INTRODUCTION

Hyperbranched polymers (HBPs) can be produced readily on an industrial scale a wide variety of raw materials, which means they are eco-friendly. Hyperbranched polymers are three dimensional structure. They have been studied widely over 20 years for their unusual properties such as low viscosity, high density of functional terminal groups, high solubility, good compatibility with other materials [1-7]. The reaction of HBPE led to various view for the upliftment of this materials in coating industries [8,9]. Hyperbranched polyester could be synthesized by easily affordable and low cost basic materials has impelled several research groups to study HBPEs in detail. Huge number of end groups offers different crosslinking method. The approximate circular structure of HBPEs makes the viscosity level low and high of molecular weight is high [10-13]. Hyperbranched polyester have attractive rheological properties and can be used in a wide variety of applications as biocides, additives, rheology modifiers, etc. [14-16]. Several HBPE with the help acrylate of methacrylate end groups have demonstrated in recent years [17-19]. The individual properties of HBPE allow extremely efficient for UV and EB curing applications, if they contain any one of the end groups (acrylate or, at least methacrylate end groups).

Now-a-days, silver nanoparticles are playing a major role in the field of nanotechnology and nanomedicine. The use of nano-sized silver particles as antibacterial agents has develop into further common as scientifically advances compose their production more inexpensive [20-22]. Nowdays, silver ions (Ag+) are used to avoid bacterial growth in a multiplicity of therapeutic applications, such as, catheters, dental work and the curing of burn wounds [23-25]. Silver cations show broad antibacterial action at very low concentrations and are previously being used for the remedial action of traumatic injuries and burn wounds. Silver ions also exhibit low levels of toxicity to humans being and are protected agents for the deduction of biofilms. Bactericidal actions of nanoparticles is accredited to the occurrence of electronic effects to are brought concerning as a result of changes in restricted electronic structures of the surfaces owing to smaller sizes. These property are measured to be contributing near development of reactivity of silver nanoparticles surfaces. The opposed charges of nanoparticles and bacteria are accredited to their union and bioactivity due to electrostatic forces. It is rational to state that compulsory of nanoparticles to the bacteria depends on the surface area accessible for communication.

Berzelius [26] reported the method of preparation of HBP resin using tartaric acid as an A,B; monomer and glycerol as a...
B-monomer not done elsewhere. In the present study, the same method of (A₂B₂ + B₃) preparative approach is followed for the synthesis of HBPE using tartaric acid as an A₂B₂ monomer and 2,2',2''-nitrilotriethanol as an B₃ monomer. The HBPE produced was highly soluble in water paves the way for its usage widely in the field of coating technology. The resulting products in the present work were analyzed using FTIR, ¹H NMR, ¹³C NMR and GPC. The molecular weight and solubility of HBPE was explained in detail. Silver nanoparticles prepared in HBPE matrix through reductive technique. The nanosilver/HBPE were analyzed by XRD, UV-visible and TEM. The anti-microbial properties of nanosilver/HBPE were evaluated against S. aureus and E. coli.

**EXPERIMENTAL**

Tri ethanol amine (>99 %) and 2,3-dihydroxy butanedioic acid had been purchased by the Sigma Aldrich. Dimethyl sulfoxide, acrylic acid and NaBH₄ was procured from SD Fine Chemicals. Silver nitrate (Merck, India) were used as received. p-Toluene sulfonic acid (p-TSA, >99 %) was purchased by Rankam Chemicals. Nutrient agar and nutrient broth was from Difco Laboratories, Detroit, 82 MI, USA. Water were purified by applying the Milli-Q system (>18 MΩ cm, Millipore).

**Characterization:** FTIR spectra of macropolester (HBPE) was taken in to account for a wave range of 4000-450 cm⁻¹ by applying JASCO 400 infrared spectrometer. ¹³C NMR and ¹H

![Scheme-I](image-url)  

**Scheme-I:** Synthesis of HBPE from 2,3-dihydroxybutanedioic acid and 2,2',2''-nitrilotriethanol
NMR spectra of HBPE were stored on a Bruker (400MHz)
NMR spectrometer was taken as a sample at room temperature
using DMSO as the solvent and trimethylsilane (TMS) as the
internal standard. Molecular weight of HBPE was analyzed
using GPC to make, Water-515 were analyzed with polyethylene
as standards. Tetrahydrofuran (THF) were taken as the
eluent and the rate of flow was kept at 1 mL/min. Thermogravimetric analysis of polymer were conducted in a tempera-
ture interval of 30-300 °C under nitrogen atmosphere with
a flow rate of 10 mL/min using a Perkin Elemer thermog-
gravimetric analyzer, Pyrisi TGA. The spectrum of nanosilver
was obtained in ethanol medium applying UV visible spectro-
scope of HITACHI U-2800 spectrophotometer. The TEM
analyses were carried out using JEOLJEM 2100 electron micro-
scope at 80KV. The resulting samples were analyzed for the
purity of the phase purity by powder XRD of make BRUKER
(Germany, D8 Advance diffract meter).

**Viscosity measurement:** The viscosity of HBPE had been
studied by using an Ostwald viscometer. Hyperbranched
polyester of various concentrations were synthesized by the
dilution of the samples. The capillary viscometer were packed
with 20 mL of sample and were equilibrated in a water bath
for 10 min at 30 ± 0.1 °C. The end samples were allowed to
pour throughout the capillary and the flow times were noted
and to analyze reduced viscosity. Three values were made for
every sample.

**Synthesis of HBPE:** Hyperbranched polyester was prepared
by melt polycondensation at 95 °C of tri ethanol amine
and 2,3-dihydroxybutanedioic acid and p-toluene sulfonic acid
(0.017 g) as an acid catalyst. The 1:1 ratio of the substance
were taken in 500 mL, four necked flask monomers equipped
with N2 inlet, using an a magnetic stirrer and a drying tube for
7 h. The reactant mixture were slowly heated and then main-
tained at 95 °C for 7 h to end the reaction. The schematic illus-
tration of the reactions is specified in **Scheme-I.**

**Hyperbranched polyester with acrylic acid**

**Modification of HBPE:** 5 g of HBPE was dissolved in
10 mL of water. It was reacted with acrylic acid in a three
necked round flask which was equipped with a magnetic stirrer
and a nitrogen gas inlet by applying p-toluene sulfonic acid
(0.017 g) as a catalyst. The reactions were carried out for 5 h
at 85 °C. The reaction is given in **Scheme-II.**

\[
\text{HBPE-OH} + \text{CH}_2 = \text{CH-COOH} \xrightarrow{85 \, ^\circ \text{C}} \text{CH}_2=\text{CH-COO-HBPE}
\]

**Scheme-II:** Synthesis of acrylic modified hyperbranched polyester

**Preparation of silver nanoparticles:** 1 g of acrylic modified
hyperbranched polyester (AHBPE) with 4 mL water had
been taken in a round bottom flask with regular stirring. 2 mL
solution of 0.1 g of AgNO3 in water was added drop-wise by
using vigorous stirring with room temperature. After comple-
tion of the addition, the reaction mixture was stirred for another
20 min. Then 0.1 g of aqueous solution of NaBH4 was added
drop-wise in to mixture The colour of resultant solution of the
polymer turned to deep brown (**Scheme-III).**

**Preparation of culture media:** The media of culture were
prepared by dissolving broth powder (1.3 g) in 100 mL water.
It were sterilized at 15 lbs pressure by autoclaving at 121 °C

**Scheme-III:** Synthesis of silver nanoparticles with in HBPE templates
for 15 min. it were cooled in a laminar hood, which were steri-
lized before hand by washing thoroughly with absolute alcohol
and followed by UV irradiation for 20 min. A sterilized wire
loop size stock microorganism were transferred in to the cold
medium below laminar flow and the conical flask were replu-
gged and the solution kept in an incubator oven at 37 °C for
24 h.

Antimicrobial activity: The nutrient agar powder (3.7 g)
was dissolved in 100 mL water. The solution were sterilized
and keep in to petridishes and cooled for adequate time to
coagulate the agar medium. The above culture broth (2 mL)
was equally spread in to entity plates applying sterile L-rod.
The 5 mm diameter of well were prepared on agar plates applying
sterilized crock borer. Different samples of Three kinds
such as silver nitrate/HBPE, nanosilver/HBPE and pure HBPE
were taken for analysis. Silver nitrate/HBPE was formed as
said in the process of nanosilver. Nanosilver/HBPE is used
for analysis by reducing the solution. The polyester is dissolved
in DMSO. Applying sterile micropipette, the solutions of
samples was poured on to every wells in all the plates. The
plates were observed for incubation for 24 h at 37 °C.

RESULTS AND DISCUSSION

The results were obtained by reacting 2,2',2"-nitrilotri-
ethanol and 2,3-dihydroxybutanediic acid via A2B2 + B3
method. Triethanolamine has a low vapour pressure and
correspondingly low odour, but evaporation of triethanolamine
from coatings is extremely slow. Tartaric acid is used in the
tanning of leather. The reaction was maintained at moderately
minimum temperature of 150 °C, with an time reaction which
is optimized to minimize unless side reactions and to overcome
gelation.

The molecular weights of HBPEs have been determined
using GPC using THF as solvent. The value of number average
molecular weight (Mn), the weight average molecular weight
and polydispersity index of HBPE are 950 g/mol, 969 g/mol
and 1.016, respectively (Fig. 1). The intrinsic viscosity of HBPE
was found to be 1.52 dL/g. The hydroxy values were found to
be 64. The HBPE prepared was found to be water soluble and
were soluble in polar solvents. Results of the elemental analysis
for HBPE are shown in Table-1.

FTIR studies: The FTIR spectra of monomers and HBPE
are shown in Fig. 2. The FTIR spectrum of triethanol amine
shows an absorption band of 3342 cm–1 due to hydroxy group
and sharp peak at 2881 cm–1 due to CH2 stretching. The peak
at 1040 cm–1 is found to C-N stretching. The FTIR spectrum
of chain extender (2,3-dihydroxybutanediic acid shows an
absorptions band of 3343 cm–1 due to the hydroxyl groups
and the peak at 1724 cm–1 due to the C=O group. The absorp-
tion peak of FTIR spectrum at 3425 cm –1 is assigned to –OH
stretch vibration and the peaks at 1723 and 1165 cm–1 are attri-
buted to the ester and C-O-R groups. These data indicate that

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<th>TABLE-1</th>
<th>ELEMENTAL ANALYSIS OF HBPE</th>
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<tr>
<td>Polymer</td>
<td>Theoretical value (%)</td>
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<tr>
<td></td>
<td>C</td>
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<tr>
<td>HBPE</td>
<td>4607</td>
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the polymers contain hydroxy groups, ester bonds, carboxylic
OH and benzene groups, which were in agreement with objective
polymers. The peak strength of hydroxyl groups decreased in
the case of acrylic modified HBPE. A peak at 1647 cm–1 related
to C=C bond presence of the introduction of acrylic group
into HBPE.

NMR studies: The structures of synthesized polymers were
identified by 1H NMR and 13C NMR spectroscopic techniques.
The 1H NMR spectra of HBPE are given in Fig. 3. The signals
and their integral areas appear around 2.2-3.4 can be attributed
to methylene proton and the peak at 2.5 ppm is due to the
solvent DMSO-d6. The signals appearing around 5.5 can be
attributed to the hydroxyl proton of the 2,3-dihydroxy butane-
dioic acid and The peak in between 4.2-4.34 ppm is taken in
account of the methylene protons attached to the ester units.
The 13C NMR spectra of HBPE is shown in Fig. 4. The peaks
at 160-172 ppm could be attributed to the carbonyl carbon of
ester and 55-60 ppm is regarding to methylene carbon of ester.
units. The numbering of atoms and the assignments of the NMR signals from different units (D, L and T) of HBPE were done according to the reported method [27]. The $^{13}$C NMR spectra of HBPE (Fig. 4) showed that the resonances from the carbons in the D, L and T units had different shifts due to the difference in their chemical environments. The percentage of T, L and D units present in HBPEs, are calculated from the integral area ratios of methylene and quaternary carbon zone of $^{13}$C NMR spectra and the value was found to be 0.5.

**Characterization of acrylic modified HBPE:** The FTIR spectra of acrylic modified HBPE is shown in Fig. 5. The band width of hydroxyl groups lowered in the case of acrylic modified HBPE indicating that the coupling reaction has proceeded. A band at 1641 cm$^{-1}$ analogous to C=C bond implies the preamble of acrylic group into HBPE. The $^1$H NMR spectra of HBPE is given in Fig. 6. $^1$H NMR (400 MHz, DMSO-$d_6$, $\delta$ (ppm): 5.5 (OH proton); 3.7- 4.1 (CH$_2$OCO). The hydroxyl peak has sharply decreased after reaction of acrylic acid indicating the removal of OH group (Fig. 6). $^{13}$C NMR spectrum of HBPE are shown in Fig. 7. $^{13}$C NMR [170-172 (-CH; COO-); 57-59 ppm (CH$_2$-OH)] showed that the hydroxy peak intensity has been reduced after adding acrylic acid (Fig. 7).

**Characterization of silvernano/HBPE:** The characteristic absorbance peak of this composite is determined with UV-visible spectrum. The UV-visible absorbance spectra of the nanoparticles is presented in Fig. 8. The final product formed are uniform in dimension and diffusion at the used ratio in present study is supported by UV-visible and TEM studies. Hence some of the challenging issues of nanoparticles formation were achieved to certain extent through this technique. The reducing agent were used to ensure absolute reduction of
Ag⁺ to Ag⁰, which is confirmed by the change reaction solution to brown and subsequent characterization of silver nanoparticles by different spectroscopic techniques. X-ray diffraction (XRD) is a very important method to characterize the structure of crystalline material. XRD pattern of silver nanoparticles is shown in Fig. 9. Here, four peaks can be seen at \(2\theta = 38.4, 44.1, 64.3\) and 77.4, which are characteristic diffraction peak of metallic silver. These peaks correspond to the four d-spacing (111), (200), (220) and (311), respectively. All diffraction peaks mentioned to the characteristic FCC silver lines [28].

From Debye-Scherrer equation, the average size of silver nanoparticle synthesized was found to be 14.7 nm. To confirm the composition of silver nanoparticles, FTIR spectra of HBPE and silver nanoparticles encapsulated with HBPE were measured. Fig. 10 shows the FTIR spectra for HBPE and silvernano/HBPE. The analysis showed that the spectral features of pure HBPE and silvernano/HBPE samples are not so different. Some differences are observed only in the intensity of their peaks. The absorption peak of C=O stretching frequency of the carboxylic ester groups of the polyester observed at 1720 cm⁻¹ shifts to 1698 cm⁻¹, which suggests that silver nanoparticles are protected by HBPE through the interaction between Ag and carbonyl group of HBPE [29].

A TEM image of the prepared silver nanoparticles is shown in Fig. 11. The silver nanoparticles are spherical in shape with a smooth surface morphology. The diameter of the nanoparticles is found to be approximately 16 nm. TEM image also shows that the produced nanoparticles are more or less uniform in size and shape. The silver nanoparticles are circular in shape with a soft surface morphology. The nanoparticle diameter is found to be approximately 15.4 nm. TEM pattern also shows that the formed nanoparticles are huge or less uniform in shape and size.

The thermogram of pure HBPE and nano-silver/HBPE is shown in Fig. 12. Evidently, the decomposition onset for nanosilver/HBPE is shifted to the higher temperature compared to the pure HBPE. The onset degradation temperature of HBPE is around 98.7 °C meanwhile it is 99.5 °C higher for nanosilver/HBPE. The overall thermal stability of HBPE is enhanced with nanosilver incorporation. The thermal properties of the systems were found to be almost similar at lower temperatures. However, the thermal stability of nanosilver/HBPE is found to be very
high at higher temperature compared to pure HBPE. This may be due to the nucleating effect of nanosilver. The silver nanoparticles in HBPE matrix act as the hardening (virtual cross linking) point in HBPE and thereby helping the soft segments to arrange in a regular pattern and thus improves the crystalline behaviour [30]. Therefore, by incorporating the silver nanoparticles within polymer, the thermal stability of the nanosilver/HBPE can be enhanced.

**Antimicrobial activity:** The antibacterial efficiency of the silvernano/HBPE against microbes was analyzed on zone of inhibition tests. After 24 h of incubation, the zone of inhibition of the silvernano/HBPE against Gram-negative and Gram-positive bacteria were found to be much superior than the zone of inhibition of AgNO3/HBPE.

**Conclusion**

Hyperbranched polyester (HBPE) was prepared in this work via A, B2 + B3 method as an acid-catalyzed esterification process by melt polycondensation from the 2,2',2''-nitro- triethanol and 2,3-dihydroxybutanedioic acid. The different generation of the samples was obtained by varying the molar monomer/core ratio. The final products are combined with acrylic acid to changing the end groups. In this article, stable silver nanoparticles, protected by HBPE, were synthesized in water by NaBH4 reducing agent. It can be concluded that HBPE is as a result of a template like dendrimers. From UV-visible spectrum and TEM micrographs of the silver nanoparticles, it can be found that the nanoparticles formed were spherical in structure. FTIR spectra analyzed that there was interaction between silver nanoparticles and HBPE played a crucial role on the stability of silver nanoparticles. Antimicrobial properties of silver nanoparticles are accredited to their whole surface area, as an enlarge surface to volume ratio of nanoparticles which provides much effect to the better antibacterial activity.

**REFERENCES**