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Research paper

Influence of Dispersion Methods on the Mechanical, Thermal and Rheological Properties of HTPB-based Nanocomposites: Possible Binders for Composite Propellants

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Abstract: The present study reports on the methods of preparation for HTPB-clay nanocomposites and their mechanical, thermal and rheological properties for their functional utility as an improved binder system for composite propellants. HTPB-clay nanocomposites were prepared by dispersing organoclay Cloisite 30B (1-3 wt.%) in the polymer matrix by magnetic stirring and high shear mixing. Critical parameters like time, temperature and RPM were optimized. These nanocomposites were cured with toluene diisocyanate in the presence of the cure catalyst DBTDL. The dispersion of the nanoclay was evaluated by using small angle X-ray scattering (SAXS) and energy dispersive X-ray (EDX) spectroscopy. EDX suggested homogeneous distribution while SAXS revealed partial exfoliation of the clay particles in the polymer matrix. Superior dispersion of the nanoclay was obtained by high shear mixing. The tensile properties of the nanocomposites prepared by high shear mixing showed 10-20% more strength and elastic modulus. The nanocomposites showed thermal stability higher than the pristine HTPB. Swelling behavior revealed increased cross linking, and the rheological behavior exhibited higher viscosity of the nanocomposites. In addition, the clay amount was increased up to 10 wt.% and its effect on the mechanical, thermal and swelling behavior was observed. Theoretical performance predictions of composite propellants with nanocomposites revealed their possible functional utility.

Keywords: nanocomposite, composite propellant, binder, dispersion, tensile strength

Supporting Information (SI), i.e. Figures S1-S8, is available at:

http://www.wydawnictwa.ipowaw.pl/cejem/Vol-16-Number-2-2019/CEJEM_00981_SI.pdf

1 Introduction

Hydroxy Terminated Polybutadiene (HTPB) prepolymer plays an important role as fuel-*cum*-binder in modern composite solid propellants for rocket motors. The network structure obtained by the curing of the prepolymers provides a continuous matrix for the inorganic oxidizer and other solid ingredients, and imparts the three-dimensional stability necessary to withstand the thermal and mechanical stress and strain that are encountered during storage and operation of propellants over a wide temperature range [1-5]. HTPB also has unique physico-chemical properties, such as an excellent solid loading capability and better shelf life than other binder systems, which makes it the work-horse polymeric binder for composite propellants. HTPB can be utilized for case bonded as well as cartridge loaded composite propellants, and accordingly its properties can be modified. However, for some specific applications like nozzle-less boosters or sleeve cast gas generators, a composite propellant requires high tensile strength and elastic modulus, with high strain capability. Although, HTPB imparts good mechanical properties and processability for both case bonded and cartridge loaded applications, it also has some limitations, such as, difficulty in achieving high strain capability with substantial tensile strength through conventional means. Therefore, there is a need for the development of a modified binder system that has the inherent merits of HTPB with improved strain capability for specific applications.

Recently, polymer-layered silicate nanocomposites (PLSN), also known as polymer-clay nanocomposites, which are based on polymers and organically modified nanoclay, has received global attention in terms of improved mechanical properties, thermal stability and barrier properties. In the last decade, many reviews have been published highlighting the various aspects of this subject [6-13], of which, a few have specifically dealt with polyurethane or thermosetting polymer based nanocomposites [14, 15]. This concept was explored almost half a century ago, but, it attained importance later when a Toyota research group disclosed improved strength, modulus, heat distortion temperature

and gas barrier properties of nylon-6 clay nanocomposites in comparison to neat nylon-6 [16-19]. Giannelis and co-workers [20, 21] revealed that the key objective in preparing polymer-clay nanocomposites is to achieve delamination of the large stacks of silicate nanoplatelets in single layers or tactoids of small numbers of layers. If this objective is achieved, then the high aspect ratio of the platelets can fully contribute to the nanocomposite's property profile. During the development of nanocomposites, it is important to know the degree of exfoliation of the nanocomposite system, which depends on the methods of dispersion and process parameters such as time and temperature [22-24].

Various methods are reported in the literature [25-27] to assess the extent of clay dispersion. Small angle X-ray scattering (SAXS), is a widely used tool for this purpose. SAXS is capable of quantifying the gallery height between adjacent silicate platelets and thus can demonstrate the extension of this distance as the matrix polymers intercalate between the galleries. The low angle diffraction band becomes wider with increasing gallery height and may disappear when the distance is significantly high. This serves as a qualitative method to measure the degree of exfoliation or intercalation of nanocomposites. Therefore, the disappearance of the SAXS diffraction band is taken as proof for complete or almost complete exfoliation of clay nano platelets [28]. In this research, SAXS was utilized as a tool to compare the extent of dispersion in samples prepared by two different techniques. Additionally, efforts have been made to confirm the homogeneity of a clay dispersion in a binder matrix by using energy dispersive X-ray (EDX) spectroscopic analysis. The extent of dispersion of the clay was assessed by sampling the concentration of silicon, a primary constituent of clay, at different locations in the cured clay composite. The silicon content was measured through multipoint mapping over the clay composite surface and gave the standard deviation of the measured concentrations. A lower standard deviation of the measured silicon concentration would represent better homogeneity or uniform dispersion of nanoclay in the binder matrix.

This concept of an HTPB-based polymer layered silicate (PLS) nanocomposite was envisaged to be of use in the field of composite propellants for the development of enhanced strain capability of the propellant and light weight insulation and inhibitor systems [29-31]. Additionally, due to the high aspect ratio and high surface area, nanoclays may also act as a burn rate modifier for composite propellants [32]. The literature revealed that various methods are available for the dispersion of nanoclay in a polymer matrix, depending upon the nature of the polymer [33-38]. In this study, two techniques *viz.* magnetic stirring and high shear mixing, were used for dispersion of the nanoclay and compared for their efficiency and suitability for the HTPB system [39].

Critical parameters like time, temperature and RPM were optimized for both techniques. Initially, in order to establish the method of dispersion, samples were prepared by using only up to 3 wt.% of nanoclay. These samples were characterized by SAXS and EDX analysis, and revealed that high shear mixing is a better technique for uniform dispersion. Hence, this technique was further used to prepare and study the effect of clay content on the mechanical and thermal properties of nanocomposites by using up to 10 wt.% of nanoclay.

The swelling and rheological behavior of these composites was also determined and found satisfactory for their functional utility and processing. The tensile properties of these nanocomposites showed a substantial improvement with up to 7 wt.% of nanoclay incorporation, but, beyond this level the tensile strength decreased significantly and the nanocomposites lost their mechanical strength. This demonstrates that, there is an optimum percentage of nanoclay for a particular polymer system, where the improvement in tensile properties will be maximized.

2 Experimental

2.1 Materials

HTPB ($M_n \approx 2600$ -2900, $-\text{OH}$ value: 40-45 mg KOH/g, functionality: 1.8-2.5, polydispersity: 1.5-2.5) was obtained from Anabond Pvt. Ltd., India; dioctyl adipate (DOA) was procured from IndoNippon Pvt. Ltd., India; toluene di-isocyanate (TDI) was obtained from BASF, Germany, and dibutyl tin dilaurate (DBTDL) was obtained from Sigma-Aldrich Co., USA. Organically modified nanoclay (Cloisite 30B) was obtained from Southern Clay Products, USA. Cloisite 30B is a natural montmorillonite modified with methyl, tallow, bis-2-hydroxy methyl, ammonium salt. This clay was selected due to the presence of the hydroxyl groups in the organic modification, which will take part in polyurethane formation and will provide physical as well as chemical reinforcement to the matrix. Figure 1 shows the chemical formula of the organic modifier and Table 1 lists the characteristics of Cloisite 30B.

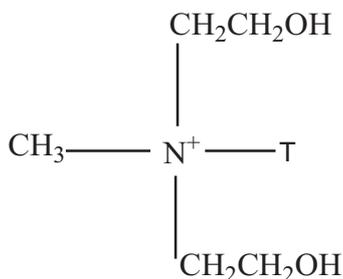


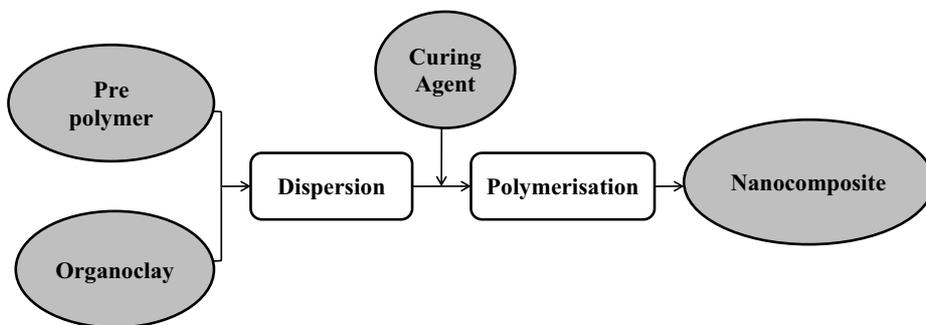
Figure 1. Organic modifier Cloisite 30B (MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium), where T is Tallow (~65% C₁₈, ~30% C₁₆, ~5% C₁₄); Anion: chloride

Table 1. Characteristics of Cloisite 30B

Property/Treatment	Value
Organic modifier	MT2EtOH
Modifier concentration	90 meq/100g clay
Density [g/cm ³]	1.98
Bulk density [g/cm ³]	0.2283
d-spacing [Å]	18.5
Moisture [%]	≤ 2

2.2 Method

HTPB-clay nanocomposites were prepared following the method described by Song *et al.* [24] and depicted in Scheme 1. Samples (PCN-1MG, PCN-3MG, PCN-1HG, PCN-3HG) were prepared by dispersion of organically modified nanoclay (Cloisite 30B) at 1 wt.% and 3 wt.%, using techniques like magnetic stirring (with IKA C-MAG HS 7 digital stirrer *cum* hot plate) and high shear mixing (with IKA T25 digital homogenizer), respectively. During dispersion, the temperature was maintained at about 50 °C. Further sample preparation was performed with higher clay contents *viz.* 5, 7 and 10 wt.% as samples PCN-5HG, PCN-7HG and PCN-10HG, respectively. Details of all the samples prepared by the different methods and with different amounts of clay are listed in Table 2. After dispersion, the samples were degassed by applying 133-266 Pa of vacuum for 15 min and then cured with TDI as a curator and DBTDL as a cure catalyst, with an equivalence ratio of 1.0, in the form of thin sheets of around 1-2 mm thickness. Samples were kept at room temperature for about 24 h in vacuum desiccators and then cured in a water jacketed oven at 60 °C for 120 h. A control sample was also prepared by curing HTPB with TDI without nanoclay.



Scheme 1. Method of preparation for HTPB-clay nanocomposites

Table 2. Detailed sample specification for various nanocomposites of HTPB/DOA 60/40

Designation ^{a)}	Cloisite 30B [wt.%]	Dispersion method ^{b)}
PCN-Base	0	–
PCN-1MG	1	Magnetic stirring for 1 h
PCN-3MG	3	Magnetic stirring for 1 h
PCN-1HG	1	Homogenization for 15 min
PCN-3HG	3	Homogenization for 15 min
PCN-5HG	5	Homogenization for 15 min
PCN-7HG	7	Homogenization for 15 min
PCN-10HG	10	Homogenization for 15 min

^{a)} PCN – polymer clay nanocomposite, MG – magnetic stirring, HG – homogenizer;

^{b)} 50°C; 25000 rpm.

The change in gallery distance of the clay was monitored with SAXS using instrument NANO-viewer, Rigaku, Japan, with Cu K α radiation at a generator voltage of 40 kV and current of 40 mA. The energy dispersive X-ray (EDX) spectroscopic analysis was performed with an EDX system from EDAX Inc., USA, attached to a Quanta 200 FEI make ESEM (Environmental Scanning Electron Microscope). FT-IR analysis was employed to determine possible intermolecular interactions between HTPB and the organo-clay using an FT-IR spectrometer, Nicolet-iS 50 from Thermo Electron Corporation, USA. Scans were taken at room temperature in the ATR mode within a range of 400-4000 cm⁻¹ for all of the samples. The tensile properties were measured using a Hounsfield H25 KS Universal Testing Machine (UTM), maximum capacity 25 kN, at a crosshead speed of 50 mm/min. Tensile strength (TS), percent elongation and elastic modulus were determined by using 4 mm thick specimens (length 115 mm and width 25 mm) as per the ASTM D-638 standard.

A mean value of five readings were taken for each composition. Thermogravimetric analysis (TGA) was carried out on an SDTA Q-600 Simultaneous Thermal Analyzer from TA Instrument, USA, over a temperature range of 30 to 600 °C at a heating rate of 10 °C/min.

Swelling experiments were carried out with $25 \times 25 \times 2$ mm³ samples by placing them in toluene at ambient temperature for 28 h. The samples were periodically removed from the test bottles, the solvent on the surface was cleaned by standard procedures and the samples were weighed immediately. The weight swelling ratio (Q_t) was determined from the weight of the sample in the unswollen and swollen states using Equation 1.

$$\%Q_t = [(W_t - W_o)/W_o] \times 100 \quad (1)$$

where Q_t is the weight swelling ratio, W_t is the weight of the sample in the swollen state and W_o is the initial weight of the sample. The crosslink density was calculated by using the number average molecular weight between crosslinks (M_c) which was calculated by the Flory-Rehner (Equation 2) [40, 41].

$$-\ln[(1 - V_r) + V_r + \chi V_r^2] = \rho V_s M_c^{-1} (V_r^{1/3} - V_{r2}) \quad (2)$$

where V_r is the volume fraction of the polymer in the swollen gel at equilibrium, χ is a polymer-solvent interaction parameter, V_s is the molar volume of the solvent, ρ is the polymer density. The crosslink density is defined as $1/(2M_c)$.

Rheological measurements were carried out using a Physica MCR 101 Rheometer by Anton Parr, USA. Dynamic oscillatory shear measurements were performed at 50 °C using a set of 25 mm diameter parallel plates of 0.5-1 mm thickness. The frequency sweep was within the frequency range of 0.01-1000 Hz at a strain of 10%.

3 Results and Discussion

3.1 Dispersion of nanoclay

3.1.1 SAXS Analysis

Dispersion of the nanoclay in the polymer matrix indicates either intercalation or exfoliation depending on the method of dispersion. In the former case, extended polymer chains are intercalated between the host layers of the clay resulting in a well ordered multilayer, where the layers of silicate retain

their structural identity. In the case of exfoliation, the polymer chains penetrate in between the layers of silicate (having nanosize thickness) and clay platelets dispersed in a continuous polymer matrix to lose their structural identity. It is well reported in the literature that exfoliated nanocomposites show better properties than intercalated nanocomposites [42, 43].

It is evident from the results summarized in Figure S1 (see SI), that dispersion of the nanoclay has taken place as the peaks are very diffuse in nature for the nanocomposite samples. In the case of samples prepared by homogenization with 3 wt.% of nanoclay (PCN 3 HG), the peak corresponding to the nanoclay is negligible, which confirms better dispersion by this technique. The samples prepared by magnetic stirring have a substantially visible peak corresponding to nanoclay, which shows that by using this method large aggregates of clay may be converted in to small aggregates that still have some structural integrity, and with homogenization maybe these aggregates also become dispersed. So, the order of dispersion can be arranged as follows: PCN-3HG > PCN-1HG > PCN-3MG > PCN-1MG. These data are further supported by the similar result from EDX analysis.

3.1.2 Energy Dispersive X-ray (EDX) Spectroscopic Analysis

Elemental X-rays, generated during SEM imaging at about 15 kV accelerating potential, from a sample surface area covering nearly 2×2 mm were collected and analyzed. EDX analysis was carried out for nanoclay, Cloisite 30B, as well as for the nanocomposite films. The powdered clay samples were made into a film over conductive adhesive tape with gentle compression and then subjected to EDX analysis. For the HTPB-clay nanocomposites, X-ray spectral profiles were collected from multiple areas over the sample surface to assess the homogeneity of nanoclay distribution. The extent of dispersion of the clay was probed by measuring the Si content and obtaining the statistical standard deviation. A lower standard deviation of silicon quantification would represent better homogeneity or uniform dispersion of the nanoclay in the binder matrix. EDX analysis data are summarized in Figures S2(a)-(f) (see SI). A polymer film of HTPB, without nanoclay was also analyzed as a control sample for comparison purposes. Figure S2(a) shows the EDX of nanoclay Cloisite 30B, where peaks for different elements like C, O, Si, Mg are clearly seen, while in Figure S2(b) only intense peaks of C and O are present, as is obvious for the control sample due to the absence of nanoclay.

Nanocomposite film samples were analyzed by multipoint mapping of a particular element to confirm the extent of dispersion. For ease of detection, Si was chosen for mapping, and data were collected from three different

points on a particular sample. The standard deviation was then calculated for the percentage of Si obtained from all of the points. A low value of the standard deviation was assumed to be confirmation of uniform dispersion. It is clear from Figures S2(c)-(f) that PCN-3HG had the smallest standard deviation (SD) of all the collected data *i.e.* 0.006, indicating greater homogeneity. This also corresponds well to the negligible peak height in the SAXS of the same sample. It thus confirms the uniform dispersion of nanoclay in the HTPB matrix. By contrast, other nanocomposite samples showed higher SD values, *viz.* 0.032 for PCN-1HG, 0.105 for PCN-1MG and 0.185 for PCN-3MG. These data also confirm the fact that high shear mixing with an homogenizer is a better technique for dispersion.

3.2 Interaction between HTPB and nanoclay

The FTIR spectrum of organo modified nanoclay, recorded as a KBr pellet, is shown in Figure S3(a) (see SI). The broad band centered at 3390 cm^{-1} is due to the presence of the -OH stretching band for intercalated water. The band at 3630 cm^{-1} is due to the -OH band stretching for Al-OH , and the shoulders and broadness of the structural -OH band are mainly due to contributions from several structural -OH groups occurring in the clay. But all of these bands, due to the presence of the -OH group in clay, are absent in the spectrum of HTPB-clay nano composites Figure S3(b) (see SI), which show that the -OH group of nanoclay is consumed in the curing reaction with isocyanate to form polyurethane linkages. Additionally, in the spectra of the HTPB-clay nanocomposites, two peaks at around 463 and 524 cm^{-1} appear, which are due to the silica backbone of clay, as shown in the FTIR spectrum of pure clay. The intensity of these peaks increased as the amount of clay was increased from 1 to 10 wt.%. No other changes due to the presence of nanoclay were observed in the FTIR spectra. This confirms that the segmented structure of HTPB has not been affected by the inclusion of organoclay.

3.3 Thermal characterization

The thermal stability of the nanocomposites under nitrogen flow (100 mL/min) was examined using SDTA as shown in Figure S4 (see SI) and Table 3. The results showed that incorporation of nanoclay does not have any adverse effect on the thermal stability: *i.e.* the decomposition onset and peak decomposition temperatures of pristine HTPB. The nanoclay composites showed progressively higher residues for samples with increasing percentages of added nanoclay. The decomposition pattern of the nanocomposites showed weight loss in two nearly overlapping steps, similar to that of the control sample 'PCN Base'.

A gradual but slow weight loss of about 2.2% was observed during the initial stage of heating (50-150 °C) of the PCN base. This may be due to loss of certain volatile matter present. The onset temperature of the 1st decomposition step of nanoclay composite PCN-1HG showed a shift towards higher temperature by about 10 °C in comparison to that of ‘PCN base’ at about 183.4 °C. However, for the rest of the nonclay composites, the onset temperature showed no significant change. An increasing onset represents improved thermal stability of the nanoclay composites. A similar increase in thermal stability has been reported by other researchers for different polymer-clay nanocomposites [44, 45]. This improvement in thermal stability of nanocomposites can be explained by high barrier properties of nanocomposites obtained by proper dispersion of nanoclay in the polymer matrix. These clay nanolayers play the role of a thermal barrier, which delays the heat transfer inside the polymer matrix [46-48]. It is important to note that, no significant changes in the maximum decomposition temperatures (T_{max}) were observed for both the first and second steps.

Table 3. TGA data for HTPB nanocomposites prepared by different techniques

Composition	Weight loss [%]		T_{max} , [°C]		Onset 1 st step, [°C]
	1 st step	2 nd step	1 st step	2 nd step	
PCN-Base	33.52	64.34	226.75	457.53	183.40
PCN-1HG	32.65	63.85	227.62	461.48	193.70
PCN-3HG	32.15	63.17	228.05	462.99	194.81
PCN-5HG	31.46	62.51	226.54	451.43	195.11
PCN-7HG	31.14	60.03	221.94	451.31	191.37
PCN-10HG	29.44	59.37	225.93	454.36	194.19

3.4 Tensile properties

The tensile properties of HTPB and HTPB-clay nanocomposites (from 1 to 3 wt.% of nanoclay) prepared by different methods are summarized in Table 4 and Figures S5(a) and S5(b) (see SI). These results show that neat HTPB exhibits low tensile strength and Young’s modulus. The incorporation of nanoclay in to the HTPB matrix shows a remarkable improvement in tensile strength as well as Young’s modulus, even at a low clay loading of 1 wt.%. It is also evident from the results that the enhancement in mechanical strength is proportional to the extent of dispersion, as the samples prepared by high shear mixing have 6-10% more tensile strength and modulus, while elongation is around 40% more, than samples prepared by magnetic stirring. Better dispersion of the nanoclay is the key reason for the improvement in mechanical properties at the same clay content.

Table 4. Tensile properties of nanocomposites prepared by different methods

Mechanical property	Nanocomposite				
	PCN-Base	PCN-1MG	PCN-3MG	PCN-1HG	PCN-3HG
Tensile Strength [MPa]	0.172	0.201	0.224	0.216	0.271
ϵ_m [%]	86	106	139	116	206
E-mod [MPa]	0.102	0.172	0.240	0.184	0.276

The amount of clay was further increased incrementally from 5 to 7 wt.% and finally up to 10 wt.%, and the dispersion of the nanoclay was carried out by homogenizer so that the effect of the clay content on the mechanical properties could be evaluated. The results are summarized in Table 5 and Figures S6(a) and S6(b) (see SI). The enhancement in properties like tensile strength and modulus up to 7 wt.% of clay can be explained on the basis of strong reinforcement of uniformly dispersed nanoplatelets within the polymer matrix, as well as strong interfacial interaction between the nanoclay and the HTPB matrix due to the very high aspect ratio of nanoclay, of the order of 200-300 [49-51]. The reduction in tensile properties at 10 wt.% clay loading is due to the decrease in the number of crosslinks from a topological perspective, as reflected by the crosslink density [52]. Surprisingly, the strain capability of these composites was also improved by inclusion of nanoclay and it is further increased by increasing the clay loading. This behaviour of nanocomposites is in contrast to the tensile behaviour of conventional elastomer composites containing micron-sized inorganic fillers, in which the tensile strength and elastic modulus are typically enhanced by compensation of the percent elongation. The literature reveals that this behaviour of nanocomposites may be a plasticizing effect of the gallery onium ions, which also contribute to dangling chain formation in the matrix [53, 54]. Thus, it is clear from these results that the extent of dispersion and the amount of clay both have a significant influence on the mechanical properties of the nanocomposites.

Table 5. Tensile properties of nanocomposites with different amounts of nanoclay

Mechanical property	Nanocomposite					
	PCN-Base	PCN-1HG	PCN-3HG	PCN-5HG	PCN-7HG	PCN-10HG
Tensile strength [MPa]	0.172	0.216	0.271	0.331	0.428	0.125
ϵ_m [%]	86	116	206	283	113	446
E-mod [MPa]	0.102	0.184	0.276	0.346	0.64	0.079

3.5 Swelling behaviour and crosslink density

The effect of clay content on the swelling behaviour of HTPB-clay nanocomposites in toluene is shown in Figure S7 (see SI). The incorporation of clay decreases the weight swelling ratio (Q_t), which indicates that the resistance to chemicals increases in nanocomposites due to reinforcement and the microstructure formed by the dispersion of the organoclay in to the polymer matrix. The crosslink density results are listed in Table 6. The results show that the presence of nanoclay reduces the rate of diffusion of solvent molecules in to the polymer matrix because of the increased crosslinking. In addition to that, the strong interaction between the clay particles and the HTPB matrix also contributes to the improved chemical resistance. However after a certain clay loading (10 wt.%), as the crosslinking decreases, the swelling ratio increases suddenly, because at this concentration dispersed platelets of nanoclay interfere with the crosslinks [55, 56].

Table 6. Crosslink density of nanocomposites with different amounts of nanoclay

Sample	Initial weight [g]	Swollen weight [g]	V_r	Crosslink density
PCN Base	1.249	9.902	0.1173	$2.863 \cdot 10^{-3}$
PCN-1HG	1.25	9.6077	0.1209	$2.936 \cdot 10^{-3}$
PCN-3HG	1.265	8.0433	0.1466	$3.441 \cdot 10^{-3}$
PCN-5HG	1.192	6.658	0.1671	$3.848 \cdot 10^{-3}$
PCN-7HG	1.284	5.44	0.2214	$4.941 \cdot 10^{-3}$
PCN-10HG	1.294	12.3429	0.0973	$2.466 \cdot 10^{-3}$

3.6 Rheological behaviour

The rheological behaviour of nanocomposites is very important from a processing point of view. The elastic modulus (G') and loss modulus (G'') of HTPB and its nanocomposites prepared by different methods are shown in Figures S8(a) and S8(b) (see SI), respectively. These figures shows that G' and G'' of HTPB-clay nanocomposites are higher compared to HTPB, whereas G' and G'' of samples prepared by dispersion of nanoclay with an homogenizer is increased more than for the samples prepared by magnetic stirring, even at the same clay loading. These results are in line with the tensile properties data. However, an increase in the modulus is more prominent in the lower frequency range than at higher frequencies, maybe because at higher frequencies, the rheological behaviour of the nanocomposites is dominated by the polymer rather than the filler [57-63].

The change in the complex viscosity of HTPB and HTPB-clay nanocomposites is shown in Figure S8(c) (see SI). The complex viscosities of HTPB-clay

nanocomposites decrease with increasing frequency, indicating shear thinning behaviour of the HTPB nanocomposites. The viscosity of nanocomposites was higher than that of pristine HTPB, and the increase in viscosity is more pronounced at the low frequency range than at the high frequency. This may be due to the flow restriction of polymer chains in the presence of clay nano particles at low frequencies while at high frequencies the viscosity of nanocomposites is similar or lower because of the alignment of silicate layers towards the direction of flow [1, 27]. The combined plots of G' and G'' of HTPB and HTPB-clay nanocomposite are displayed in Figure S8(d) (see SI), which shows G'' larger than G' for both of the samples in the entire frequency range. This reflects a prominent liquid-like or viscous behaviour of HTPB which does not become affected by the inclusion of nanoclay.

Table 7. Theoretical performance parameters of various propellant compositions with HTPB-clay nanocomposites

Composition ^{a)}	Base	CP-1	CP-3	CP-5	CP-7	CP-10
Performance parameter						
Enthalpy of combustion [kJ/kg]	-2405.31	-2420.38	-2450.48	-2476.86	-2491.13	-2505.38
Mol. wt. [kg/mol]	24.79	24.88	25.07	25.26	25.36	25.45
Specific heat [kJ/(kg·K)]	2.9532	2.9570	2.9655	2.9772	2.9828	2.9886
Flame temperature [K]	3243	3250	3263	3277	3283	3290
Specific heat ratio, γ	1.1494	1.1489	1.1480	1.1471	1.1466	1.1461
Characteristic velocity C^* [m/s]	1577.3	1575.8	1572.7	1569.9	1568.4	1566.8
Specific impulse I_{spvac} [s]	276.9	276.6	276.1	275.7	275.4	275.2
Specific impulse $I_{sp70:1}$ [s]	260.6	260.3	259.9	259.5	259.2	259

^{a)} Base – AP/Al/Binder, 67/17/16, CP-1 to CP-10 = composite propellants with PCN-1HG to PCN-10HG, respectively.

3.7 Theoretical predictions for composite propellants

HTPB clay nanocomposites are anticipated to be of use in composite propellant formulations. The theoretical performance of composite propellant formulations containing HTPB-clay nanocomposites was predicted by the NASA CEC-71 code before actual processing of the same. All of the predictions were done for chemical equilibrium conditions at a chamber pressure of 7 MPa. The ratio of the nozzle exit area (A_e) and the nozzle throat area (A_t) values was chosen as 7 for all of the compositions. The combustion efficiency and nozzle efficiency was assumed to be 100% for all predictions. The detailed results are presented in Table 7 and reveal that HTPB-clay nanocomposites can be used in composite propellants for their advantageous improved mechanical strength and thermal stability, by having marginal compensation towards the specific impulse (I_{sp}).

4 Conclusions

Hydroxyl terminated polybutadiene (HTPB)-clay nanocomposites with intercalated and exfoliated structures have been prepared successfully by employing high shear mixing and magnetic stirring. The nanocomposites prepared by high shear mixing have better dispersion of the nanoclay, which is supported by successive improvements in tensile properties. HTPB-clay nanocomposites have better mechanical strength, thermal stability and chemical resistance than neat HTPB, without adversely affecting the original elastomeric properties of the polymer. Rheological studies revealed that the nanocomposites exhibit a more liquid-like behaviour and shear thinning, similar to the inherent behaviour of HTPB. Theoretical performance predictions and this comprehensive study conclude that HTPB-clay nanocomposites could be possible binder candidates for preparing composite propellants with superior tensile strength and high strain capability. However, for a detailed understanding of their effect on ballistic properties and processing difficulties, they need to be evaluated in actual propellant formulations.

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