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# Viscoelastic Behaviour of Solid Propellants based on Various Polymeric Binders

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**ABSTRACT**

The dynamic mechanical properties of different binders and corresponding propellants are studied in terms of storage modulus and loss tangent. The binders investigated are HTPB, CTPB, PBAN, HEF-20 and ISRO polyol. The viscoelastic behaviour is investigated using Rheovibron viscoelastometer at 35 Hz covering a wide temperature range (-100 °C to 100 °C). The properties of the binder and corresponding propellant are compared in terms of the parameters, tan $\delta_{max}$, $T_g$ and the trend of their master relaxation modulus curves. It is found that polybutadiene binders exhibit lowest $T_g$ (around -60 °C) and ISRO polyol the highest (near -20 °C). The propellants have higher moduli than the binders at any temperature. The master relaxation modulus curve is influenced by the type of propellant.

## 1. INTRODUCTION

Various polymers, such as carboxyl terminated polybutadiene (CTPB), hydroxyl terminated polybutadiene (HTPB), lactone terminated polybutadiene (HEF-20), terpolymer of butadiene, acrylonitrile and acrylic acid (PBAN), ISRO polyol, etc. are used as fuel binders in composite solid propellants[1]. These propellants are viscoelastic due to the polymeric binder. It is known that the viscoelastic properties of polymeric systems are dependent on various factors, like nature of polymer, curative type and level, filler loading, additives, etc. In this paper, the dynamic mechanical properties of crosslinked binders, like HTPB, CTPB, PBAN, HEF-20 and ISRO polyol are evaluated. The behaviour of propellant and the corresponding binder is compared in terms of temperature of the transition from glassy to rubbery state ($T_g$), modulus, damping and master relaxation modulus curves.

## 2. EXPERIMENTAL DETAILS

The polymeric binders, HTPB, HEF-20 and ISRO polyol were produced at VSSC, Thiruvananthapuram, while CTPB and PBAN were procured from commercial sources. For evaluating dynamic behaviour, the resins were hand-mixed with suitable curatives in stoichiometric proportions, degassed, cast and cured in moulds to obtain 5 mm thick slabs. The propellants containing the binder, ammonium perchlorate, *Al* powder, etc. were prepared following usual processing techniques. The details of binders, curatives used, cure conditions, etc. are given in Table 1.

**Table 1. Details of binders and propellants**

| Binder | Curative | Cure condition | | Solid loading (%) |
|---|---|---|---|---|
| | | Binder | Propellant | |
| CTPB | MAPO, Gy 252 | 60 °C, 48 h | 60 °C, 8 days | 86 |
| HTPB | TDI | 60 °C, 48 h | 60 °C, 5 days | 86 |
| HEF-20 | MAPO | 60 °C, 48 h | 60 °C, 12 days | 84 |
| PBAN | Gy 252 | 60 °C, 48 h | 75 °C, 12 days | 86 |
| ISRO polyol | TDI | 60 °C, 48 h | 60 °C, 5 days | 86 |

ISRO polyol: polyol based on 12-hydroxy stearic acid and trimethylol. propane; MAPO: tris (1-(2 methyl) aziridinyl) phosphine oxide; Gy 252 : diepoxide of bisphenol A; TDI : toluene diisocyanate.

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The dynamic properties, namely storage modulus ($E'$), loss modulus ($E''$) and loss factor (tan $\delta$) were determined using Rheovibron viscoelastometer DDV-III-C over a wide temperature range (-100 °C to 100 °C). The specimen size used was 50 mm × 10 mm × 5 mm. The dissipation factor (tan $\delta$ ) is directly read whereas the complex modulus is computed using

$$E^* = \frac{L}{8ADS} \times 10^{12} \text{ dyne/sq cm}$$

where $L$ is specimen length, $S$ is cross-sectional area, $A$ and $D$ are instrument parameters. The storage and loss moduli are then calculated using

$$E' = E^* \cos\delta \text{ and } E'' = E^* \sin\delta$$

The theoretical aspects and terminology relating to dynamic mechanical properties have been discussed by several authors[2-4].

## 3. RESULTS AND DISCUSSION

### 3.1 Comparison of Binders

$E'$ vs temperature and loss tangent versus temperature plots for cured HTPB, PBAN and ISRO polyol binders are shown in Figs. 1 & 2. It is observed that $E'$ exhibits sharp fall around -60 °C, -40 °C and -20 °C respectively corresponding to $T_g$ of the binder. As evident from Fig. 2, the loss tangent shows peak at temperatures corresponding to $T_g$. The difference in $T_g$ of the binders can be related to the nature of the backbone, with HTPB (largely hydrocarbon) exhibiting the lowest $T_g$ and ISRO polyol with polar ester groups in the backbone showing the highest $T_g$. PBAN exhibits intermediate $T_g$. The storage modulus values of the binders decrease to very low values and are out of measurement range. Hence data at room temperature (RT, 27 °C) are not available for the binders.

The $T_g$ and tan $\delta_{max}$ values for the binders are shown in Table 2. It is observed that binders having polybutadiene backbone (viz., CTPB, HTPB and HEF-20) have nearly same $T_g$ values (around -55 °C). The $T_g$ of HTPB cured with TDI shown in Table 2 is higher than that of IPDI-cured HTPB reported as -83 °C by Stacer and Husband[5].

### 3.2 Comparison of Binder and Propellant

Dependence of storage modulus and loss tangent data of PBAN propellant and binder on temperature are compared in Figs 3 & 4. It is observed that at any temperature the modulus of the propellant is higher than that of the binder. This is due to the incorporation of high level of solids in the propellant. The shift in the propellant curve towards the right indicates volume replacement and stiffening due to fillers combined with effect on viscoelastic behaviour[6].

For the same reason, the tan $\delta_{max}$ value of propellant is lower than that for the binder. Above $T_g$, the loss tangent curve of the propellant exhibits broad peak covering wide temperature range (-20 °C to 60 °C). This may be associated with the existence of mechanically impeded interphase filler particles[5-8]. Within the interphase, segmental mobility of polymer network is restricted due to weak adsorption to the filler surface. The small increase in $T_g$ of the propellant (filled

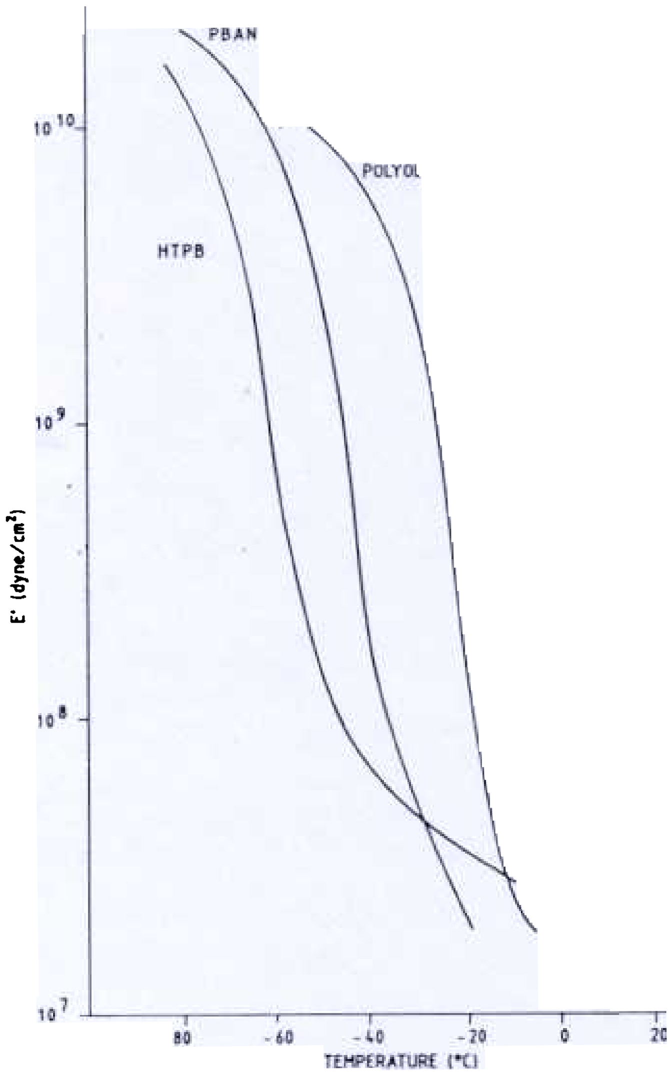



Figure 1. Dependence of storage modulus ($E'$) on temperature at 35 Hz for different polymeric binders.

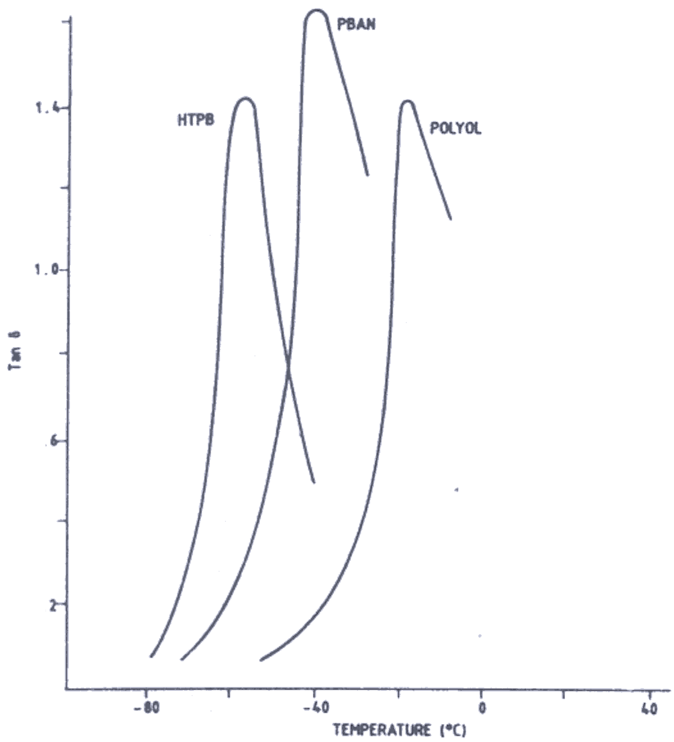



**Figure 2. Dependence of loss tangent on temperature at 35 Hz for various polymeric binders.**

polymer) is in agreement with the observations of Stacer and Husband[5].

**Table 2. Loss factor and glass transition temperature ($T_g$) of polymers and corresponding propellants**

| Description | Binder | | Propellant | |
|---|---|---|---|---|
| | tan $\delta_{max}$ | $T_g$ (°C) | tan $\delta_{max}$ | $T_g$ (°C) |
| HTPB (cured with TDI) | 1.42 | -57 | 0.45 | -48 |
| CTPB | 1.43 | -53 | 0.34 | -52 |
| HEF-20 | 0.84 | -54 | 0.65 | -47 to -37 |
| PBAN | 1.63 | -38 | 0.75 | -28 to -80 |
| ISRO polyol | 1.42 | -18 | 0.78 | -8 |

The storage moduli and loss tangent data of three different propellants are compared at different temperatures in Figs 5 & 6. Tan $\delta_{max}$, corresponding to $T_g$, is the highest for PBAN propellant and the lowest for HTPB propellants. At temperatures above $T_g$, the damping behaviour of the three propellants is quite interesting. In HTPB propellant, a broad hump with magnitude close to tan $\delta_{max}$ is observed between -10 °C and 80 °C. Above $T_g$, HEF -20 (1) propellant exhibits sharp decrease in loss tangent and remains nearly constant (but for a shoulder around 50 °C). The behaviour of loss tangent of PBAN propellant is qualitatively similar to that of HTPB propellant. However, above $T_g$, the hump is much broader in the latter than in the former.

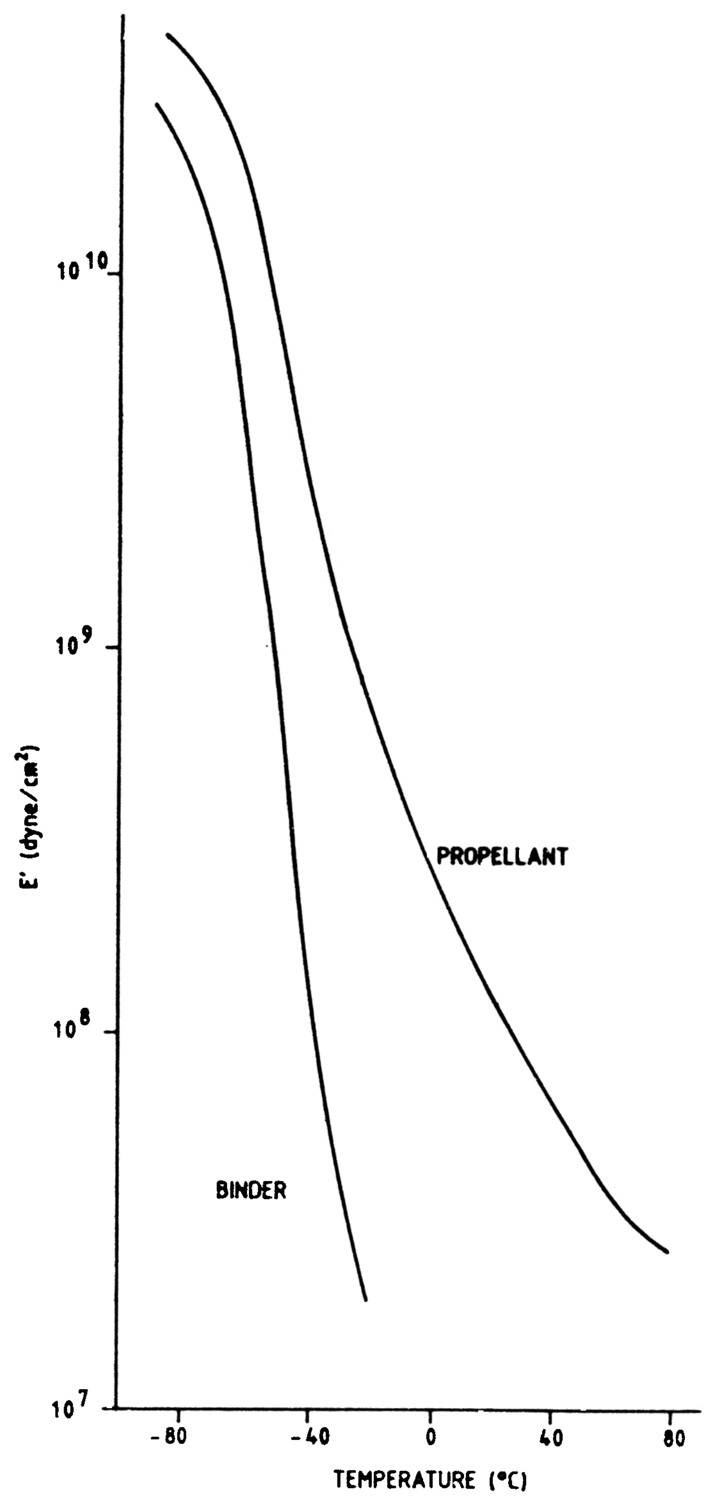



**Figure 3. Comparison of storage modulus of PBAN propellant and binder at different temperatures at 35 Hz.**

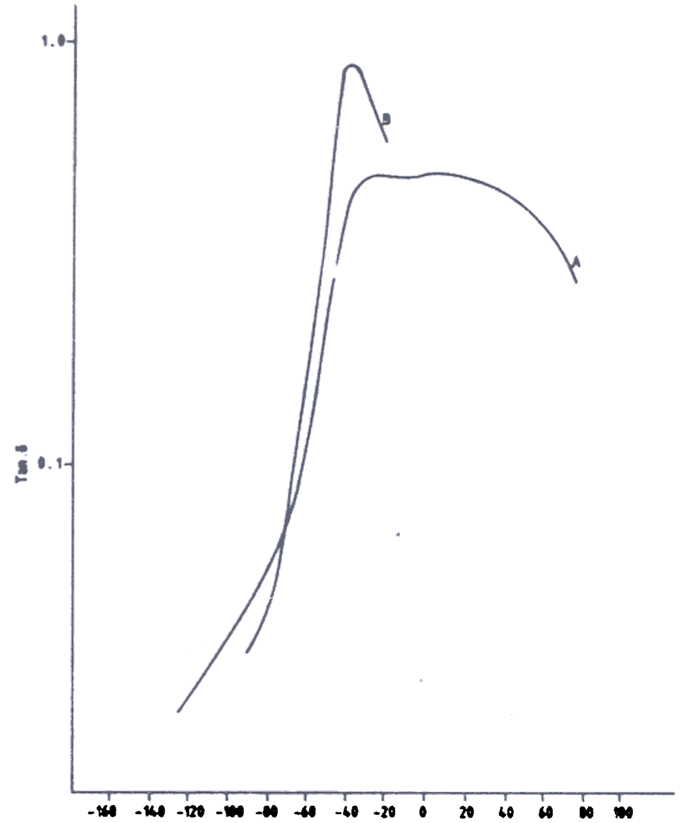



**Figure 4. Comparison of loss tangent of PBAN propellant (curve A) and binder (curve B) at different temperatures at 35 Hz.**

From Fig. 5, it is observed that the storage modulus of all the propellants exhibits sharp decrease around -40 °C. Subsequently, the decrease in $E'$ is gradual, resulting in the highest values of $E'$ for HEF-20(1) propellant and the lowest for PBAN propellant at temperatures above 50 °C.

The dynamic properties of the various propellants are detailed in Table 2. It is observed that the $T_g$ of the propellants is higher than that of the corresponding binder. The increase in $T_g$ is slightly larger in PBAN, HEF-20(1) and ISRO polyol systems than in HTPB propellant. The tan $\delta_{max}$ values of the propellants are lower than those of the binders. This behaviour is usual with filled systems[2,6].

### 3.3 Master Curves

The modulus-temperature data for the propellants determined at different frequencies are converted to modulus-time data at different frequencies and superposed using time-temperature superposition principle[2,4,9]. The shift factors ($a_T$) at different temperatures were determined according to

$$a_T = t/t_o$$

where $t$ and $t_o$ are times at temperatures $T$ and $T_o$ (ref. temperature). For HTPB-based propellants, WLF equation is found to be given by[2,4]

$$\log a_T = \frac{-6\,(T - 300)}{157 + T - 300}$$

where the reference temperature $T_o$ is 300 K. Here the WLF constants are $C_1 = 6$ and $C_2 = 157$. These constants are different for different polymeric binders[4,5]. Based on the shift factors, the master modulus curve is generated as plots of $E'$ versus reduced time $\log(t/a_T)$. A typical master curve is shown in Fig. 7. It is observed from Fig. 7 that the modulus covers a wide range of time, namely $10^{-10}$ to $10^4$ s. The modulus at short times determines the response of the propellant during ignition pressurisation whereas the ageing characteristics govern the long-time response of the propellant[10]. The master curves are essential inputs for evaluating the margin of safety of solid propellants.

The master curves for different propellants are compared in Fig. 8. It is observed that the decay of modulus with reduced time is slower in HEF-20(1) propellant than in the other propellants. HEF-20 resin is produced by degradation of polybutadiene rubber. In the case of HTPB, CTPB and PBAN, the resin is obtained by polymerisation of the corresponding monomer. Further, the molecular weight of HEF-20 resin is higher than that of the other resins. Also, HEF-20 resin contains considerable amount of plasticiser added during manufacture. This could be the reason for the slower decay of $E'$ with time in HEF-20(1) propellant. From Fig. 8, it is observed that the modulus of HTPB propellant is higher than that of PBAN propellant at very short times (less than $10^{-6}$ s) as well as at long times (beyond $10^2$ s). However, at intermediate times, opposite/reverse behaviour is observed.

## 4. CONCLUSIONS

The dynamic properties of binders and propellants based on HTPB, CTPB, PBAN, HEF-20 and ISRO polyol were studied. The glass transition temperature ($T_g$) of polybutadiene binders is nearly same around -55 °C. The $T_g$ of binders follows the order

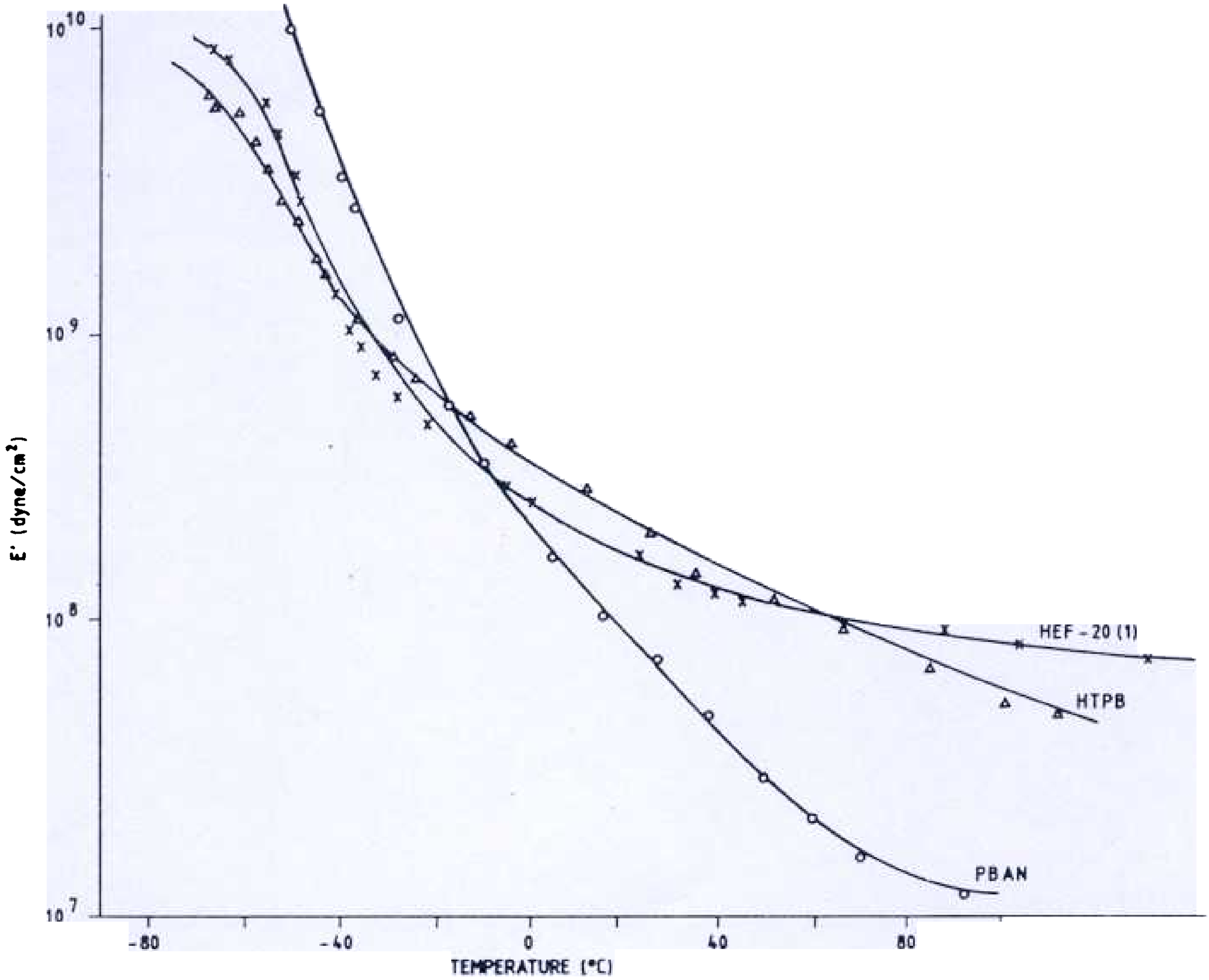



Figure 5. Dependence of storage modulus ($E'$) on temperature for different propellants at 35 Hz.

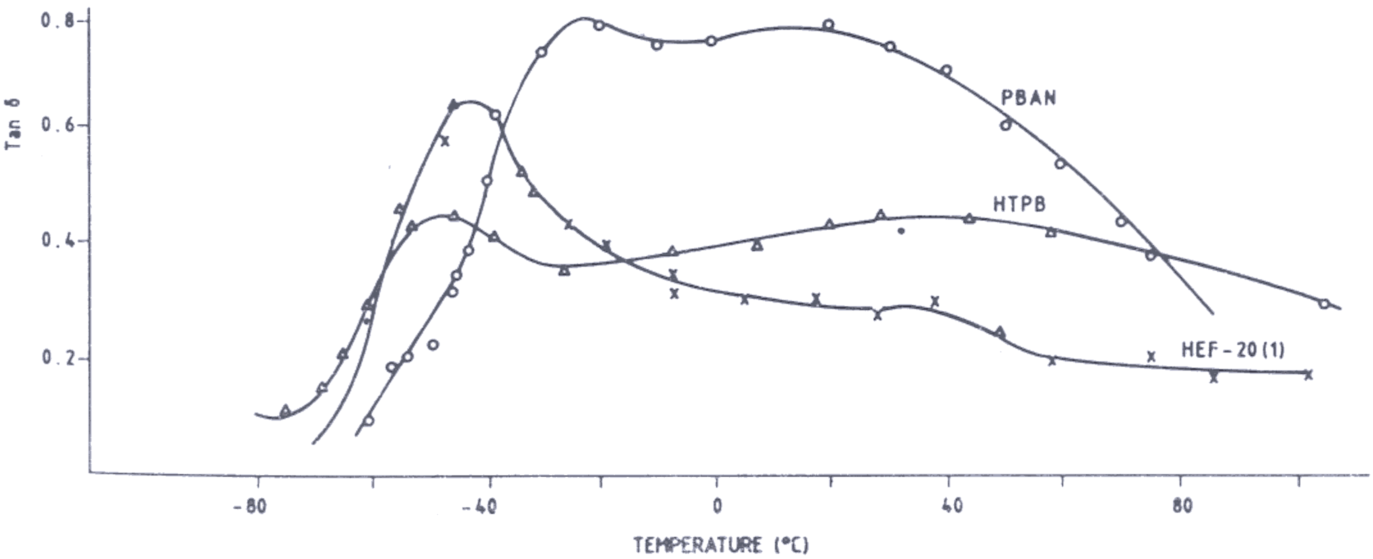
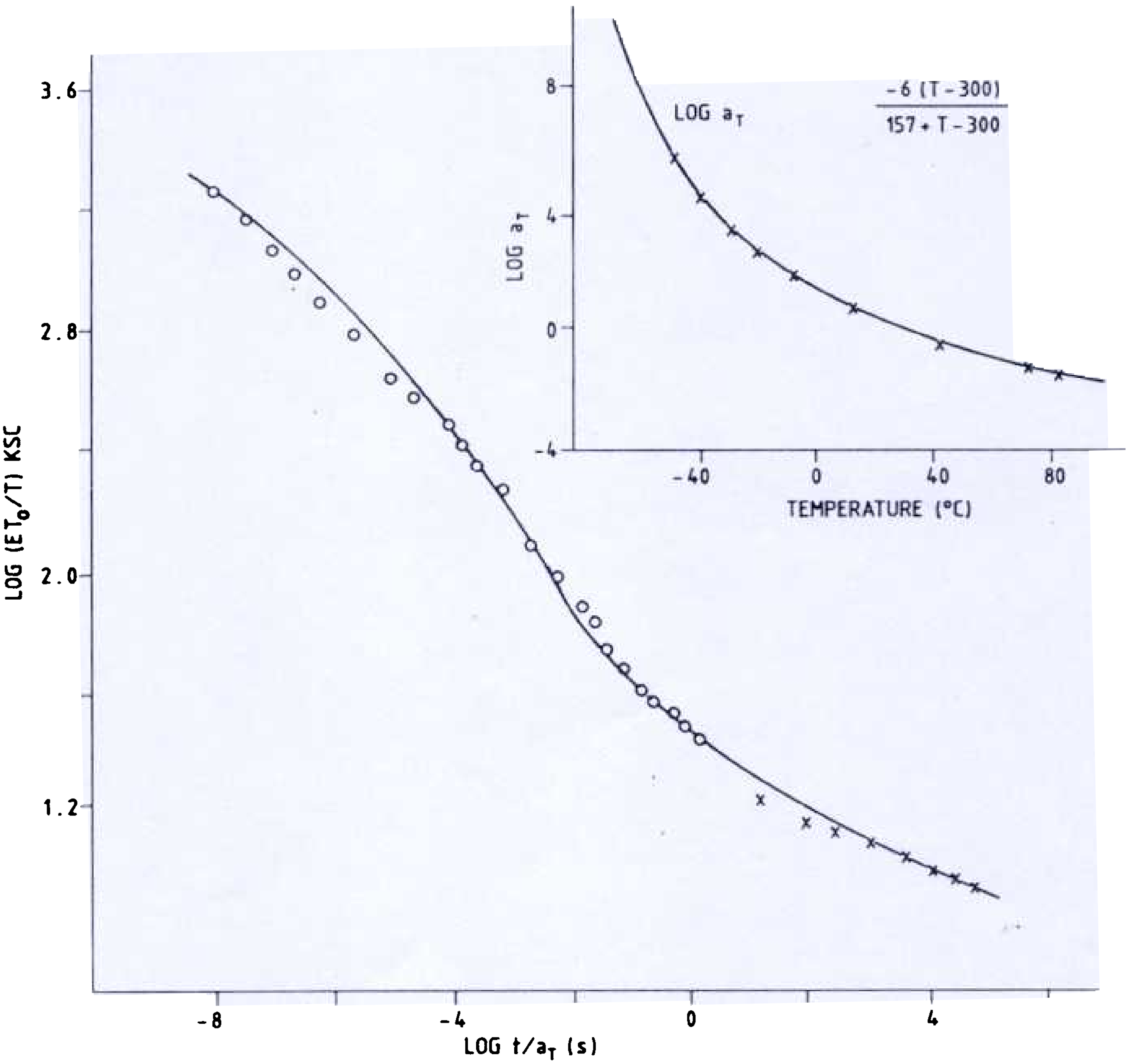



Figure 6. Comparison of loss tangent data of different propellants at different temperatures at 35 Hz.




Master curve for HTPB propellant using 300 K as reference temperature. Inset figure shows dependence of shift factor ($a_T$) on temperature

ISRO polyol > PBAN > HTPB. The $T_g$ of propellant is higher than that for the corresponding binder. The storage modulus is higher and the loss tangent lower

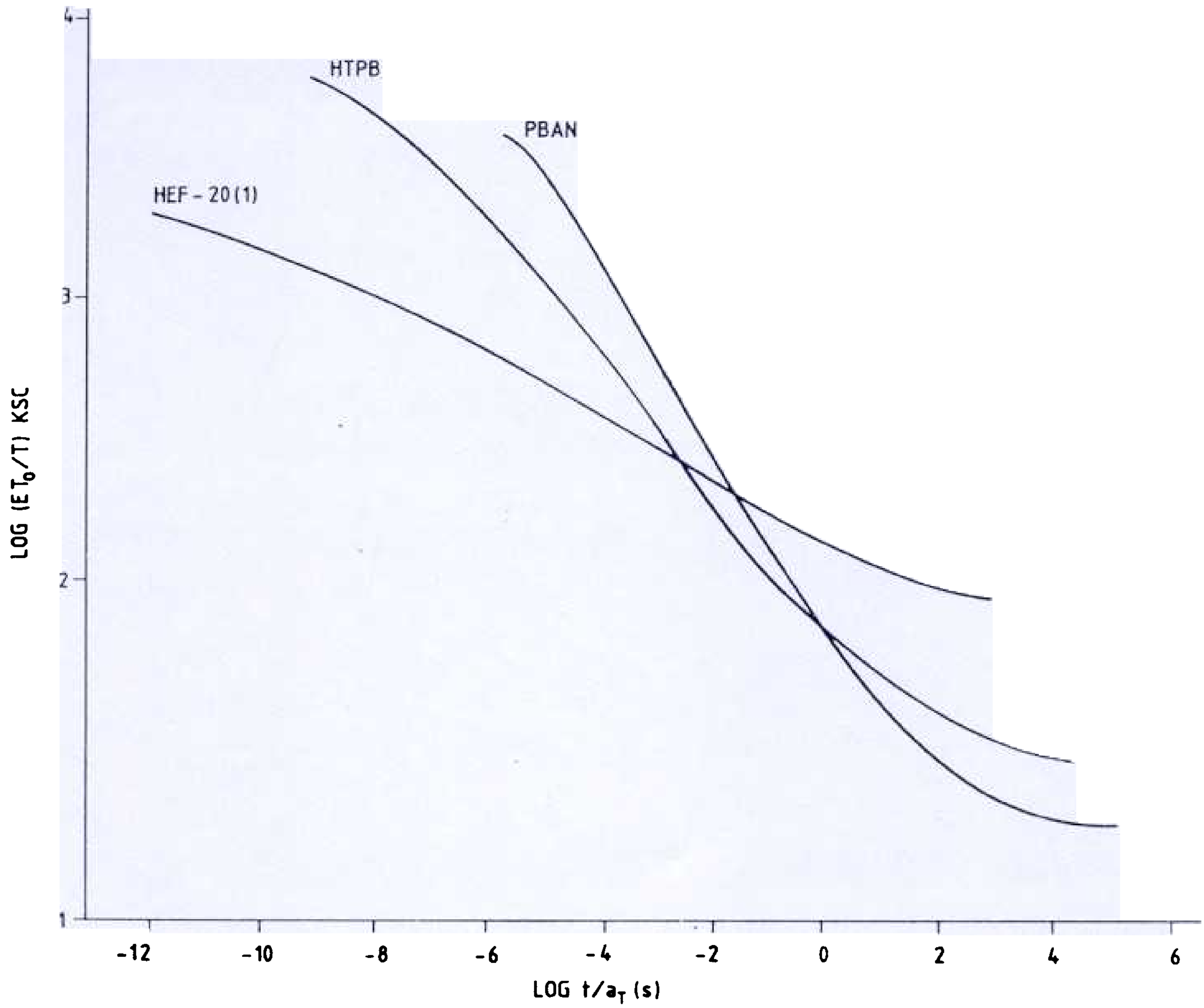



**Figure 8. Comparison of master curves for three propellants.**

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