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RESEARCH PAPER

Shear Thickening Behaviour of Composite Propellant Suspension under Oscillatory Shear

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ABSTRACT

Composite propellant suspensions consist of highly filled polymeric system wherein solid particles of different sizes and shapes are dispersed in a polymeric matrix. The rheological behaviour of a propellant suspension is characterised by viscoplasticity and shear rate and time dependant viscosity. The behaviour of composite propellant suspension has been studied under amplitude sweep test where tests were performed by continuously varying strain amplitude (strain in %, γ) by keeping the frequency and temperature constant and results are plotted in terms of log γ (strain amplitude) vs logG′ and logG″ (Storage modulus and loss modulus, respectively). It is clear from amplitude sweep test that dynamic moduli and complex viscosity show marked increase at critical strain amplitude after a plateau region, infering a shear thickening behaviour.

Keywords: Shear thickening, amplitude sweep, packing fraction, composite propellant, rheology

NOMENCLATURE

γ	Strain
γ_c	Critical strain
γ_m	Strain at maximum complex viscosity
η^*	Complex viscosity
G'	Storage modulus
G''	Loss modulus
ϕ_m	Maximum packing fraction
ϕ/ϕ_m	Reduced packing fraction
AP	Ammonium perchlorate
Al	Aluminium powder
HTPB	Hydroxyl-terminated polybutadiene

1. INTRODUCTION

Composite propellant consists of suspension of solid particulates of oxidiser (ammonium perchlorate, AP) and metallic fuel in a polymeric binder system, usually based on hydroxyl-terminated polybutadiene (HTPB). To maximise the performance of composite propellant, the concentration of solid particulates is often kept close to maximum packing fraction. Such highly filled suspensions of composite propellant exhibit complex rheological behaviour. The study of its rheology is vital since it affects various manufacturing processes such as mixing, casting, etc. as well as the end product properties of these suspensions. The rheological behaviour of propellant suspension is generally characterised by viscoplasticity and shear rate and time dependant viscosity which is affected by viscosity of binder, particle size, shape and size distribution of solid particles[1] as well as measurement conditions[2]. Further, the efficiency of distributive and dispersive mixing of the ingredients of suspensions significantly controls the microstructure and rheological behaviour of suspension. Furthermore, the rheological characterisation is also complicated by occurrence of wall slip and flow instabilities[2,3]. Slip flow behaviour of composite propellant occurs due to formation of binder rich region near the wall due to particle migration away from the high shear region, thus forming a 'slip layer' near the wall. Thus, development of apparent slip flow behaviour of propellant slurry has an important effect in characterisation of rheological properties as well as on its processing and quality control.

The literature reveals that a number of studies on rheology of composite propellant suspensions have been reported based on steady shear but not much has been revealed of their oscillatory shear behaviour. Miller[4], *et al.* have reported two class of propellant compositions using steady and dynamic rheometry. Kalyon[3], *et al.* have reported the rheological behaviour of solid propellant stimulant using torsional and capillary rheometry. Further, Muthiah[1], *et al.* have developed generalised correlations for various rheological parameters of HTPB based propellant system as a function of volume fraction of solids, cure time and temperature based on steady shear experiments. Kohga and Hagihara[5] have studied the viscosity of AP/HTPB based composite propellant with concentration of AP at upper limit applicable in propellant. The studies have also been reported on modelling of viscosity of propellant composition based on morphology of particle. Erisken[6], *et al.* have developed a model based on Furnas's theory for obtaining

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composition of particulates leading to maximum packing density with minimum viscosity for a given solid loading. However, the above mentioned studies of composite propellant suspensions have been largely limited to steady shear rheology rather than oscillatory shear.

Further, at higher shear stress, it has been reported by many investigators that concentrated suspensions shows shear thickening behaviour beyond a critical shear rate, the reason being ordered to disordered transition of layers of suspensions[7], formation of hydroclusters[8] and dilatancy[9]. Early observations on shear thickening phenomena include Hoffman's extensive experiments using monodispersed polyvinylchloride dispersions in dioctylphthalate with the help of light scattering wherein he showed that a sudden jump in viscosity occurs at a critical shear rate, when the transition from ordered to disordered state takes place. According to Barnes[10] , all concentrated suspensions of solid particles exhibit shear thickening, if measured in the appropriate shear rate range and stated that the actual nature of shear thickening depends on the parameters of the suspended phase, viz., phase volume, particle size, size distribution, particle shape, as well as those of the suspending phase. It has also been found that particle size and volume fraction of dispersed solids affect the critical shear rate corresponding to onset of shear thickening. Yilmazer and Kalyon[11] have shown dilatancy in concentrated suspension of ammonium sulphate in Newtonian matrix using torsional rheometry with results corrected for apparent slip. The computer simulations performed on concentrated dispersions surveyed by Boersma[12], *et al.* have shown this type of transition. Berezov[13], *et al*. have concluded that changes in the balance between hydrodynamic and interparticle forces are responsible for shear thickening properties of the plastisols. Lee and Wagner[14] have reported dynamic properties of shear thickening colloidal suspensions of 40 wt % colloidal silica dispersion whereas Chang[15], *et al.* have studied shear thickening mechanism of 58 vol.% colloidal dispersion of styrene/acrylate particle in ethylene glycol using transient and steady rheometry. Xu[16], *et. al.* have studied the shear thickening in highly viscous granular suspensions using oscillatory shear and attributed the shear thickening to the dilation of suspension against the confining interface. They have also concluded that shear thickening stops when maximum confining stresses from surface tension have reached.

The exhaustive literature survey reveals that a very scanty information is available on study of shear thickening transition of composite propellant suspensions by dynamic oscillatory test using rheometer. Therefore, a systematic study has been carried out on four different propellant compositions based on HTPB binder system loaded with different fractions and particle size of AP under oscillatory shear.

2. EXPERIMENTAL

2.1 Materials

Ammonium perchlorate (AP) of size 300 μm was procured from Pandian Chemicals Ltd, Cuddalore, India, and fine fractions were obtained by grinding coarser particles. HTPB, manufactured by free radical solution polymerisation and has molecular weight (Mn) of 2300-2900 with hydroxyl value of 43 mg KOH/g, was procured from Anabond Pvt Ltd Chennai. Aluminium powder (Al), having average particle size of 15 μm, procured from Metal Powder Company, Madurai, was used as such. Dioctyl adipate (DOA) and toluene diisocyanate (TDI) were procured from trade and used without further modifications. The slurry obtained from these mixed ingredients was used for amplitude sweep test using rheometer.

2.2 Procedure

All the experimental mixing of composite propellant was carried out at 5 kg batch level in a vertical planetary mixer. A general method for the preparation of propellant composition is described as follows. A mixture of binder which includes prepolymer resin HTPB, plasticiser DOA and other minor ingredients were mixed in a vertical planetary mixer. The ingredient addition sequence followed for mixing was first liquid binder ingredients, aluminum powder followed by AP of 6 μm, 50 μm and 300 μm. The overall mixing temperature was maintained at 40± 2 °C. After addition of all solid ingredients, the mixing of the composition was further carried out under vacuum. Finally, TDI was added and mixed further for another 30 minutes. After completion of final mixing, the propellant suspension samples were used for rheological testing.

2.3 Characterisation

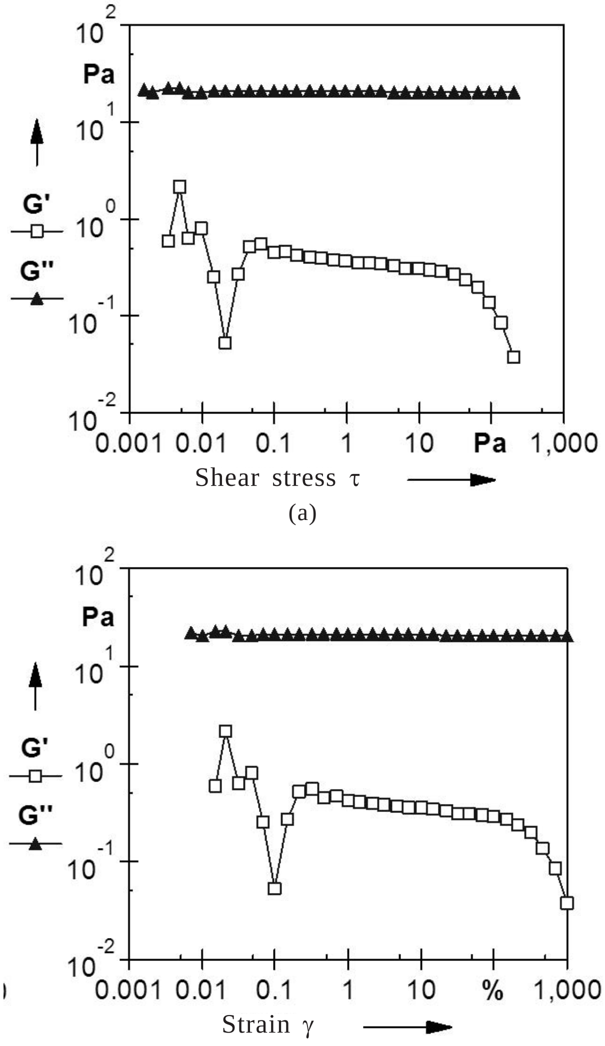
The amplitude sweep tests were performed on rheometer (MCR 101 Anton Parr make) with parallel plate geometry with 50 mm plate diameter (PP50), bottom plate of which was fixed and the other one was free to move. The maximum stress generated by PP50 plate was 5000 Pa. The plate surface was serrated to negate the slip effects. All the tests were carried out at 40 °C. Peltier system of rheometer was used for maintaining the temperature conditions for the samples. Around 10g -15g of propellant suspension sample was taken on the parallel plate attachment and tests were carried out with 2 mm gap between the plates. A preshear is applied to the sample before starting the test to minimise the effects of sample loading. Fresh samples were used for each test. The normal force was allowed to die down to zero. For each sample, the amplitude of the strain was varied from 0.001 to 1000% at 1 Hz and results were analysed.

3. RESULTS AND DISCUSSION

Initially, only HTPB, which is used as a binder, was studied under amplitude sweep test using rheometer as reference sample and results obtained are presented in Fig. 1. Later on, the behaviour of propellant slurry which was obtained by mixing AP and Al in HTPB, with compositions A to D as shown in Table 1 were studied by amplitude sweep test on rheometer and the findings are presented in Figs. 2 - 4.

3.1 Behaviour of HTPB under Amplitude Sweep Test

Prior to the study of propellant suspension, the behaviour of HTPB, which is a major binder ingredient was studied under the strain sweep from 0.001 to 1000%, as it is known to affect the rheological behaviour of propellant suspension and mechanical properties of cured propellant. The curves of G′ and G″ were plotted against the value of strain varying



(a)

(b)

Figure 1. Behaviour of HTPB under amplitude sweep test (a) Dynamic moduli (G′and G″) versus strain, (b) Dynamic moduli (G′ and G″) versus shear stress.

Table 1. Details of propellant compositions

Composition (wt%)	A	B	C	D
Binder*	14	15	15.5	20
Al	18	18	18	2.5
AP, 300 μm	52.5	23	20	6.5
AP, 50 μm	15.5	24	20	0
AP, 6 μm	0	20	26.5	71
Volume fraction of solids, %	73.3	71.7	70.9	65.3
Burning rate at 7 MPa, mm/s	5	13	19	25

*Binder comprises HTPB, DOA, TDI and other minor ingredients.

from 0.001 per cent to 1000 per cent at 1 Hz frequency and presented in Fig. 1. It is clear from Fig. 1 (a) and (b) that a straight line is obtained for G″(loss modulus) values while G′ (storage modulus) values show a plateau region till 100 per cent, which is considered to be the linear-viscoelastic range for HTPB. Thus, the unfilled system of HTPB shows linear visco-elastic behaviour upto 100 per cent strains and 100 Pa stress.

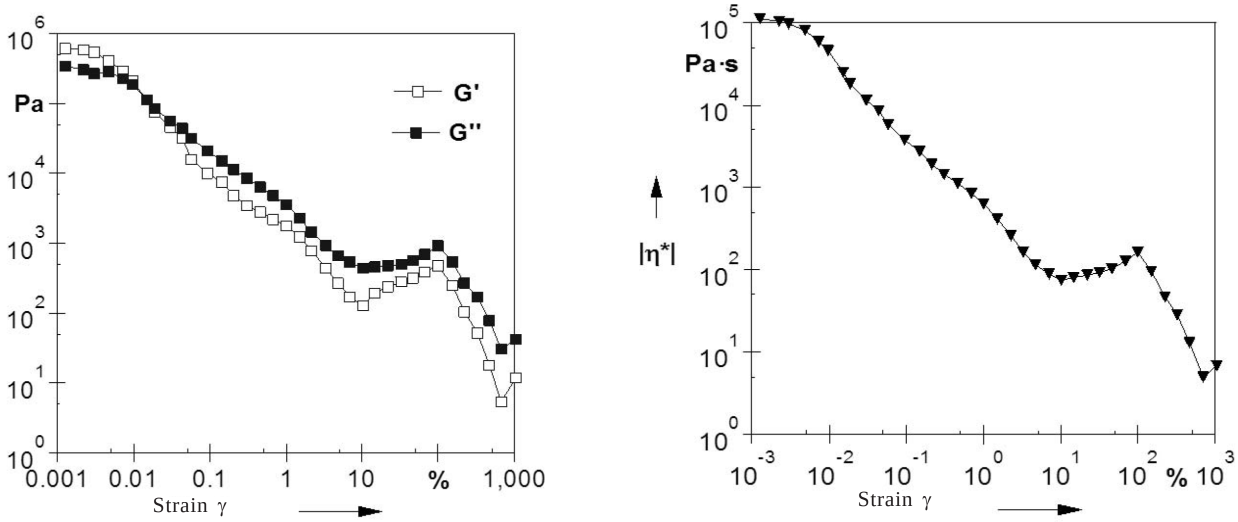
3.2 Behaviour of Propellant Slurry (HTPB Filled With AP and Al) under Amplitude Sweep Test

During the amplitude sweep, a periodic sinusoidal strain is imposed on the samples and response is measured in terms of the complex modulus given by $G^{*}= G' + iG''$. The real part of the complex modulus (G′) represents storage modulus whereas the imaginary part (G″) represents the loss modulus. The storage modulus signifies the energy stored as potential energy during deformation whereas, the loss modulus signifies the energy dissipated as heat. The complex viscosity is the frequency dependant viscosity function given by $\eta^{*} = G^{*}/\omega$. The amplitude sweep tests were performed on propellant compositions A to D as listed in Table 1. The strain amplitude was varied from 0.001 per cent to 1000 per cent at frequency (ω) of 1 Hz. The response of propellant compositions was plotted in terms of dynamic moduli G′ and G″ against strain (γ). For low strains, both G′(γ) and G″(γ) curve for all the compositions display constant plateau values. The range of strains with plateau values of dynamic moduli is the linear viscoelastic limit for the propellant suspensions. The amplitude sweep test for all the compositions indicates the linear viscoelastic limit upto 0.01% strain. The very low and almost same limit for all the propellant compositions is due to very high volumetric loading of solid which is close to maximum packing fraction. At higher strain amplitude, the non liner effects become significant and the stress response deviated from a sinusoidal curve. However, for the present study, it is assumed that the contributions of higher harmonics are less than 15 per cent to the measured response[17,18].

Further, the results were also plotted as complex viscosity (η*) versus strain. The curve represented in Fig. 2(a) for composition A, indicates that the plateau values of G′ and G″ start decreasing after 0.01 per cent of strain, and further deepening down till 10 per cent strain. Beyond 10 per cent strain, both G′ and G″ begin to increase till 100 per cent strain. Similarly, the complex viscosity versus strain curve in Fig. 2(b) shows first a decreasing trend for complex viscosity followed by a sudden increase in viscosity after 10% strain.

This behaviour of an order of magnitude rise in complex viscosity beyond 10 per cent strain (γ_c) is attributed to the shear thickening of the compositions at critical strain levels. The shear thickening behaviour was further found to be reversible, i.e., the response of amplitude test with strain sweep in forward (0.001 -1000%) was the same as in strain sweep reverse direction (1000-0.001%) as shown in Fig. 3. It infers that the propellant suspension under study is found to exhibit a reversible shear thickening behaviour. The shear thickening is attributed to the formation of hydroclusters[8] which is well studied for many colloidal systems. During hydroclusters formation, particles are brought close to each other due to hydrodynamic forces. These clusters due to near contact between particles increase the resistance to shear resulting in shear thickening behaviour.

The similar trends were also observed for propellant compositions B, C and D with clear indication of initial shear thinning followed by increase in complex viscosity with higher strains. Figure 4(a) and 4(b), shows the results for the compositions B to D in terms of dynamic moduli against strain and complex viscosity against strain. Further, all



(a) (b)

Figure 2. Strain amplitude sweep test response for composition A (a) Dynamic Modulli (G′ and G″) vs Strain; (b) Complex viscosity *vs* strain.

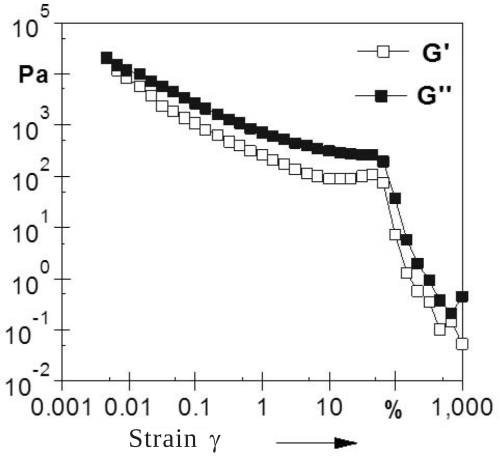
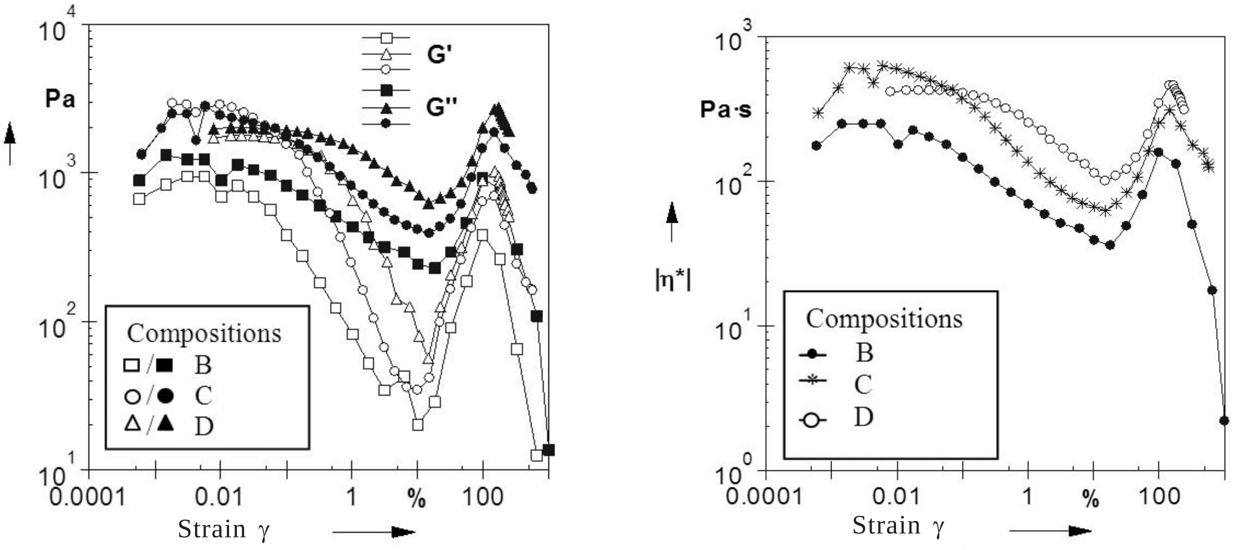


Figure 3. Strain amplitude sweep test response in reverse direction (from 1000% strain to 0.001%) for composition A.

the compositions also show a strain limit γ_m with maximum complex viscosity which is upper limit of shear thickening. After the maximum strain limit, the propellant slurry again shows apparent shear thinning behaviour. The apparent shear thinning was due to visible slippage of sample at very high strains. Under wall slip conditions, the strains measured by the rheometer are apparent strains and it is found that true strain and shear rates are lower than the apparent strain and shear rates. The difference between true and apparent values depends upon the slip velocities. The slip velocities increase with increasing shear stress[4]. Thus, at higher shear stress, the actual strains are lower than the measured apparent strains. These apparent strain values beyond γ_m results in lower values of complex viscosities and exhibits apparent shear thinning behaviour[11]. However, below γ_m, the apparent slip effects were insignificant. This was confirmed by carrying out oscillatory strain sweep with multiple gap height of parallel plate fixture.



(a) (b)

Figure 4. Strain amplitude sweep test response for compositions B, C and D (a) dynamic Moduli (G′and G″) *vs* strain; (b) Complex viscosity *vs* strain.

By varying gap heights, the response was unchanged which indicate absence of apparent slip effects.

3.3 Effect of Reduced Packing Fraction and Particle Size on Shear Thickening

Shear thickening in concentrated suspensions is reported to be dependant of particle size, size distribution and volume fraction of solids[10]. The combined effect of these parameters is expressed in terms of reduced packing fraction which is a ratio of volume fraction of solids to the maximum packing fraction[11]. Hence maximum packing fraction for all the four propellant compositions was determined experimentally. The maximum packing fraction was determined by preparing the suspensions with varying volume fractions of solid and measuring the viscosity of resulting suspensions. The inverse of suspension viscosity was plotted against volume fraction of solids. The x- intercept of the curve was obtained by interpolation, which gives the maximum packing fraction of solids.

The various parameters related to shear thickening regime such as strain at onset of shear thickening and strain and shear stress at which maximum viscosity attained are compared for the propellant compositions A to D. These parameters along with reduced packing fraction and mass mean particle size of AP are given in Table 2.

Table 2. Comparison of shear thickening regimes for different compositions

Characteristics/Composition	A	B	C	D
γ_c	10	10.4	10.2	14
Maximum Packing fraction, ϕ_m	79.6	77.5	76.6	69.4
Reduced packing fraction, ϕ/ϕ_m	0.92	0.928	0.93	0.94
Mass mean diameter of AP, μm	234	122.6	107.6	30.6

The strain at the onset of shear thickening is lowest for composition A and highest for composition D. As stated earlier, the shear thickening phenomenon is attributed to the formation of clusters due to hydrodynamic forces. The hydrodynamic forces increase with particle size, thus, resulting in higher hydrodynamic forces for larger particles[8]. In composition A, the hydrodynamic forces seem to dominate at lower strain levels due to higher mass mean particles. Similarly, composition D with lowest mean particle size shows highest strain required for onset of shear thickening and cluster formation. Further, the dependency of onset strain on maximum packing fraction is also noted. Composition D is having highest reduced packing fraction was found to show highest onset strain.

3.4 Effect of Frequency on Critical Strain

The amplitude sweep tests were also carried out at different frequencies 0.1, 0.5, 1 and 10 Hz. The critical strain was found to be unchanged with increasing frequency. This could be the low frequency regime[14] where critical strain is not affected by frequency. The high frequency regime where strain is inversely proportional to frequency could not be found. The high frequency testing could not be done as sample integrity during test was not ensured at higher frequencies due to significant inertia and slippage of materials.

3.5 Implications of Shear Thickening in Propellant Processing

Shear thickening in concentrated suspension is known to serious ramifications in many industrial processes. The shear thickening is closely related to jamming where particle clustering takes place. The shear thickening causes increased flow resistance and pressure drop in pressure driven flows of propellant such as in extrusion or pressure casting. The increased mixer loads during mixing of propellant suspension may be encountered[8]. Further, the jamming of particles associated with shear thickening can cause filtration of binder especially during flow through narrow geometries encountered during extrusion resulting in aggregation of particles posing increased safety hazards. Thus, the shear thickening characterisation is essential for optimising the process parameters and propellant compositions.

4. CONCLUSION

The amplitude sweep test of different propellant slurries has been carried out successfully. The data reveal that these propellant compositions exhibit a distinct shear thickening behaviour at critical strain. The shear thickening behaviour may be attributed to the formation of hydroclusters. The onset strains of shear thickening are found to be higher for compositions with low mass mean particle diameter and higher reduced packing fraction of solids. Further, all the compositions show an apparent second shear thinning behaviour beyond γ_m. This shear thinning behaviour may be due to apparent slip of the suspension during measurement. Also, the shear thickening is found to be reversible and independent of strain cycling. The findings of this study may be useful for optimising propellant processing conditions.

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In the current study, he has contributed in the conceiving of idea and implementation.