intermolecular forces as reported by other researchers also[10-13].

Refractive index of prepolymers without DOA/ HTPB at 20°C

Further to this, a detailed study was also carried out by taking 90-100% HTPB and DOA while adduct percentage was varied for 1-10 percentage maximum

TABLE 6 : Data on refractive index of conventional prepolymers at 20°C

Sr. no.	HTPB,%	DOA,%	ADDUCT,%	R.I.
Mixture -1	9.50	3.0	0.12	1.5001
	10.06	3.0	0.12	1.5007
	10.50	3.0	0.12	1.5014
	11.0	3.0	0.12	1.5020
Mixture-2	10.06	2.5	0.12	1.5029
	10.06	3.0	0.12	1.5007
	10.06	3.5	0.12	1.4988
	10.06	4.0	0.12	1.4966
Mixture-3	10.06	3.0	0.07	1.5011
	10.06	3.0	0.09	1.5008
	10.06	3.0	0.12	1.5007
	10.06	3.0	0.15	1.5005

and RI of prepolymer prepared in this fashion was determined at standard temperature i.e. 20°C and data thus obtained are presented in TABLES 4 and 5. It is clear from the TABLE that as percentage of the ingredients changes RI also changes. These data are very useful for quantifying the percentage of liquid ingredients. Further, these data may be referred as standard and based on the standard value any change in percentage of liquid ingredients can be correlated which directly provides the exact percentage of liquid ingredients present in the prepolymer.

Refractive index of prepolymers using conventional ratio at 20°C

In order to use refractometry technique further, the binder matrixes having the near about percentage of liquid ingredients (HTPB/DOA/Adduct) were also prepared as it is being used in composite propellant processing. At present composite propellant processing uses HTPB in the range of 9.0% to 11% and DOA content varies from 2-4%. However, the percentage of adduct generally remains constant for different compositions and its percentage in binder matrix is 0.12 %(max). Based on these input, polymer matrix were prepared having HTPB and DOA in different ratio while adduct percentage was also studied from 0.07 to 0.12%. Thus, three different prepolymer mixtures were prepared by keeping the ratio of two liquid ingredients constant while varying the third one and vice versa. The RI of pre

pared binder matrix or prepolymer was determined at 20^0C and data obtained are presented in TABLE 6. It is clear from the TABLE that the standard composition having HTPB/DOA/Adduct in the ratio of 10.06 /3.0/ 0.12 shows value of RI at 20^0C is 1.5007. Further, if the percentage of DOA changes from 3 to 4 in the same binder matrix the value of RI changes to 1.4966 at the same temperature. Furthermore, prepolymer mixture 3 reveal that although the % of adduct is very less but minor change in its percentage i.e. from 0.07 % to 0.09% also brings out change in RI value at 4th place i.e. from 1.5011 to 1.5008. In the same way, the value of RI also decreases from 1.5007 to 1.5005 on increasing the percentage of Adduct from 0.12% to 0.15%. This finding infer that even slight change in percentage of HTPB, DOA or adduct, the value of RI changes, which directly envisages the importance of RI as a new tool to quantify the percentage of the liquid ingredients present in the binder matrix and also confirms the accuracy and sensitivity of the instrument used.

Based on this study, it is clear that exact quantification of liquid ingredients present in binder matrix can be determined successfully. Further to this, if a unknown binder matrix is subjected to this technique, the exact percentage of binder matrix can be quantified based on RI value at 20^0C.

The prime interest to carry out this study is to develop a technique /method to detect any error occurred inadvertently during the weighment of liquid ingredients or charging to mixer as mechanical properties are mainly governed by these ingredients after curing with diisocyantes like TDI/IPDI. Further, this technique not only controls the quality of the finished products but has also enhanced our morale and confidence to process big motors at large scale (Ton level).

CONCLUSION

A new method has been developed successfully to quantify the exact percentage of liquid ingredients present in the binder matrix using refractometry technique. This technique has enhanced our confidence to process large size case bonded motors based on composite propellant in large scale (ton level). This method will be highly advantageous in bulk production of propellants where raw material sources are identified and are available in bulk. The slight changes in RI value at 4th place of decimal also provide important input about any change in the percentage of liquid ingredients while weighing or charging in the mixer. Further, the developed technique has been included in the text of routine quality checks of binder matrix before addition of solid ingredients during the processing of composite propellant.

ACKNOWLEDGMENT

The authors thank Dr. A.Subhananda Rao, Director, High Energy Materials Research Laboratory for his support and encouragement during the course of this study.

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