International Journal of
Nanotechnology

International Journal of Nanotechnology

ISSN online: 1741-8151 - ISSN print: 1475-7435
https://www.inderscience.com/ijnt

Research progress of adoption of hyperbranched polymer nano materials in textile industry

Ruihang Huang, Xiaoming Yang, Wen Zhang

DOI: 10.1504/IJNT.2023.10056478

Article History:

Received:	05 August 2021
Last revised:	18 February 2022
Accepted:	02 March 2022
Published online:	31 May 2023

Research progress of adoption of hyperbranched polymer nano materials in textile industry

Ruihang Huang, Xiaoming Yang*
and Wen Zhang

College of Humanities,
Donghua University,
Songjiang, Shanghai, 201620, China
ORCID: 0000-0001-9042-1762
Email: 1209125@mail.dhu.edu.cn
Email: 1037234058@qq.com
Email: zw18302168165@163.com
*Corresponding author

Abstract: Hyperbranched polymers have broad adoption prospects in coatings industry, rheological modifier, nano technology and the nearly spherical three-dimensional structure, many internal cavities, low viscosity, and high reactivity. From the perspective of the textile industry, the fabric dying and fabric antibacterial of hyperbranched polymer nano materials are studied, as well as its adoption as fibre leather fatliquoring agent in the process of leather fatliquoring, to review the adoption of hyperbranched polymer in textile industry. The adoption of polymer in textile industry, massive documents has been referred for analysis. From the perspective of dying, hyperbranched polymer can be applied to polypropylene dyeing, salt-free dyeing, dispersant-compound dyeing, and anti-staining through modification and polymerisation. Nano-Ag is modified by hyperbranched polymer to obtain the colloidal solution, after which the silk undergoes antibacterial treatment, and the finished fabrics all show strong antibacterial properties. Nano-Ag treatment of silk by steaming method can achieve better antibacterial properties. The polyamide-type hyperbranched polymer go through hydroxyl activation, and the linear-hyperbranched polymer is obtained by acylation reaction, which can be further modified by esterification reaction and compounding methods. After it is adopted in leather fatliquoring, the collagen fibres of the leather are filled, thereby increasing the softness and thickening rate of the leather.

Keywords: hyperbranched polymer; textile industry; dyeing; antibacterial property; leather fatliquoring.

Reference to this paper should be made as follows: Huang, R., Yang, X. and Zhang, W. (2023) ‘Research progress of adoption of hyperbranched polymer nano materials in textile industry’, *Int. J. Nanotechnol.*, Vol. 20, Nos. 1/2/3/4, pp.303–322.

Biographical notes: Ruihang Huang is a Doctoral student at Donghua University. His research direction is the scientific and technological development of textile nano materials.

Xiaoming Yang is a Doctoral supervisor and Professor of Donghua University, Shanghai, China. Textile technology is the research direction of textile science.

Wen Zhang is a Doctoral student at Donghua University, Shanghai, China. His research direction is the scientific and technological development of textile nanomaterials.

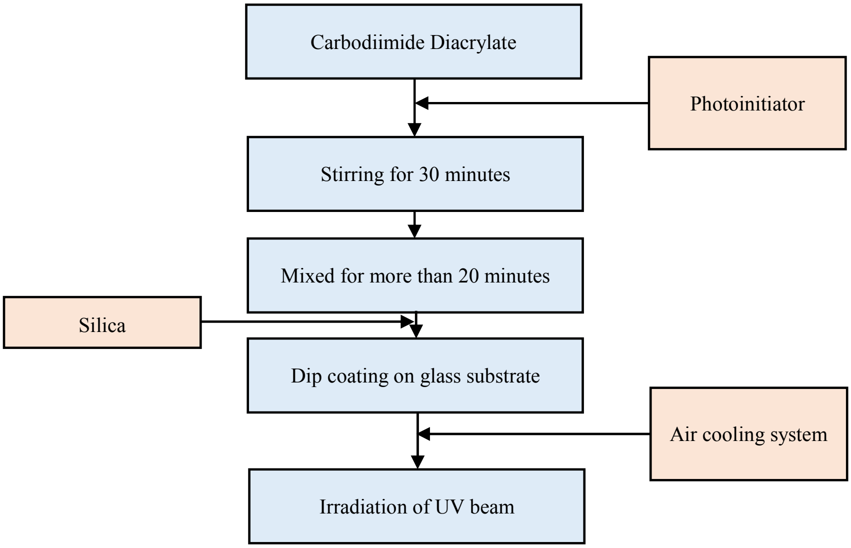
1 Introduction

Hyperbranched polymer is a kind of polymer with a highly branched three-dimensional structure, which is different from traditional linear polymers, and is a kind of dendrimer. Hyperbranched polymers and dendrimers are both called dendritic polymer and their structures and properties are similar [1, 2]. Dendritic macromolecules gradually and repeatedly react through the multifunctional monomer AB_n (branching unit, where $n \geq 2$) to obtain macromolecules with a dendritic highly branched structure. The molecular structure includes a multi-arm trigger core, an inner body composed of repeating units, and multiple functional groups wound on the outer surface layer [3, 4]. The structure of dendrimers is regular with high symmetry. In addition, the volume of the dendrimer, the types of functional groups, and the number of functional groups are all controllable. The molecular weight distribution is relatively dispersed and the surface functional groups present a higher density.

The spherical super-macromolecules are tight on the outside and loose on the inside. Although there are branched structures, they are relatively regular. Therefore, there are obvious differences in performance from linear polymers, the molecular chains are not entangled too tightly, the viscosity of solutions and molecules configured based on dendrimers is lower and the activity of dendrimers is higher [5]. The reaction of dendrimers requires protective measures, separation and purification steps, the process is more complicated [6]. To complete the reaction, it is necessary to purchase a lot of auxiliary facilities, so the cost is high, which is not conducive to mass production. From the adoption level, there is no need for a spherical structure to be between similar dendritic macromolecular structures. When it is utilised as a functional reagent, many terminal functional groups are required, so hyperbranched polymers with similar structures have attracted the attention of many researchers in this field [7, 8]. The synthesis process of hyperbranched polymer is relatively simple relative to dendrimers. Most of the synthesis steps do not require separation and purification. The internal molecules of the polymer are ellipsoidal, and the degree of branching is much lower than that of standard dendrimers [9]. However, it maintains performance characteristics similar to those of dendrimers, and thus has many unique properties, including good fluidity, low viscosity, and film-forming properties. The flowchart for synthesis and preparation of hyperbranched polymer is shown in Figure 1.

Due to its unique structure and performance, hyperbranched polymer shows attractive adoption prospects in the textile field. Giving that the hyperbranched polymer has many functional groups and has a good affinity for dye molecules, the dye molecules can be extracted to realise the purification of dye wastewater [10, 11].

Figure 1 Flowchart for synthesis and preparation of hyperbranched polymer (see online version for colours)



1.1 *Adoption of hyperbranched polymer*

As a functional polymer, hyperbranched polymer has broad adoption prospects. It has shown high adoption value in nano materials, drug slow release, coatings and textile fields [12, 13].

By analysing the main parameters that the design of organic nanostructured systems is influence sensitively, limitations and emerging approaches in the various fields of nanotechology. Correction and harmonisation of unwanted processes is one of the major challenges of the next decades and a deeper knowledge and understanding of the key factors are required that drive the formation of nanomaterial.

i *Adoption of hyperbranched polymer in printing and dyeing*

The interaction between hyperbranched polymer and dyes such as static electricity, hydrogen bonding, coating, etc. can pre-treat the fabric. For example, the adoption of reinforcing fibres and the combination of dyes can enhance the binding degree of dye. Hyperbranched polymer and dyes can also form insoluble salts, thereby reducing its water solubility and improving the washing and friction resistance of the dyed fabric.

ii *Adoption of hyperbranched polymer in the leather field*

As mentioned earlier, hyperbranched polymer has a unique molecular structure. Modifying it can give the polymer many new functions and uses. Then, various new needs in the processing of leather products are met, for it can be adopted as various auxiliary reagents in leather products, including main tanning agents and finishing agents [14, 15]. Microfibre can be utilised as the best substitute for natural leather. The leather made of this type of fibre has a lighter weight and natural luster. The deficiency is that the density of the tissue is low, the fabric is lighter and easy to fade. The main reason is that the microfibre lacks active groups, which affects the adsorption and dyeability of synthetic leather [16].

iii *Adoption of hyperbranched polymer in sustained release of drugs*

Hyperbranched polymer has relatively irregular molecular chains, so its branches can be expanded arbitrarily. The groups at the ends of the molecules are packed tightly, and many closed cavities are generated inside the molecules. It can be utilised as a carrier of small molecules to greatly enhance its anti-interference ability to the external environment [17]. There are two ways of binding between drug molecules and hyperbranched polymer. First, the hyperbranched polymer forms a covalent bond with the drug molecule during the formation process. Second, the hyperbranched polymer forms a physical coating with the drug molecule [18]. The former can effectively control the sustained release of the drug, thereby maintaining the chemical properties of the drug molecule. Hyperbranched polymer is employed as a drug carrier to deliver chemical drugs into the tumour. The drug carrier can provide a narrow particle size distribution, protect the drug molecule from the outside world based on the new characteristics of the drug, and can also carry multiple drug therapeutic agents.

iv *Adoption of hyperbranched polymer in the preparation of nano materials*

Hyperbranched polymer is a kind of highly branched polymer with three-dimensional structure. Due to its unique molecular internal nanopores, it can chelate ions, adsorb small molecules, or act as a catalyst for small molecule reactions. On the one hand, hyperbranched polymer can be utilized as a template material to synthesise nano materials, and the structure and size of hyperbranched molecules can be adjusted to generate nanoparticles of different sizes. On the other hand, hyperbranched polymers modify nano materials, which can reduce the specific surface energy of nanoparticles, that is, reduce the surface polarity of nanoparticles, and improve their solubility in aqueous solutions.

Contribution: This paper details the most relevant approaches for incorporating such nanoparticles into synthetic fabrics in the textile industry. From the perspective of the textile industry, the fabric dying and fabric antibacterial of hyperbranched polymer nano materials are detailed and analysed. Its adoption as fibre leather fatliquoring agent in the process of leather fatliquoring and the adoption of hyperbranched polymer in textile industry are also detailed. The adoption of polymer in textile industry and the massive documents has been referred for analysis.

Organisation: The rest of the paper is organised as follows. Section 2 provides the review of existing work by many researchers. Research methodology adopted in this work is discussed in Section 3 followed by the Result analysis in Section 4. The complete paper is concluded in Section 5.

2 Literature review

In recent years, many researchers have conducted research on hyperbranched polymer. Since Kim utilised the polycondensation method to prepare hyperbranched polyphenyl organics, the preparation of various hyperbranched polymers has been proposed one after another. According to the type of monomer used, it is classified into single monomer method and double monomer method. The single monomer method uses AB_n type monomers for polymerisation, including polycondensation, self-condensation vinyl polymerisation (SCVP), atom transfer radical polymerisation (ATRP), proton transfer polymerisation (PTP), and ring-opening polymerisation (SCROP). The double monomer method uses two monomers or a pair of monomers for polymerisation, such as the 'A1 + B2' type monomer polymerisation. However, when this method is adopted for polymerisation, crosslinking and gelation will occur, so the single monomer method is mainly used for polymerisation. Such methods include the following synthetic preparation methods, as shown in Table 1.

Table 1 The synthetic preparation methods

Method	*Advantages*	*Disadvantages*	*References*
AB_n type monomer polycondensation	The synthesis method is simple Only one-time required raw materials are added to the reactor for synthesis	Low output, wide molecular weight distribution Molecular weight is not easy to control	Lee et al. [19]
Selfcondensing vinyl polymerisation	The vinyl monomers commonly used in the industry are added into the synthesis of hyperbranched polymers	There are side reactions in the system Gelation will occur when the reaction time is long	Kumar et al. [20]
Atom transfer radical polymerisation	The reaction efficiency is high, and the system concentration is not required	Requirements for functional group compounds are high, elements are required	Xinyu et al. [21] and He et al. [22]
Proton transfer polymerisation	The reaction process is faster and the product has less impurities	The monomer must contain the nucleophilic group A	He et al. [23] and Wickham [24]
Ring-opening polymerisation	It is easy to prepare hyperbranched polymer with high molecular weight	It requires reactants such as Lewis acid or bases	Liu et al. [25, 26] and Xue et al. [27]

Zhang et al. prepared a polypropyleneimine dendrimer modified with end group fatty amide. The molecule can exist in the form of soluble monomolecular micelles in toluene-based non-polar organic solutions. The toluene solution containing polypropylene imine dendrimers can adsorb acid dyes in the aqueous solution. When the solution was alkaline, it released the acid dye adsorbed by itself. Koninck et al. [28] connected long link branches on hyperbranched polyethyleneimine. The linked polymer products can form monomolecular micelles in organic solvents, thereby transferring dye components in water. Such performance was significantly superior to that of linear polymer under the same conditions [29]. The unique structure of hyperbranched polymer makes it possible to modify it to produce more properties, and expand broader adoption prospects in other aspects of the textile field.

Rajesh and Venkatesan [30] designed a variety of hyperbranched polyester quaternary ammonium salts and utilised them for the treatment of printing and dyeing wastewater and the test of alkali reduction of silk. Shao et al. [31] designed a hyperbranched polymer with an amino terminal and modified it to further generate the quaternary ammonium salt of amino-terminated hyperbranched polymer (HBP-HTC), which is adopted in cotton fabrics [32]. It is found that after HBP-HTC is applied, the dyeing performance of cotton fabrics is significantly improved.

Aldosari et al. [33] made full use of the multiple groups at the end of the hyperbranched polymer and its high reaction production activity, and employed it to modify ultrafine fibres. The thickness of the modified microfibre-leather product was significantly increased and the water vapour permeability was also greatly enhanced.

Srnová-loufová et al. [34] adopted amino hyperbranched polymer and polylactic acid to synthesise high-performance drug carrier, which was then adopted to generate nanoparticles. It was used as a carrier of anti-tumour agents for rabies, so as to effectively improve the contact duration of anti-tumour agents and tumour cells, and thus enhance the therapeutic effect of anti-tumour agents [35].

Jiang et al. [36] synthesised a monomer structure with hyperbranched polyamide as the core and polyvinyl alcohol as the shell, to form an amphiphilic modified hyperbranched polymer with a core-shell structure that is hydrophobic inside and hydrophilic outside. It was employed as a carrier to prepare a dispersion system containing nano-zinc oxide, and the particle size of the zinc oxide of the system was only 3~5 nm. Service [37] adopted the sol-gel method, and they employed MEA as a cross-linking agent and combined nano-zinc oxide with HBPI. The particle size of ZnO in this system was less than 10 nm, which was much smaller than the wavelength of incident light, and the composite film emitted relatively stronger fluorescent [38]. Some scholar utilised the branched structure of hyperbranched polymer macromolecules to reduce Ag ions, and the prepared nano-Ag solution had a particle size of 8.5 nm. Moreover, after being placed for 4 months, the particle size was still around 30 nm, with favourable stability.

3 The proposed methods

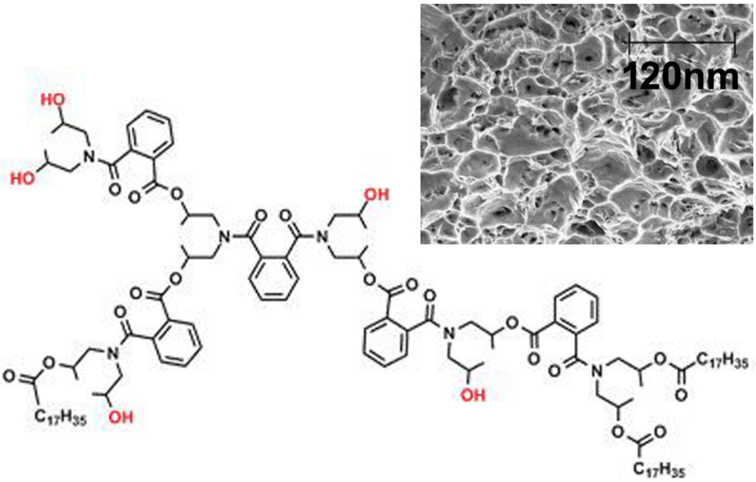
3.1 Preparation of controllable nano materials based on hyperbranched polymer

The cavity in internal branched of hyperbranched polymer provides an ideal place for preparing controllable nano materials. After graft modification, the hyperbranched polymer has a ‘core-shell’ structure. The outer shell has an enhanced effect on the generation of controllable nano materials, that is, the outer shell serves as a template for preparing nano materials. In addition, the hyperbranched polymer has many functional groups distributed inside and outside, which can participate in the preparation of nano materials, and has a coordinated effect on the preparation of controllable nano materials. Hyperbranched polymer not only controls the generation of nano materials, but also effectively protects the prepared nano materials, thereby maintaining the stability of nano materials. Moreover, in the adoption of nano materials prepared based on hyperbranched polymer, hyperbranched polymer can not only provide auxiliary effects, but also enhance the bonding force between nano materials and the substrate.

3.2 Preparation of nano-Ag

To prepare nano-Ag with hyperbranched polymer, hyperbranched polymer with amino group and its modified polymer are usually adopted. Ag ion is captured into the hyperbranched polymer by the complexation of the amino group to the Ag ion. Then, the Ag ion is reduced to nano-Ag by the reducing agent or the reducing action of the amino group itself. In addition, the size of nano-Ag can be well controlled because of the external protective effect of hyperbranched polymer. Molecular formula and SEM image of nano-Ag prepared with hyperbranched polyamine is shown in Figure 2.

Figure 2 Molecular formula and SEM image of nano-ag prepared with hyperbranched polyamine (see online version for colours)



Xu et al. [39] utilised 2,4,6-trichloro-1,3,5-triazine and 4,4-dianiline as raw materials to synthesise hyperbranched polyamines by the A2 + B2 double monomer method [40]. $NaBH_4$ was employed as a reducing agent to obtain nano-Ag particles in a DMSO environment, and the antibacterial properties were also studied, as illustrated in Figure 3.

Chen et al. [41] prepared nano-Ag particles using hyperbranched polyamines in supercritical CO_2 with hydrogen as the reducing agent. The nano-Ag had a particle size of 3.4±0.8nm and had a smaller particle size distribution, as presented in Figure 4. The nano-palladium was prepared by adopting this method and the nano-particles obtained by this method had relatively stable physical properties in the hyperbranched polymer, and can be prepared into a dry powder state and then dissolved in a suitable solvent [42].

Li et al. [43] grafted hyperbranched ethyleneimine end groups with long alkane chains to generate amphoteric hyperbranched polymers, thereby preparing controllable nano-Ag particles. The prepared nano-Ag particles had a particle size of about 1.6 nm and exhibited favourable antibacterial properties. Wang et al. [44] reduced the PAMAM dendrimer to generate controllable nano-Ag under light radiation without reducing agent, and studied its aggregation state in solution [45]. It was proved that the amino group in the macromolecule had a good reduction effect on Ag ions, and the nano-Ag particle size was commonly at about 3.0 nm.

Figure 3 Preparing process of nanoparticles by hyperbranched polyamines assisted by supercritical CO_2 (see online version for colours)

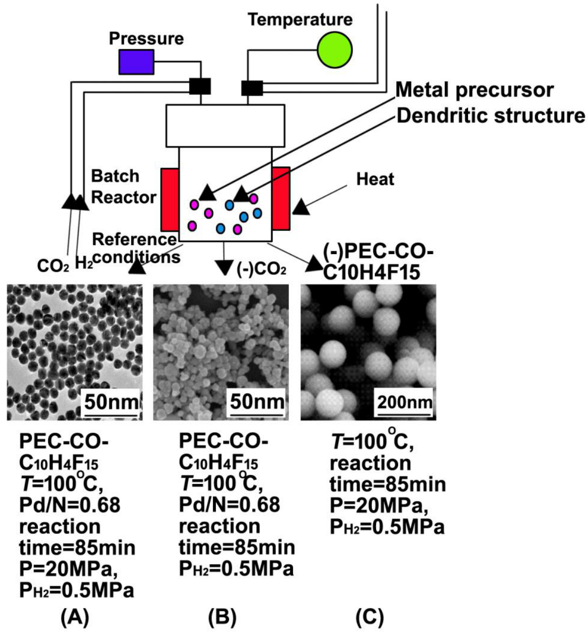
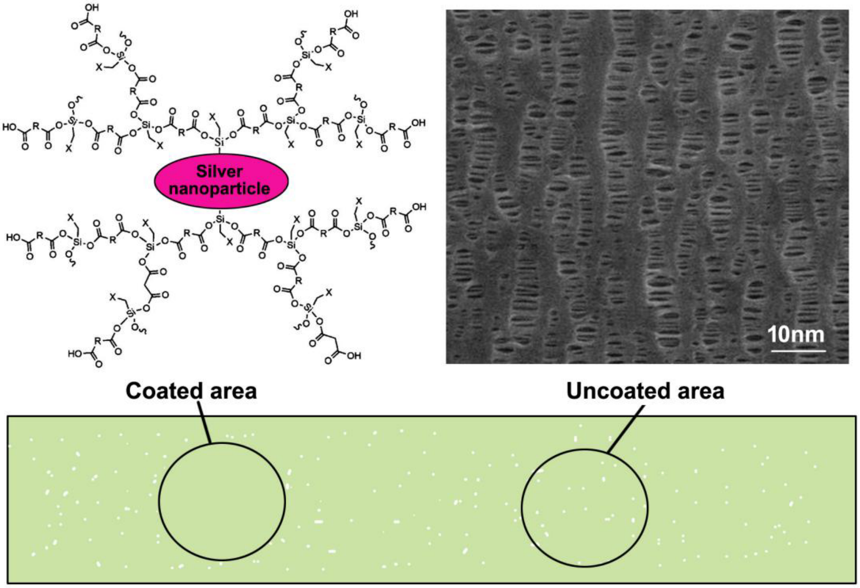


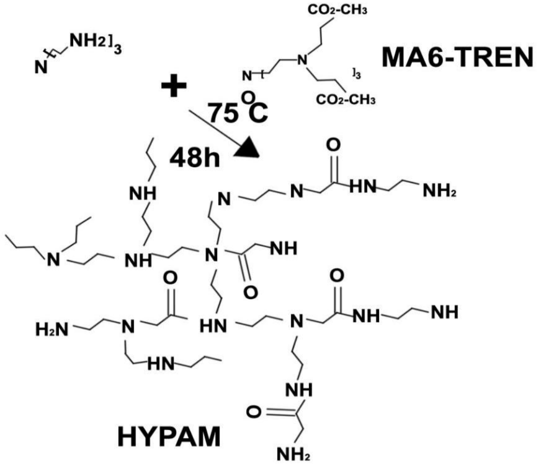
Figure 4 Comparison of antibacterial properties of amphoteric hyperbranched polyethyleneimine-nano-ag and conventional nano-Ag (see online version for colours)



3.3 Preparation of nano-Au

Adopting hyperbranched polymer to prepare nano-Au has the same principle as preparing nano-Ag. Generally, chloroaurate ions are attached to the inside of the hyperbranched polymer, and nano-Au is obtained via the reducing agent. Luo et al. [46] prepared hyperbranched polyamide-amino groups with different molecular weights by controlling the reaction conditions, to obtain aqueous solutions of nano-Au [47]. In the process, the reaction conditions (including solution concentration and solution pH) were changed to test its influence on the formation and stability of Au nanoparticles, as illustrated in Figure 5.

Figure 5 Reaction process of hyperbranched polyamide-amine to prepare Ag nanoparticles (see online version for colours)

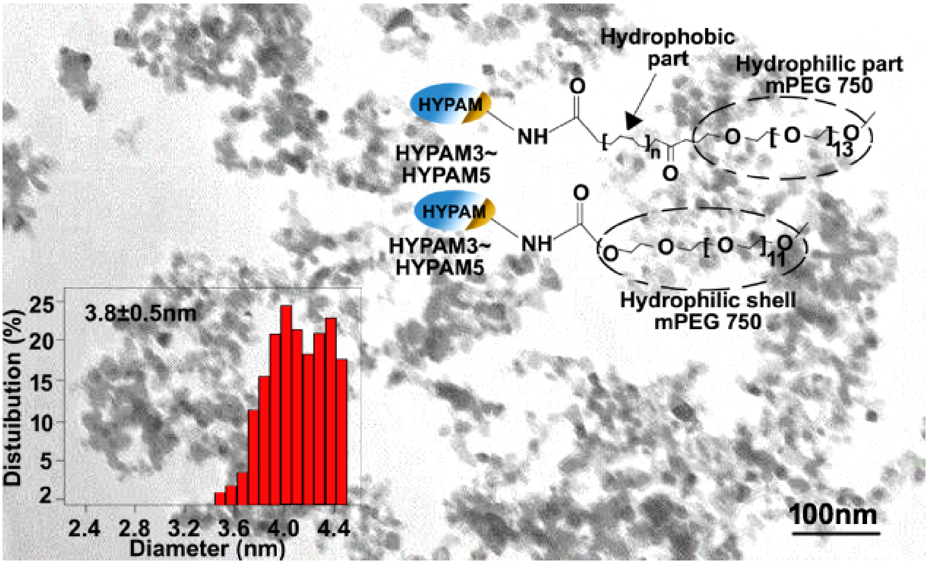


In the reaction process shown in Figure 5, the particle size of the nano-Au can be adjusted by adjusting the ratio of chloroauric acid and polymer. In addition, the stability of the nano-Au is affected by the molecular weight and pH of the polymer.

3.4 Preparation of nano-ZnO

The hyperbranched polymer is adopted to prepare controllable nano-ZnO. In the previous literature, the inert gas was injected first, the organic salt of Zn was dispersed in the hyperbranched polymer to make it hydrolyse naturally in the air, and then nano-ZnO was generated in the hyperbranched polymer. Zhang et al. linked polyethylene glycol to the end groups of hyperbranched polyamide-amine to prepare hyperbranched polymers with ‘core-shell’ and ‘core-multi-shell’ structures [48]. The organic salt of Zn was hydrolysed inside the polymer to generate nanometer ZnO, thereby controlling the particle size of the product, as shown in Figure 6.

Figure 6 The reaction products and some physical properties of hyperbranched polyamide-amine to prepare nano-ZnO (see online version for colours)



4 Results and discussion

4.1 Adoption of hyperbranched polymer in textile dyeing

As mentioned earlier, due to its unique structure, hyperbranched polymer has been widely adopted in many fields, such as polymer processing aids, curing agents, drug release agents, and functional film materials. It can also be widely adopted in the whole textile dyeing industry.

4.2 Adoption of hyperbranched polyester in polypropylene dyeing

Polypropylene fibre has low density, stable chemical properties, strong mechanical properties, and abrasion resistance. Moreover, the material has abundant reserves, low price, simple production process, and low energy consumption. It has become a synthetic fibre variety. However, polypropylene contains saturated carbon bonds, and the molecule does not contain polar or reactive groups, so it is highly hydrophobic and lacks affinity for general dyes. The advantages of polypropylene fibre are high crystallinity, tighter structure, and it is difficult for dye molecules to enter the crystal area. Therefore, it is difficult for general dyes and conventional dyeing methods to work on polypropylene fibres. Srimagal et al. [49] adopted a modification method to modify the hyperbranched polyester with hexadecanoyl chloride [50, 51]. The thermogravimetric analysis showed that the alkyl-modified hyperbranched polyester had strong stability. It can meet the temperature requirements of polypropylene spinning, the proportion of alkylation was changed, and the dyeing rate of modified polypropylene fibres was increased.

4.3 Dyeing adoption of hyperbranched polymer in inorganic salt

In the traditional process of cotton fabric reactive dyes, a large amount of inorganic salt needs to be added to improve the dyeing rate and fixation rate of the dye. However, the addition of salt will cause deterioration of water quality and destruction of the ecological environment [52]. The cationisation of cotton fibre can be adopted, that is, the chemically combined spinning cationic compound is adsorbed on the fibre, thereby increasing the exhaustion rate and fixing rate of the dye. At the same time, amino-terminated hyperbranched polymer (HBP-NH_2) is combined with cotton fibre via van der Waals force, hydrogen bond, and other forces, thereby improving the dyeing ability of cotton fibre-amino hyperbranched polymer.

4.4 The compounding effect of hyperbranched polymer in dispersant

In practical adoptions, a single surfactant is relatively rarely utilised, while mixed surfactants are usually adopted to obtain products with better performance. In practice, employing a mixed active agent can achieve better performance compared to a single surfactant, and produce a synergistic effect after the surfactant is compounded. Some studies compounded hyperbranched dispersant HPD and non-ionic surfactant Tween-80 in a certain proportion to obtain pigment particles. The particle size tested was 2100 nm, and the stability of the overall system reached 83.6%. However, when HPD was combined with an anionic surfactant TBS, the particle size obtained was 2039 nm, and the overall system stability exceeded 90%. It proved that the compounding effect of hyperbranched dispersant and anionic surfactant was better. Part of the reasons was that the two compound molecules involved in the compound had an electrostatic repulsion effect, which worked together on the pigment particles to obtain smaller and more uniform pigment particles.

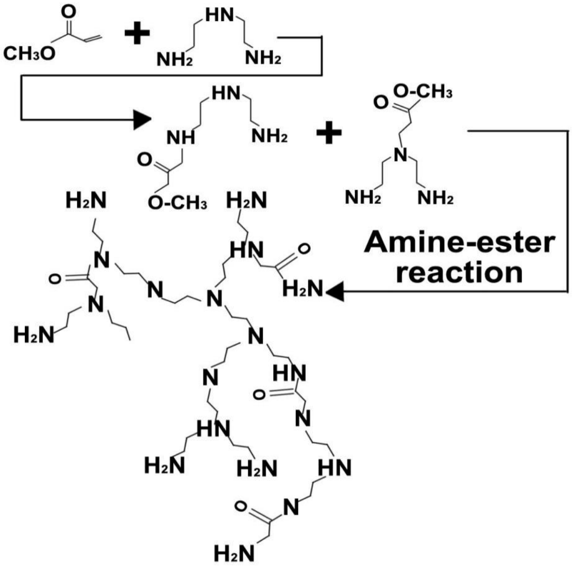
4.5 Adoption of hyperbranched polymer in textile antibacterial property

People usually call materials that can kill or inhibit the growth of bacteria as antibacterial materials. The definition of antibacterial is broad, that is, if a material has similar functions, the material has certain antibacterial properties. The research time in the field of antibacterial agents in China is relatively short, and the understanding of the classification of antibacterial agents and antibacterial principles needs to be further improved. The advanced foreign researches are referred for discussion.

Antibacterial agent, as a kind of medicine that can kill or inhibit bacteria and other microorganisms, can be added to the material to make the material have antibacterial properties. There are currently more than 500 types of antibacterial materials. Antibacterial agents include organic antibacterial agents, inorganic antibacterial agents, and natural antibacterial agents. According to different chemical structures, organic antibacterial agents are classified into more than 20 kinds, mainly including organic acids, esters, phenols, and alcohols. At present, the most widely adopted antibacterial agents include quaternary ammonium salts/polymer antibacterial agents, quaternary phosphate salts/polymer antibacterial agents, and organotin/polymer antibacterial agents. According to the different antibacterial mechanism, inorganic antibacterial agents include two types. One is antibacterial agents with heavy metals/metal ions as the main component. The other category is non-dissolvable antibacterial agents with photocatalytic activity. Natural antibacterial agents are effective ingredients extracted from natural substances to achieve antibacterial effects, including animal antibacterial agents, plant antibacterial agents, and mineral antibacterial agents.

Some studies modified the amino hyperbranched compound (HBP). 100g diethylenetriamine was weighted and placed in a three-necked flask. After the ice bath, 80 g methyl acrylate and 100 mL methanol solution were mixed, and then slowly dropped into the three-necked flask. During the dripping, nitrogen gas was introduced, the mixture was stirred constantly, and reacted at room temperature for 5 h. Methanol was removed during the depressurisation, and the reaction was continued at 170°C for 5 h to obtain a pale yellow viscous hyperbranched compound HBP-NH_2, as provided in Figure 7.

Figure 7 Synthesis of hyperbranched amino-terminated hyperbranched compound (HBP-NH_2)



HBP-NH_2 obtained in Figure 7 is added with methyl acrylate dropwise at room temperature. After the reaction, methanol solutions containing different volumes of HBP-NH_2 (3.56g, 1.69g, and 0.84g) are added to the solution, respectively. Then, the methanol is removed after the pressure is reduced. The temperature is raised to 170°C, and the reaction lasts for 5 h to obtain three modified hyperbranched compounds, namely NHBP-1, NHBP-2, and NHBP-3. The effect of modified hyperbranched polymers with different molecular weights on nano-Ag particle size is explored. The same concentration (0.65g/L) of NHBP-1, NHBP-2, and NHBP-3 reacts with a constant concentration (0.16g/L) $AgNO_3$ solution, denoted as a, b, and c, respectively. UV-Vis analysis is implemented. Figure 8 discloses that the characteristic absorption peaks of nano-Ag appear at 426 nm, 433 nm, and 438 nm in different nano-Ag colloidal solutions, which proves the production of solution nano-Ag. It is also revealed that the half-peak width of the absorption curve gradually increases, and it is inferred that the nano-Ag particle size gradually decreases, as presented in Figure 9.

Figure 8 Ultraviolet-visible light absorption spectra of nano-Ag colloidal solutions based on different amino-modified hyperbranched compounds (see online version for colours)

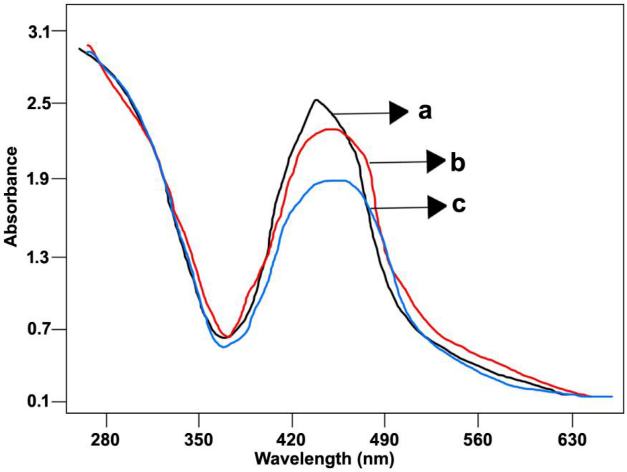
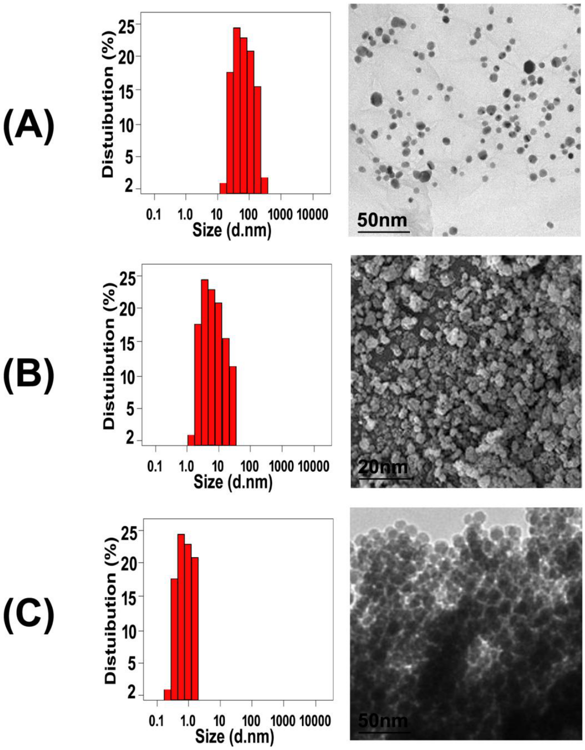


Figure 9 Particle size and TEM images: (A) NHBP-1; (B) NHBP-2 and (C) NHBP-3 (see online version for colours)



In Figure 9, the particle sizes of nano-Ag prepared with NHBP-1, NHBP-2, and NHBP-3 are 13–120 nm, 1.0–50 nm, and 0.5–6 nm, respectively, which are the same as the results predicted by UV-Vis. Furthermore, it proves that the nano-Ag is coated by modified hyperbranched polymer. The average particle size of NHBP-2 is only 5.6 nm, and the particle size of different particles is not much different. It means that the modified hyperbranched polymer-nano-Ag has higher stability, so NHBP-2 is chosen to prepare nano-Ag.

In the experiment, the Oxford cup diffusion is adopted, and nano-Ag prepared with 0.16 g/L $AgNO_3$ solution and 0.65 g/L NHBP-2 is employed for antibacterial testing. The antibacterial performance of different Ag solutions on Staphylococcus aureus and Escherichia coli is compared in Figure 10.

Figure 10 Antibacterial effect of distilled water on different bacteria: (A) Staphylococcus aureus; (B) Escherichia coli; (C) $AgNO_3$-Staphylococcus aureus; (D) the prepared nano-Ag-E. coli (see online version for colours)

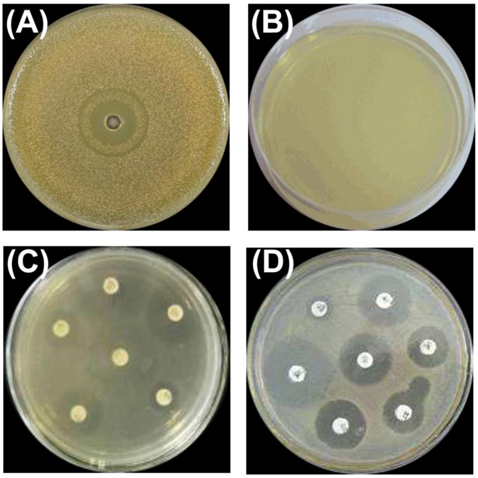


Figure 10(C) and (D) shows that the Ag ion solution forms an inhibition zone. The corresponding inhibitory diameters are 6.5 nm and 7.8 nm, respectively. Compared with the conventional $AgNO_3$ solution, the nano-Ag exerts a better antibacterial effect.

4.6 Adoption of hyperbranched polymer in leather fatliquoring

It is a process in which animal, plant, or synthetic materials are added as fatliquoring agent to leather in the process of leather making, so that grease or synthetic materials can penetrate into the leather fibres, thus the leather is softer and comfortable to use. Most fatliquoring agents are modified natural oils, and sulphated, sulfited, and phosphorylated natural oils. However, the modified product produces a large amount of waste liquid during the processing, thereby reducing the utilisation rate of grease, and the waste liquid pollutes the environment.

Some people have turned their attention to mineral oil and paraffin. Utilising carbon products for fatliquoring is more commonly. However, it is necessary to conduct in-depth research on leather fibres. Such fibre reduces the interaction between collagen fibres via the polar groups between collagen fibres, thereby increasing the non-polarity of molecular chains and strengthening the spacing between fibres. As a result, relative slippage occurs between the molecular chains, which in turn leads to a trend of decline in mechanical properties of the leather fibre. Scholars tried adopting synthetic grease to modify the hyperbranched polyamide (HPT), and employed the acid chloride reaction to generate linear-hyperbranched polymer (HPT-3), which was taken as an intermediate to perform a phosphorylation reaction on the unchanged hydroxyl group. That is, P_2O_5 was utilised as the phosphorylation reagent and CCl_4 as the dispersant, the esterification reaction was carried out under the action of THF, and then a certain amount of water was added for hydrolysis to obtain the linear-hyperbranched phosphate polymer (HPT-3-P). After the hyperbranched polymer is applied to the leather fatliquoring, Figure 11 shows that compared with the leather without fatliquoring, the spacing between collagen fibres increases obviously and the fibre bundle decreases after the HPT-3 and HPT-3-P are added.

Figure 11 SEM image corresponding to different leathers: (A) leather without fatliquoring; (B) HPT-3 treated leather; (C) HPT-3-P treated leather; (D, E) and is magnification of A, B, and C, respectively

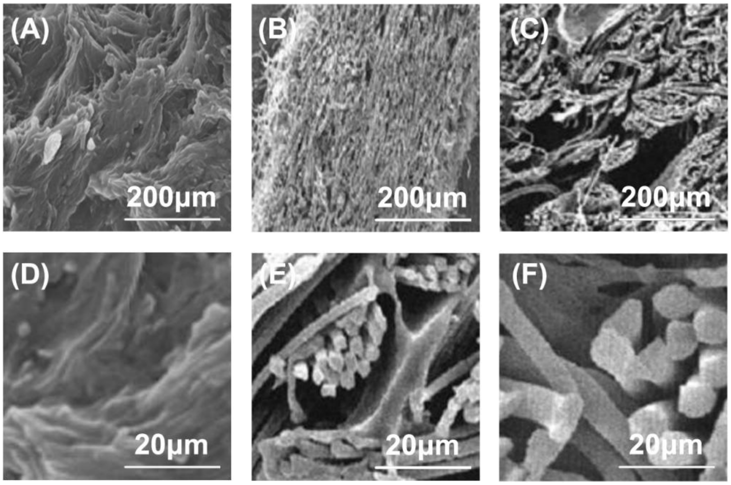


Figure 12 suggests that the leather sample without fatliquoring has the highest degradation rate at 280.6°C, with a degradation rate of 0.52%/min. When the temperature reaches 580°C, the weight loss tends to balance, and the residual amount of the sample is 21.85%. The leather samples treated with HPT-3 had the highest degradation rate at 373.5°C, and the degradation rate reached 0.46%/min. When the temperature reaches 580°C, the weight loss tends to balance, and the residual amount of the sample is 18.70%. The leather samples treated with HPT-3-P had the highest degradation rate at 332.6°C, and the degradation rate reaches 0.45%/min. When the temperature further rises to 580°C, the weight loss tends to balance, and the residual amount of the sample is 20.47%.

Compared with the blank leather, the degradation rate of the leather samples decreases after the hyperbranched ester polymer is added. This is because the introduction of HPT-3 and HPT-3-P changes the degree of aggregation among leather collagen fibres, which in turn changes the leather fibres, indicating that HPT-3 and HPT-3-P can form strong intermolecular forces with collagen fibres. To find out whether the preparation of fatliquoring agent affects the mechanical properties of leather, further demonstrations are made on different samples, as presented in Figure 13.

Figure 12 DTG analysis of different leather products after fatliquoring (see online version for colours)

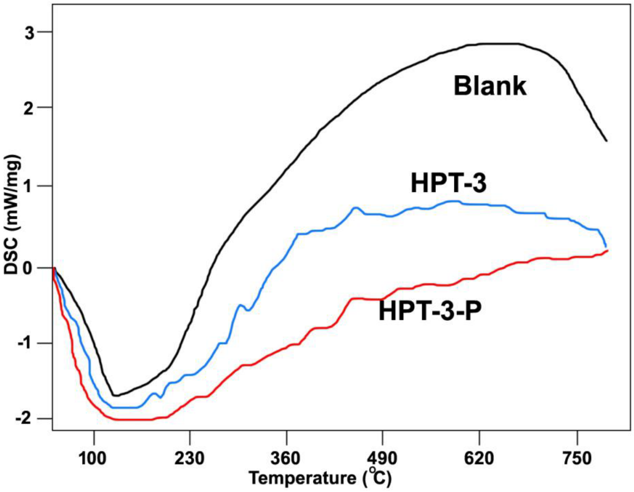
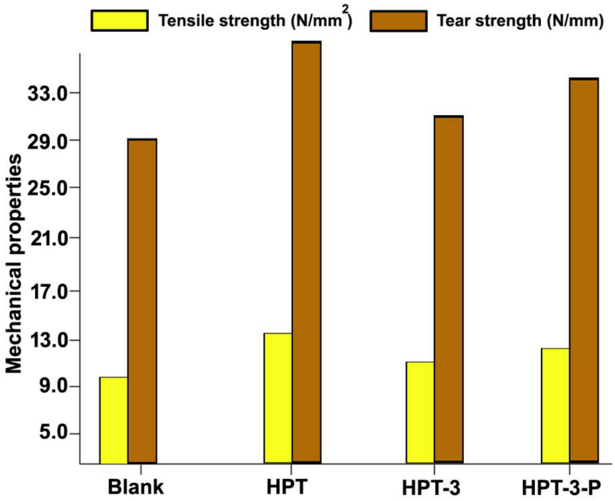


Figure 13 Comparison of the mechanical properties of different hyperbranched polymers after fatliquoring (see online version for colours)



It is inferred in Figure 13 that after the prepared ester compound is added the finished leather product has a significant increase in tensile strength and tear strength. This is because there are a large number of hydroxyl groups on the periphery of the hyperbranched structure, which can form hydrogen bonds with hydroxyl groups and amino groups on the collagen fibres. However, after the long-chain alkyl group is grafted, the tensile strength and tear strength of the material will be decreased. The reason is that after the long-chain alkyl groups in the leather replace part of the hydroxyl groups of the hyperbranched compounds, the number of hydroxyl groups naturally appears to be significantly reduced, and the hydrogen bond force is correspondingly weakened, thereby reducing the mechanical properties of the ester compounds. The leathers added with esters (HPT-3 and HPT-3-P) are compared. Then, the leather samples after treatment with phosphate are further compared in terms of tensile strength and tear strength. The tensile strength and tear strength of HPT-3-P treated leather are stronger than those of leathers treated with intermediate product HPT-3.

5 Conclusion

Hyperbranched polymers have broad adoption prospects in coatings industry, rheological modifier, nano technology, and biomedical materials due to their abundant terminal functional groups, the nearly spherical three-dimensional structure, many internal cavities, physical and chemical characteristics of high solubility, low viscosity, and high reactivity. Compared with the blank leather, the degradation rate of the leather samples decreases after the hyperbranched ester polymer is added. The thermo gravimetric analysis shows that the alkyl-modified hyperbranched polyester has strong stability. It can meet the temperature requirements of polypropylene spinning, the proportion of alkylation is changed, and the dyeing rate of modified polypropylene fibres is increased. The compound effect of hyperbranched dispersant and anionic surfactant is favourable. When hyperbranched polymer is applied in inorganic antibacterial agents, the Ag ion solution can be employed to form a bacteriostatic zone, and the corresponding bacteriostatic diameter is smaller. The prepared nano-Ag can exert a better antibacterial effect relative to the conventional $AgNO_3$ solution. After the prepared ester compound is added, the prepared leather finished product has obvious improvement in tensile strength and tear strength.

New approaches will be studied and analysed in future for incorporating such nanoparticles into synthetic fabrics in the textile industry. It will be future concern for providing solution to textiles traditional problems for microorganism growth onto fibres, flammability, robustness against ultraviolet radiation, and many others.

Acknowledgements

This work was supported by the year 2018–2019 Fundamental Research Funds for the Central Universities and Graduate Student Innovation Fund of Donghua University " Research on the development of sizing technology in China" (Project No., CUSF-DH-D-2019105) stage of achievements.

References

1 Ng, Y.H., Leung, Y.H., Liu, F.Z., Ng, A.M.C., Gao, M.H., Chan, C.M.N., Djurišić, A.B., Leung, F.C.C. and Chan, W.K. (2013) 'Antibacterial activity of Zno nanoparticles under ambient illumination – the effect of nanoparticle properties', *Thin Solid Films*, Vol. 542, pp.368–372.

2 Cao, B., Cao, S., Dong, P., Gao, J. and Wang, J. (2013) 'High antibacterial activity of ultrafine Tio2/graphene sheets nanocomposites under visible light irradiation', *Mater. Lett.*, Vol. 93, 15 February, pp.349–352.

3 Kavitha, C. and Dasan, K.P. (2013) 'Nanosilver/hyperbranched polyester (hbpe): *synthesis*, characterization, and antibacterial activity', *J. Coat. Technol. Res.*, Vol. 10, No. 5, pp.669–678.

4 Wan, C. and Li, J. (2016) 'Cellulose aerogels functionalized with polypyrrole and silver nanoparticles: in-situ synthesis, characterization and antibacterial activity', *Carbohydr. Polym.*, pp.362–367.

5 Saadati, Z. (2013) 'Synthesis, characterization and antibacterial activity of silver nanoparticles in laboratory waste', *FEYZ*, Vol. 179, No. 23, pp.7264–7273.

6 Xie, G., Luo, P., Deng, M., Wang, Z. and Gong, R. (2017) 'Hyperbranched polyamine as nano-plugging agent used in water-based drilling fluid', *Nanosci. Nanotechnol. Lett.*, Vol. 29, No. 3, pp.506–513.

7 Yasin, S., Behary, N., Giraud, S. and Perwuelz, A. (2016) 'In situ degradation of organophosphorus flame retardant on cellulosic fabric using advanced oxidation process: a study on degradation and characterization', *Polym. Degrad. Stab.*, Vol. 126, April, pp.1–8.

8 Tsuzuki, T. and Wang, X. (2010) 'Nanoparticle coatings for UV protective textiles', *Res. J. Text. Appar.*, Vol. 14, No. 2, pp.9–20.

9 Zhong, J., Wu, L., Lan, J., Waqas, M., Sun, M, Fan, Y., Chen, W., Liu, L. and Yang, J. (2020) 'Worm-like Pt nanoparticles anchored on graphene with S, N co-doping and Fe_3O4 functionalization for boosting the electrooxidation of methanol', *Int. J. Hydrog. Energy*, Vol. 45, No. 43, pp.22929–22937.

10 Rehan, M., Mashaly, H.M., Mowafi, S., Abou El-Kheir, A. and Emam, H.E. (2015) 'Multi-functional textile design using in-situ ag nps incorporation into natural fabric matrix', *Dyes Pigm.*, Vol. 118, pp.9–17.

11 Sertkol, M., Koeseoglu, Y., Baykal, A., Kavas, H. and Toprak, M.S. (2010) 'Synthesis and magnetic characterization of Zn0.7Ni0.3Fe2O4 nanoparticles via microwave-assisted combustion route', *J. Magn. Magn. Mater.*, Vol. 322, No. 7, pp.866–871.

12 Zhang, L., Guan, H., Dong, Q. and Gao, D. (2014) 'Synthesis and characterization of Ni0.7Zn0.3Fe2O4 and Mn0.7Zn0.3Fe2O4 nanoparticles by water-in-oil microemulsion', *Integr. Ferroelectr.*, Vol. 154, No. 1, pp.103–109.

13 Sudheesh, K.P.T., Lakshmanan, V.K., Raj, M., Biswas, R., Hiroshi, T., Nair, S.V. and Jayakumar, R. (2013) 'Evaluation of wound healing potential of β-chitin hydrogel/nano zinc oxide composite bandage', *Pharm. Res.*, Vol. 30, No. 2, pp.523–537.

14 Singletary, K. (2014) 'Clove: Overview of potential health benefits', *Nutr. Today*, Vol. 52, No. 3, pp.93–111.

15 Miyaki, N., Tomita, I. and Endo, T. (2015) 'Three-component coupling polymerization of bisallene, aryl dihalides, and nucleophiles via π-allylpalladium complex. II. effect of nucleophiles on polymerization', *J. Polym. Sci. A: Polym. Chem.*, Vol. 35, No. 21, pp.1211–1218.

16 Fossum, E. (2011) 'Book review of hyperbranched polymers: synthesis, properties, and applications', *J. Am. Chem. Soc.*, Vol. 133, No. 37, pp.14840–14840.

17 García-Alonso, J., Khan, F.R., Misra, S.K., Turmaine, M., Smith, B.D., Rainbow, P.S., Luoma, S.N. and Valsami-Jones, E. (2011) 'Cellular internalization of silver nanoparticles in gut epithelia of the estuarine polychaete nereis diversicolor', *Environ. Sci. Technol.*, Vol. 45, No. 10, pp.4630–4636.

18 Battin, T.I., Kammer, F.V.D., Weilhartner, A., Ottofuelling, S. and Hofmann, T. (2009) 'Nanostructured Tio 2: transport behavior and effects on aquatic microbial communities under environmental conditions', *Environ. Sci. Technol.*, Vol. 43, No. 21, pp.8098–8104.

19 Lee, S.W., Kim, S.M. and Choi, J. (2009) 'Genotoxicity and ecotoxicity assays using the freshwater crustacean daphnia magna and the larva of the aquatic midge chironomus riparius to screen the ecological risks of nanoparticle exposure', *Environ. Toxicol. Pharmacol.*, Vol. 28, No. 1, pp.86–91.

20 Kumar, G., Malhotra, S., Shafiq, N., Pandhi, P. and Sharma, S. (2011) 'In vitro physicochemical characterization and short term in vivo tolerability study of ethionamide loaded PLGA nanoparticles: potentially effective agent for multidrug resistant tuberculosis', *J. Microencapsul.*, Vol. 28, No. 8, pp.717–728.

21 Yang, X., Gondikas, A.P., Marinakos, S.M., Auffan, M., Liu, J., Hsu-Kim, H. and Meyer, J.N. (2012) 'Mechanism of silver nanoparticle toxicity is dependent on dissolved silver and surface coating in caenorhabditis elegans', *Environ. Sci. Technol.*, Vol. 79, No. 2, pp.1119–1127.

22 He, G.J., Li, G.Q., Ying, H., Guo, Y.S. and Fang, W.J. (2015) 'Palmitoyl hyperbranched polyglycerol as a nanoscale initiator for endothermic hydrocarbon fuels', *Fuel*, Vol. 161, pp.295–303.

23 He, G., Shen, Y., Li, J., Zhang, L., Guo, Y., Dionysiou, D.D. and Fang, W. (2017) 'Solubilization of the macroinitiator palmitoyl modified hyperbranched polyglycerol (phpg) in hydrocarbon fuels', *Fuel*, Vol. 200, 15 July, pp.62–69.

24 Wickham, D.T., Engel, J.R., Hitch, B.D. and Karpuk, M.E. (2012) 'Initiators for endothermic fuels', *J. Propuls. Power*, Vol. 17, No. 6, pp.1253–1257.

25 Liu, J., Huang, W., Pang, Y., Zhu, X., Zhou, Y. and Yan, D. (2010) 'Self-assembled micelles from an amphiphilic hyperbranched copolymer with polyphosphate arms for drug delivery', *Langmuir*, Vol. 26, No. 13, pp.10585–10592.

26 Liu, J., Pang, Y., Huang, W., Zhu, X., Zhou, Y. and Yan, D. (2010) 'Self-assembly of phospholipid-analogous hyperbranched polymers nanomicelles for drug delivery', *Biomaterials*, Vol. 31, No. 6, pp.1334–1341.

27 Xue, Y.N., Huang, Z.Z., Zhang, J.T., Min, L., Min, Z., Huang, S.W. and Zhuo, R.X. (2009) 'Synthesis and self-assembly of amphiphilic poly (acrylic acid-b – dl – lactide) to form micelles for ph-responsive drug delivery', *Polymer*, Vol. 50, No. 15, pp.3706–3713.

28 Koninck, M.D. and Bélanger, D. (2003) 'The electrochemical generation of ferrate at pressed iron powder electrode: comparison with a foil electrode', *Electrochim. Acta*, Vol. 48, No. 10, pp1435–1442.

29 Zhang, X., An, J., Guoa, Q., Zhaoa, Y. and Li, C. (2015) 'Colloids and surfaces a: physicochemical and engineering aspects', *Colloids Surf.*, Vol. 482, pp.98–108.

30 Rajesh, R. and Venkatesan, R. (2012) 'Encapsulation of silver nanoparticles into graphite grafted with hyperbranched poly(amidoamine) dendrimer and their catalytic activity towards reduction of nitro aromatics', *Mol. Catal.*, Vol. 359, pp.88–96.

31 Shao, S., Ma, Z., Ding, J., Wang, L., Jing, X. ad Wang, F. (2012) 'Spiro-linked hyperbranched architecture in electrophosphorescent conjugated polymers for tailoring triplet energy back transfer', *Adv. Mater.*, Vol. 24, No. 15, pp.2009–2013.

32 Li, Q., Xu, B., Zhuang, L., Xu, X., Wang, G., Zhang, X., and Tang, Y. (2018) 'Preparation, characterization, adsorption kinetics and thermodynamics of chitosan adsorbent grafted with a hyperbranched polymer designed for Cr (VI) removal', *Cellulose*, Vol. 25, No. 6, pp.3471–3486.

33 Dosari, A., Haila, M., Ayesh and Ahmad, I. (2013) 'Nanocluster production for solar cell applications', *J. Appl. Phys.*, Vol. 114, No. 5, p.063107.

34 Srnová-loufová, L.F., Gemperle, A. and Gemperlová, J. (2000) 'Coreshell (ag)au bimetallic nanoparticles: analysis of transmission electron microscopy images', *Langmuir*, Vol. 16, No. 25, pp.9928–9935.

35 Emira, H.S.A. (2013) 'High performance alkyd paints based on platy kaolin for corrosion protection of steel', *J. Coat. Technol. Res.*, Vol. 10, No. 2, pp.199–208.

36 Jiang, L., Kong, X., Lu, Z. and Hou, S. (2015) 'Preparation of amphoteric polycarboxylate superplasticizers and their performances in cementitious system', *J. Appl. Polym. Sci.*, Vol. 132, No. 4, pp.78–87.

37 Service, R.F. (2003) 'Nanomaterials show signs of toxicity', *American Chemical Society Meeting*, 11 April, 2003. Science, Vol. 300, No. 5617, p.243.

38 Fu, J., Wang, L., Yu, H., Haroon, M., Haq, F., Shi, W., and Wang, L. (2019) 'Research progress of UV-curable polyurethane acrylate-based hardening coatings', *Prog. Org. Coat.*, Vol. 131, pp.82–99.

39 Xu, J., Luo, S., Shi, W. and Liu, S. (2006) 'Two-stage collapse of unimolecular micelles with double thermoresponsive coronas', *Langmuir the Acs Journal of Surfaces & Colloids*, Vol. 22, No. 3, pp.989–997.

40 Zhu, J., Hou, J., Zhang, Y., Tian, M., He, T., Liu, J. and Chen, V. (2018) 'Polymeric antimicrobial membranes enabled by nanomaterials for water treatment', *J. Membr. Sci.*, Vol. 550, pp.173–197.

41 Chen, T., Wang, Q., Chen, R., Zhang, B., Chen, K.P. and Maklad, M. (2012) 'Distributed hydrogen sensing using in-fiber Rayleigh scattering', *Appl. Phys. Lett.*, Vol. 100, No. 19, pp.57–67.

42 Mashouf Roudsari, G., Mohanty, A.K. and Misra, M. (2017) 'Green approaches to engineer tough biobased epoxies: a review', *ACS Sustain. Chem. Eng.*, Vol. 5, No. 11, pp.9528–9541.

43 Li, F.S., Labreche, Y., Lively, R.P., Lee, J.S., Jones, C.W. and Koros, W.J. (2014) 'Poly(ethyleneimine) infused and functionalized torlon-silica hollow fiber sorbents for post-combustion co2 capture, *Polymer*, Vol. 55, No. 6, pp.1341–1346.

44 Wang, H., Wang, S., Su, H., Chen, K-J., Armijo, A., Lin, W-Y., Wang, Y., Sun, J., Kamei, K-i., Czernin, J., Radu, C. and Tseng, H-R. (2009) 'A supramolecular approach for preparation of size-controlled nanoparticles. *Angew. Chem., Int. Ed.*, Vol. 48, pp.4344–4348, https://doi.org/10.1002/anie.200900063

45 Sun, T.Y., Mitrano, D.M., Bornhöft, N.A., Scheringer, M., Hungerbühler, K. and Nowack, B. (2017) 'Envisioning nano release dynamics in a changing world: using dynamic probabilistic modeling to assess future environmental emissions of engineered nanomaterials', *Environ. Sci. Technol.*, Vol. 51, No. 5, pp.2854–2863.

46 Luo, Y., Hui, P., Wu, J., Sun, J. and Wang, Y. (2011) 'Novel amphoteric ph-sensitive hydrogels derived from ethylenediaminetetraacetic dianhydride, butanediamine and amino-terminated poly(ethylene glycol): design, synthesis and swelling behavior', *Eur. Polym. J.*, Vol. 47, No. 1, pp.40–47.

47 Zhang, L., Qiao, M., Han, Q. and Yu, M. (2021) 'Recent advances in enhancing the anti-uV properties of aramid fibers with nanomaterials: a review', *Polym. Test.*, 107138.

48 Zhang, H. and Xue, X. (2019) 'The research progress on corrosion and protection of silver layer', *SN Appl. Sci.*, Vol. 1, No. 5, pp.1–8.

49 Srimagal, A., Mishra, S. and Pradhan, R.C. (2017) 'Effects of ethyl oleate and microwave blanching on drying kinetics of bitter gourd', *J. Food Sci. Technol. - Mysore*, Vol. 54, No. 5, pp.1–7.

50 Li, Q., Xu, B., Zhuang, L., Xu, X., Wang, G., Zhang, X., and Tang, Y. (2018) 'Preparation, characterization, adsorption kinetics and thermodynamics of chitosan adsorbent grafted with a hyperbranched polymer designed for Cr (VI) removal', *Cellulose*, Vol. 25, No. 6, pp.3471–3486.

51 Kausar, A. (2019) 'Applications of polymer/graphene nanocomposite membranes: a review', *Mater. Res. Innov.*, Vol. 23, No. 5, pp.276–287.

52 Zhang, Y., Hao, N., Lin, X. and Nie, S. (2020) 'Emerging challenges in the thermal management of cellulose nanofibril-based supercapacitors, lithium-ion batteries and solar cells: a review', *Carbohydr. Polym.*, Vol. 234, 115888.