Def Sci J, Vol 39, No. 2, April 1989, pp 147-155

Energetics and Compatibility of Plasticizers in Composite Solid Propellants

Rm. Muthiah, U.I. Somasundaran, T.L. Verghese and V.A. Thomas

Propellant Engineering Division, Vikram Sarabhai Space Centre, Trivandrum–695 022

ABSTRACT

In this paper a comparative analysis on the energetics of ester type plasticizers such as dioctyl adipate (DOA), dioctyl phthalate (DOP), dibutyl sebacate (DBS), isodecyl pelargonate (IDP), trioctyl phosphate (TOF), diethyl phthalate (DEP), tricresyl phosphate (TCP) and dibutyl phthalate (DBP) and hydrocarbon type plasticizers such as polybutene (PB), spindle oil, naphthenic oil, polymer extender oil (PEO) and poly isobutylene (PIB) and the impact of some of the plasticizers on the workability, pot life and mechanical properties of propellants based on two selected polymeric binders namely polybutadiene-acrylic acid-acrylonitrile (PBAN) ter polymer and hydroxyl terminated polybutadiene (HTPB) have been reported. The compatibility of all the plasticizers on HTPB binder was also studied at different concentration levels and temperatures using Brookfield viscometer and reported. The mechanism of plasticization is also reviewed.

1. INTRODUCTION

Composite solid propellant is a heavily solid loaded system, comprising of discrete solid particles of ammonium perchlorate (oxidizer) and aluminium powder (metallic fuel) embedded in a highly viscous polymeric binder. Plasticizers are essentially used in propellant manufacture for improving the processability of the propellant slurry and mechanical properties of the cured propellant. They are relatively low m.wt. non-volatile liquids such as esters and hydrocarbons and are of primary type plasticizers. The selection of a plasticizer for a propellant system calls for a hard compromise of the factors such as energetics, compatibility, availability and cost potential.

Received 17 May 1988

Most modern composite propellants are comprised of high solid loading of 85–90 per cent for advanced launch vehicles. Ammonium perchlorate and aluminium particles in the propellant system are uniformly embedded in a highly viscous polymeric binder of meagre concentration of 7 to 10 per cent. Such a heavily solid loaded system necessitates the incorporation of suitable, compatible plasticizers to achieve amenable processability and reasonable mechanical properties.

Plasticizers generally used in composite propellants are low molecular weight, non-volatile, non-reactive esters or hydrocarbons which are compatible with the binder system. The fuel value of the plasticizer is also an important factor since the plasticizer is part of the fuel content in the propellant.

In this paper we have made an attempt to compare the influence of ester type plasticizers such as DOA, DOP, DBP, IDP, TOF. etc. and hydrocarbon type plasticizers such as PEO, PIB, PB etc. on the processability of the propellant slurry and mechanical properties of the cured propellant and energetics. Two types of typical polymeric binders used for making composite solid propellants – PBAN and HTPB were selected for the present study.

2. PLASTICIZER CHARACTERISTICS

The characteristics of the plasticizers used for this study are listed in Table 1. The physico-chemical characteristics and energetics listed in the table are of much importance in the selection of the plasticizer for propellant system.

The analytical data of various plasticizers show that hydrocarbon plasticizers have more fuel value as seen from their calorific values compared to ester type plasticizers. Though ester type plasticizers give low calorific values, most of the plasticizers listed in the table show lower viscosity. But the selection of a plasticizer calls for a hard compromise of many factors such as energetics, compatibility, processability, availability and cost potential. This was achieved through experimentation in the propellant system.

The compatibility of 11 different plasticizers such as dioctyl adipate (DOA) isodecyl pelargonate (IDP), trioctyl phosphate (TOF), tricresyl phosphate (TCP), polymer extender oil (PEO), dibutyl sebacate (DBS), polybutene (PB), dioctyl phthalate (DOP), dibutyl phthalate (DBP), spindle oil and naphthenic oil with HTPB resin was studied.

Six different concentration levels of all the plasticizers listed above were experimented with HTPB resin and the mix viscosity at each concentration level was measured at 50°C using Brookfield Viscometer. Viscosity vs. concentration graphs of all the 11 plasticizers with HTPB resin are given in Figs. 1(a) and 1(b).

3. ENERGETICS

It could be noted from the Table 1 that hydrocarbon plasticizers such as polybutene, polyisobutylene, polymer extender oil etc. give higher energetics than the ester type plasticizers as seen from their calorific values. The high hydrogen to carbon ratio in hydrocarbon plasticizers contributes more towards the fuel value which

Table 1. Characteristics of plasticizers

Name of plasticizer	Viscosity at 25°C (cp)	Viscosity at 50°C (cp)	Density (g/cc)	Cal. value (cal/g)
(a) Ester type				
1. Dioctyl adipate (DOA)	14.0	8.0	0.932	8150
2. Dioctyl phthalate (DOP)	59.0	37.0	0.985	8010
3. Dibutyl sebacate (DBS)	7.6	3.7	0.935	7810
4. Isodecyl pelargonate (IDP)	6.2	2.9	0.862	9120
5. Trioctyl phosphate (TOF)	12.0	4.9	0.924	8300
6. Diethyl phthalate (DEP)	11.0	4.0	1.11	6080
7. Tricresyl phosphate (TCP)	98.0		1.165	7400
8. Dibutyl phthalate (DBP)	14.8		1.046	7380
(b) Hydrocarbon type				
1. Polybutene (PB)	47.0	13.0	0.839	10800
2. Spindle oil	15.0	6.0	0.859	10560
3. Naphthenic oil	57.0	21.0	0.880	10510
4. Polymer extender oil (PEO)	10800	610.0	1.01	9650
5. Polyisobutylene (PIB)	3.7	1.9	0.798	10450

is contributing to the overall efficiency of the rocket motor. The less energetic ester group reduces the fuel value of ester type plasticizers.

4. PROPELLANT EXPERIMENTATION

The influence of plasticizers, ester type as well as hydrocarbon type on the processing characteristics and end properties were evaluated using standard propellant formulation for HTPB and PBAN systems. HTPB formulations contain a solid loading of 87 per cent with 18 per cent aluminium and PBAN at 86 per cent with 18 per cent aluminium. The propellant processings were carried out in a 4 kg sigma type mixer. The processing was carried out at 40°C for HTPB propellants and 50°C for PBAN propellants and a duration of three hours mixing time was adopted. The premix containing the prepolymer was charged to the mixer, followed by aluminium addition and then two grades of ammonium perchlorate namely coarse grade and fine grade were charged at regular intervals. Sample cartons were cast under vacuum and cured at 60°C. The viscosity build up data of slurry was generated using Brookfield Viscometer and mechanical properties for the cured propellant were generated using Instron Table Model–1121 using die of ASTM specification D–412–68 (Type–C) at a cross head speed of 50 mm/minute at 25°C.

5. RESULTS AND DISCUSSIONS

A regular trend of reductions in viscosity with increase in concentration of the plasticizer from 10 to 50 phr of HTPB resin is shown in Figs. 1(a) and 1(b). The

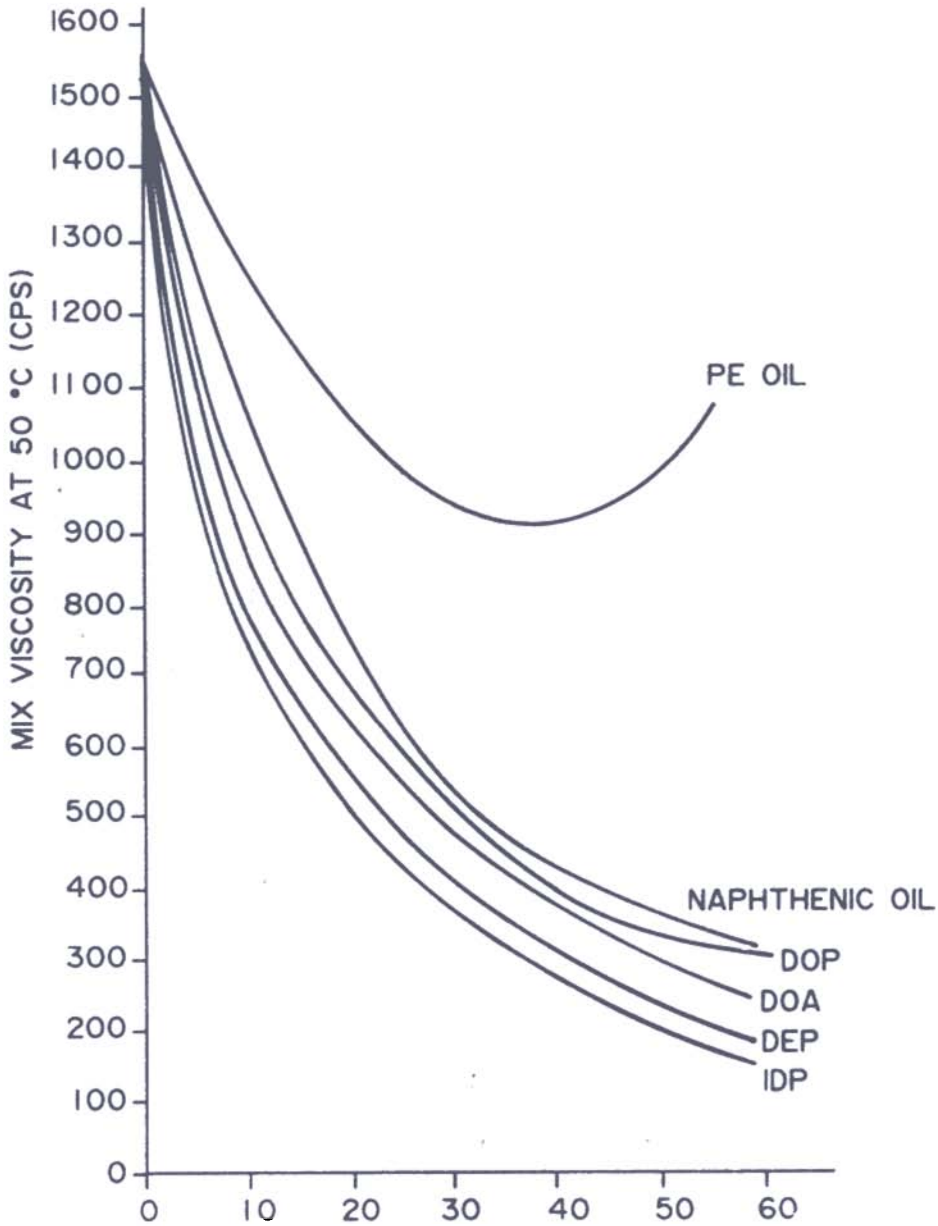

Figure 1(a). Effect of plasticizer level on HTPB resin.

maximum viscosity reduction was found with IDP and the least with PEO. In the case of PEO, viscosity reduction was found upto 36 phr of HTPB resin, beyond which viscosity increases linearly with increase in concentration and this could be due to the change over the function of a primary plasticizer to a secondary plasticizer, having limited miscibility, beyond the level of 36 phr and also due to the high inherent viscosity of PEO. The reduction in viscosity in all the other cases shows good compatibility with HTPB resin and it was more pronounced from zero to 20 phr level beyond which less influence was noticed.

Figure 2 depicts the viscosity and viscosity build up data of HTPB propellant with different plasticizers used for the study. All the plasticizers were used at a concentration level of 3 per cent. IDP, DOA and TOF show lower EOM viscosity and slow build up which is very much desirable for the processing of large rocket

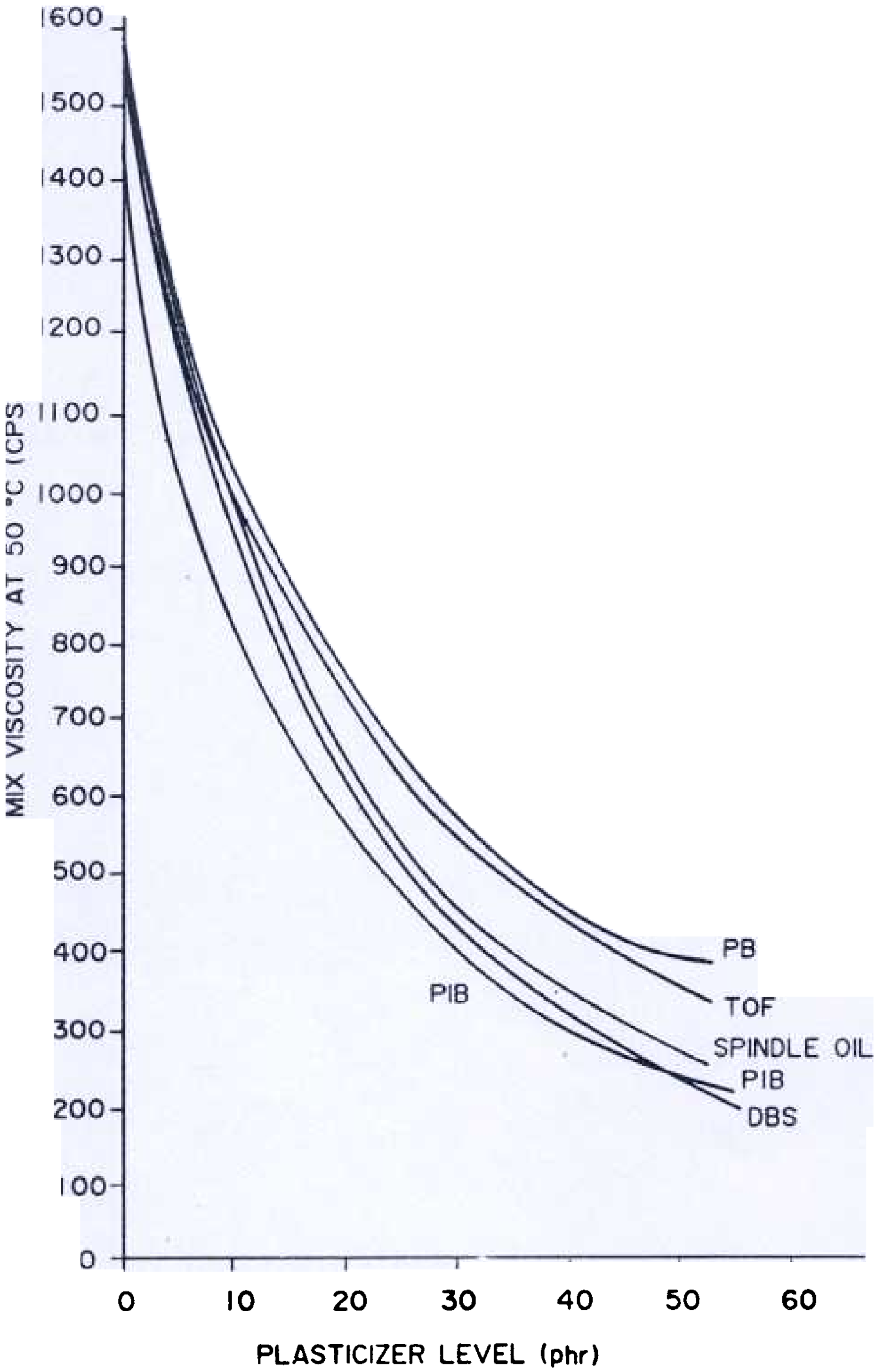

Figure 1(b). Effect of plasticizer level on HTPB resin.

motors compared to others. The faster reaction rate of other plasticizers could be due to the presence of reactive functional groups as impurities. From the processability point of view, IDP and DOA are most suitable plasticizers.

The influence of concentration is shown in Fig. 3. The studies at concentration levels of 2, 3 and 4 per cent of both DOA and IDP show a regular decrease in EOM viscosity and viscosity build up with increase in plasticizer concentration. IDP at 4 per cent level gives the lowest EOM viscosity and viscosity build up.

The mechanical properties of the cured propellant using different plasticizers at concentration level of 3 per cent is shown in Table 2. The results with DOA and IDP are presented at 3 different concentrations. DOA, IDP, TOF, DBP give lower tensile strength and higher elongation. The mechanical properties are quite comparable for TCP, PEO, PB, Spindle oil and Naphthenic oil. But we have seen earlier that DOA and IDP give better processability and pot life. Tensile strength can be improved at the expense of elongation by adjusting curing agent level in propellant formulation. Also it was seen that the change in the concentration of IDP and DOA modifies the properties as seen from the Table 2. The usual practice is to adjust the level of plasticizer and curing agent to achieve the required properties. This method has been reported in the development of HTPB propellants using plasticizers such as DOA, PB and TOF[1].

The impact of DOA, TOF, IDP, PB, PEO and PIB on PBAN propellant at a concentration level of 3 per cent is shown in Table 3. From the processability point of view (Fig. 4), IDP and PIB are better plasticizers compared to others. The mechanical properties are also comparatively good for these plasticizers. The superior

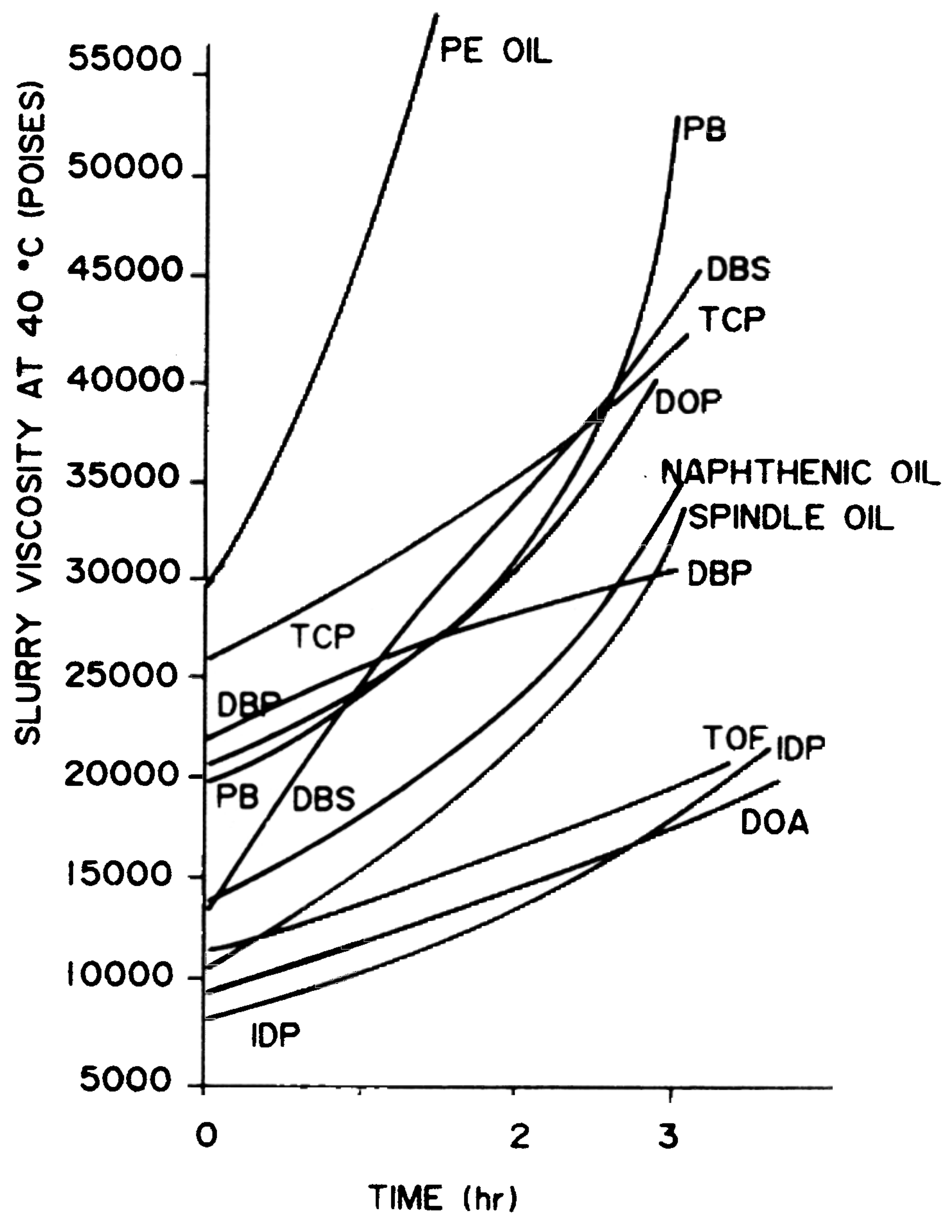

Figure 2. Effect of plasticizers (3%) on slurry viscosity (HTPB propellant).

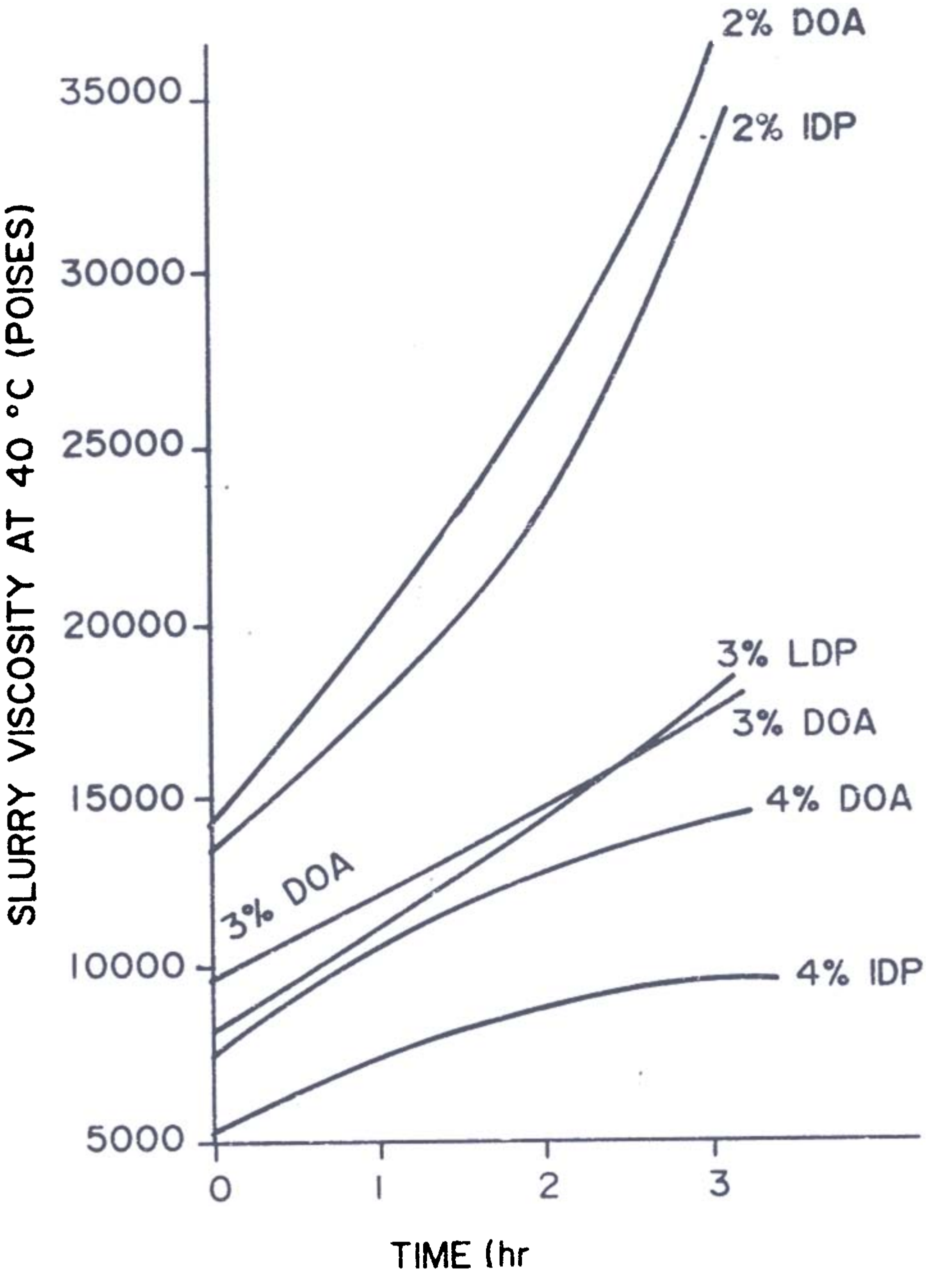

Figure 3. Effect of plasticizer concentration on slurry viscosity (HTPB propellant).

mechanical properties with PEO is more than offset by high EOM viscosity and poor pot life.

The concept of a 'like dissolving like' could be applied to explain compatibility of various plasticizers. From thermodynamic point of view, the cohesive energy densities must be alike for a plasticizer to be compatible with a system[2]. The lubrication theory as well as the gel theory of solvation of polymer chain with plasticizer holds good to explain the low EOM viscosity of PBAN and HTPB propellant slurries with ester type plasticizers. The exceptions to this could be explained by the free volume theory, according to which an increase in the size of the molecule (as reflected in the higher viscosity of some ester plasticizers) reduces the free volume, which in turn lowers the plasticizer efficiency. The behaviour of hydrocarbon plasticizers also could be explained in a similar manner.

Table 2. Effect of plasticizers on HTPB propellants

Name of plasticizer	Propellant slurry characteristics: EOM viscosity (Ps at 40°C)	Viscosity after 3 hrs (Ps at 40°C)	Propellant mechanical properties: T.S. (KSC)	Elong. (%)	Modu. (KSC)	Hardness (SAH)
DOA (2%)	14080	36480	5.5	35	36	65
DOA (3%)	9600	17280	4.8	36	28	60
DOA (4%)	7680	14080	4.3	39	21	50
IDP (2%)	13440	33920	5.1	31	36	60
IDP (3%)	8000	17600	3.7	41	20	54
IDP (4%)	5440	9600	3.6	42	19	50
TOF (3%)	11200	18880	4.7	33	33	55
TCP (3%)	26240	41600	6.3	25	49	65
PEO (3%)	29440	Beyond 64000	5.8	32	42	64
DBS (3%)	21760	30720	3.2	30	19	45
PB (3%)	19840	53440	6.1	31	45	65
DOP (3%)	21120	36480	6.7	22	60	67
DBP (3%)	21760	30720	4.0	49	20	50
S'oil (3%)	10880	32640	5.7	34	39	64
N'oil (3%)	13760	34500	5.9	31	40	61

Table 3. Effect of plasticizers on PBAN propellants

Name of plasticizer	Propellant slurry characteristics: EOM viscosity (Ps at 50°C)	Viscosity after 3 hrs (Ps at 50°C)	Propellant mechanical properties: T.S. (KSC)	Elong. (%)	Modu. (KSC)	Hardness (SAH)
DOA	7360	11520	4.6	28	39	58
IDP	5120	7360	4.6	32	30	57
TOF	6080	10240	3.5	34	21	52
PB	8000	12800	4.3	30	29	55
PIB	5120	9600	4.0	32	23	54
PEO	12480	23680	6.1	40	39	62

CONCLUSION

Plasticizer compatibility study with various plasticizers on HTPB resin show drastic decrease in viscosity at lower concentration. From processability point of view IDP seems to be the most suitable plasticizer for HTPB and PBAN systems.

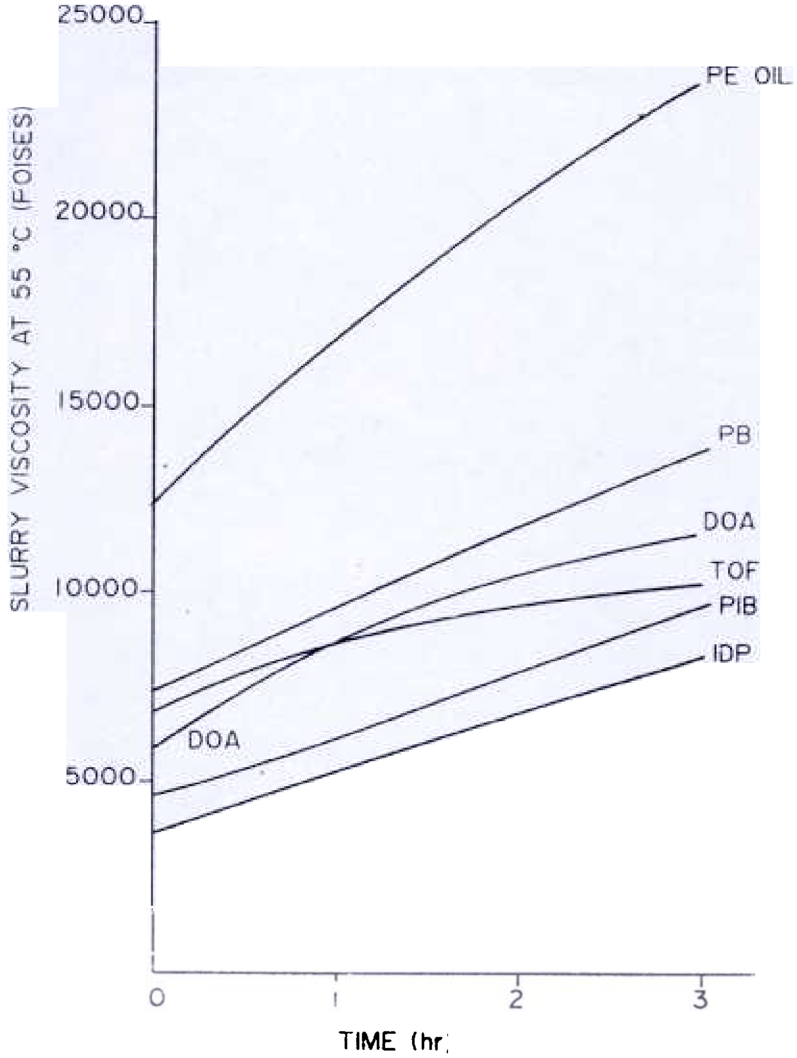

Figure 4. Effect of different plasticizers on slurry viscosity (PBAN propellant).

Increase in the plasticizer (DOA and IDP) from 2 to 4 per cent improves the processability and pot life of HTPB propellant. Both DOA and IDP give comparable mechanical properties with HTPB and PBAN propellants. The impact of PE oil on PBAN propellant is well evidenced from the superior mechanical properties, but at the expense of processability.

Hence the overall selection of a plasticizer in a propellant system depends on its energetics, compatibility with the binder system, impact on processability, pot life of propellant slurry, mechanical properties of the end product and finally on availability and cost. The desired mechanical properties could be very well achieved by adjusting the concentration level of plasticizers and curing agent in a propellant system.

REFERENCES

1 Smith, P.L. & Bankaitis, H., HTPB Propellants for Large Booster Applications, AIAA, No. 71-708, 1971.

2 Sears, J. Kern & Darby, Joseph R., The Technology of Plasticizers, USA, 1982