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Research Progress of Polymer Fire Extinguishing Gel and Its Application in Forest Fire Prevention

Zhifeng XU, Nianci ZHANG *

Heilongjiang Forest Protection Research Institute, Harbin 150040, China

Abstract The paper summarizes the structure and water-absorbing mechanism, classification, and preparation method of polymer fire extinguishing gel, and prospects for its application in aerial firefighting, forest ground fire extinguishing, opening of firebreaks, and mitigating human casualties in forest fire extinguishing.

Key words Polymer fire extinguishing gel; Water-absorbing mechanism; Forest fire prevention

1 Introduction

Since the 1980s, China has been experiencing continuous development in science, technology, economy, and culture, leading to an increased awareness of ecological and environmental protection. As a result, research has been conducted in various fields to enhance the utilization rate of water resources. Against this background, Super Absorbent Polymer (SAP) have emerged as a new type of polymer functional material that plays an important role in various fields, including agriculture, coal mining, construction, health, medical care, transportation, sewage treatment, and desertification control. This paper summarizes the structure and water-absorbing mechanism, classification, and preparation method of polymer fire extinguishing gel, and also explores its potential application in the field of forest fire prevention.

2 Structure and water-absorbing mechanism of polymer fire extinguishing gel

The polymer fire extinguishing gel is a material that disperses a specific superabsorbent resin into water and forms a gel-like substance after absorbing water and swelling. SAP, also known as ultra absorbent polymer, is a type of novel water absorbent material. It is fast-absorbing, retains water for a long time, and is environmentally friendly. SAP molecules have numerous polar hydrophilic functional groups, including $-OH$, $-COOH$, $-CONH_2$, and $-SO_3H$. These groups are cross-linked during the reaction to form a three-dimensional (3D) network structure. Such a "grid" can hold water hundreds of times its own mass, forming a polymer fire extinguishing gel[1]. SAP material is known for its fast water absorption, high water absorption capacity, durable water retention capacity, and environmental friendliness. These characteristics are not found in general water absorption materials. At the same time, these materials retain moisture even under high temperature and high pressure conditions, while also exhibiting excellent stability in light, cold, heat, acid, and base environments[2]. Therefore, the use of polymer fire extinguishing gel has great potential in preventing and extinguishing forest and grassland fires.

2.1 Structure From a molecular structure perspective, the fire extinguishing gel is primarily composed of a polymer 3D framework, polar water-absorbing functional groups, and water molecules. The framework of this material consists of moderately cross-linked network structures, as illustrated in Fig. 1. The polar functional groups responsible for water absorption are hydrophilic, such as $-OH$ and $-SO_3H$. The molecular structures of these groups exhibit varying states in different molecular monomer systems. Makamura *et al.* [3] investigated the presence of water in SAP microstructures using analytical methods such as DSC and NMR. They observed that water typically exists in SAP in two states: bound water and free water, with free water occupying a significant portion. It can be concluded that SAP exists as a 3D network structure, and the key factor that leads to water absorption is the osmotic pressure inside and outside the network structure.

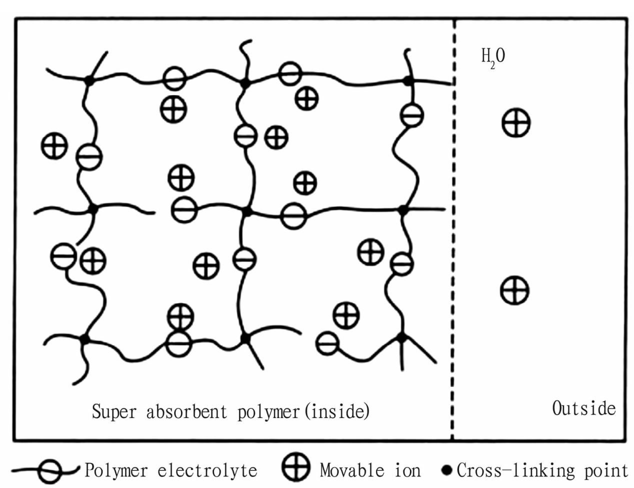

Fig. 1 Network structure of polymer fire extinguishing gel

The water absorption and swelling of polymer fire extinguishing gels are influenced by three main factors: (i) the free energy of mixing water and SAP during the absorption process; (ii) the

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* Corresponding author. E-mail: yunbing22098@126.com

elastic contraction capacity of the 3D network-like structure of SAP; and (iii) the types of polar functional groups in the SAP structure.

2.2 Water absorption mechanism The process of forming polymer fire extinguishing gel through SAP absorption of water and swelling involves two methods of water absorption. The first method involves water molecules diffusing freely to reach the capillaries on the surface of the absorbent polymer, while the second method involves water molecules combining with the hydrophilic groups of SAP through hydrogen bonding to form bound water. Both types of water absorption play a crucial role in the formation of polymer fire extinguishing gels, and the hydrogen bonding, in particular, is of utmost importance[4].

When SAP absorbs water using the first method, water molecules can slowly enter the interior through capillary adsorption and free diffusion. Prior to the introduction of water molecules, the SAP's skeletal structure is rigidly fixed, and the polar functional groups exist in an ionic state. As water molecules enter, the hydrophilic functional groups within the 3D mesh structure form a flexible plastic structure with water molecules. At this time, the hydrophilic groups start to ionize when exposed to water. The 3D network expands rapidly, creating an ionic concentration difference between the skeletal mesh layer frameworks that diffuses inwardly and outwardly due to the osmotic pressure of water molecules (Fig. 2)[5].

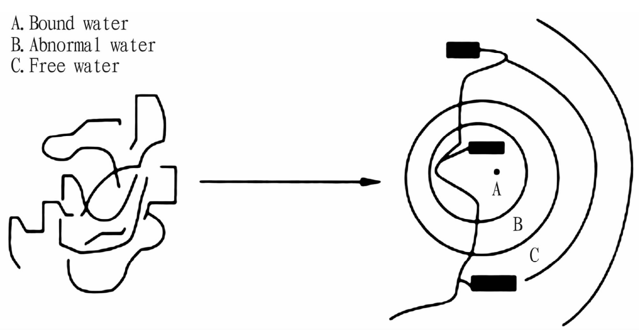

Fig. 2 Structure model of water around hydrophilic groups in polymer fire extinguishing gel

When SAP absorbs water using the second method, the hydrophilic group turns the molecular chain outward to bond with water molecules, while the hydrophobic group folds inward, forming locally insoluble particulate units. The polar effect locally deactivates water molecules that have already entered the skeleton molecules, immobilizing them at the particulate units. As additional water molecules enter the skeletal structure, the osmotic pressure difference between the interior and exterior of the molecules gradually decreases. The reaction continues until dynamic equilibrium is reached, at which point the skeleton molecules are fully saturated. This marks the completion of the water absorption process in the polymer fire extinguishing gel[6]. Comparing and analyzing the water absorption of different functional group molecules reveals that the higher the content of hydrophilic groups with stronger polarity, the faster the water absorption of SAP and the better the water retention durability. Meanwhile, it is necessary to match a moderate degree of cross-linking.

3 Classification of polymer fire extinguishing gels

SAP research started in the 1960s. The earliest research was on starch grafting acrylonitrile, conducted by Russell at the Northern Research Institute of the United States Department of Agriculture in 1961. SAP was used as a water retention agent in agriculture and gardening at that time. Since then, research on SAP has flourished, contributing to generation of varieties.

3.1 Classification by raw material source SAP was first derived from starch. SAP can be categorized into four types based on the raw materials used: starch, cellulose, synthetic, and organic-inorganic composites. The primary groups for grafting onto starch are acrylonitrile, acrylate, and acrylamide. Some varieties directly carboxymethylate the main starch chain, while others produce starch xanthate grafted acrylate and starch, acrylic acid, acrylamide, and maleic anhydride grafted copolymerization. Cellulose and starch share major grafting groups. Cellulose has various grafting options, including hydroxymethylation, etherification, esterification, xanthate grafted acrylates, and cellulose carboxymethylation of epichlorohydrin cross-linking varieties. The synthetic system comprises mainly of polyacrylic acid and polyvinyl alcohol varieties. In addition, it includes organic and inorganic composite types such as kaolin, bentonite, attapulgite clay, mica, and diatomaceous earth.

3.2 Classification by hydrophilic groups Hydrophilic groups are generally composed of cationic anions, zwitterions, non-ions and a variety of hydrophilic group systems.

Tertiary and quaternary amines are common cationic species, while carboxylic, sulfonic, and phosphoric acids are common anionic species. Zwitterionic species include carboxylic acid-quaternary amine and sulfonic acid-tertiary amine. Common nonionic species include hydroxyl and amide groups. Hydrophilic groups include those containing hydroxyl-carboxylic acid, hydroxyl-carboxylic acid group-amide group, and sulfonic acid-carboxylic acid group.

4 Preparation of polymer fire extinguishing gel

With the continuous development of technology, the preparation of SAP involves various methods, including solution polymerization, reversed phase suspension polymerization, reversed phase emulsion, liquid polymerization, and radiation polymerization. Among these, solution polymerization and reversed phase suspension polymerization have been extensively studied[7].

4.1 Solution polymerization Solution polymerization is an easily operated and controlled reaction method. The reactant is dissolved in the appropriate solvent, and the initiator and crosslinker are added sequentially for polymerization under heating or radiation. This method can be further subdivided into homogeneous and heterogeneous polymerization. In the former case, the solvent dissolves both the monomer and polymer, resulting in a polymer solution that only requires cross-linking to produce the final product. In the latter case, the monomer is soluble in the solvent while the polymer is insoluble. As a result, the SAP precipitates due to particle formation. Post-processing is required, including filtering, washing, drying, and pulverizing.

Solution polymerization offers a simple and easy process, but it also presents some drawbacks, such as high viscosity, low polymerization rate, low molecular weight, and heat dissipation difficulties during the middle and late stages of polymerization.

4.2 Reversed phase suspension polymerization Reversed phase suspension polymerization is a polymerization process where the initiator is dissolved in the aqueous phase, with the solvent (oil phase) acting as the dispersing medium, and the water-soluble monomer or polymer presenting as an aqueous droplet or particle. This method typically employs hydrophilic or water-soluble monomers and water-soluble initiators. The resulting SAP products are typically bead or granular in shape and have a regular structure.

Currently, the most commonly used method for synthesizing SAP is the reversed phase suspension method. Its advantages include a high polymerization rate, high molecular weight, mild reaction conditions, and few side reactions. This method overcomes the shortcomings of the solution polymerization system, which has high viscosity and poor heat dissipation. However, a disadvantage of the suspension polymerization method is the difficulty of solvent recovery.

4.3 Inverse emulsion polymerization Inverse emulsion polymerization is a chemical synthesis method that disperses water-soluble reactants in an oily medium and emulsifies them through strong stirring with the aid of an emulsifier. The method's remarkable feature is that the monomer is a hydrophilic or water-soluble substance. In other words, the water-soluble monomer is dispersed in an oily medium, and the aqueous monomer is formed into a latex particle, which belongs to the water-in-oil emulsion system. Inverse emulsion polymerization is often used due to the frequent use of hydrophilic monomers for SAP preparation.

The main distinction between inverse emulsion polymerization and reversed phase suspension polymerization lies in their respective mechanisms. Inverse emulsion polymerization follows the emulsion polymerization mechanism, while reversed phase suspension polymerization adheres to the aqueous solution or bulk polymerization mechanism. The former is the monomer initiation in the oil phase by an oil-soluble initiator, and the resulting monomer free radicals form droplet micelles for chain growth and chain termination in droplets or particles. The latter uses water-soluble initiator for monomer initiation, chain growth and chain termination in droplets.

4.4 Radiation polymerization Radiation polymerization is a method of synthesizing cross-linked structures between molecules using radiation energy, such as light, microwave, high-energy rays, and cross-linking agents. This method has gained popularity in laboratory basic research due to its uniformity, high speed, high efficiency, and lack of environmental pollution. However, industrial production is not yet feasible.

5 Application prospects of polymer fire extinguishing gel in forest fire prevention field

In recent years, the state has vigorously advocated for the use of water to fight forest fires. This method has several advantages, including convenient water access, low cost, no pollution to the environment, and benefits to forest growth. However, the utilization rate of water resources is still low. Applying polymer fire extinguishing gel to prevent forest fires can significantly improve the utilization of water resources and enhance fire extinguishing speed, efficiency, and safety. This is due to its high water absorption rate, long water retention time, and environmental friendliness.

5.1 Application in aerial firefighting Aerial firefighting is an effective method for combating large-scale forest fires. The aircraft can carry a significant amount of water at once, and the water can be injected from top to bottom to directly extinguish the fire. However, only a small amount of water carried by aircraft reaches the target fire extinguishing location due to the fast flight speed of the aircraft, the influence of wind speed, failing to extinguish and block the fire.

The super water absorption and retention properties of polymer fire-extinguishing gel, along with its gel state and biodegradability, make it a promising material for aviation firefighting. The fire extinguishing gel made of polymer addresses several issues, including spray drift, low water utilization rate, and adverse effects on soil. The gel state increases the viscosity of the substance, and it can absorb water to a significant extent, allowing it to carry thousands of times its own weight in water. Besides, water retention can cause the polymer fire extinguishing gel to adhere to the surface of flammable materials, effectively extinguishing and blocking fires for an extended period of time. The polymer fire extinguishing gel's environmental friendliness makes it a suitable soil water retention agent that does not harm the environment. Therefore, the use of polymer fire extinguishing gel shows promise in aerial firefighting.

5.2 Application in forest fire ground extinguishing Forest firefighters use a variety of tools to fight surface fires, including wind extinguishers, reciprocating water guns, fine water mist extinguishers, and No. 2 tools. However, these tools have low efficiency in extinguishing fires, and the embers may reignite in the fire area.

Polymer fire extinguishing gel is recognized for its ability to quickly absorb water, retain it for a long time, and maintain good thermal stability. When combating a forest fire, applying polymer fire extinguishing gel to the surface of the combustible can rapidly isolate the air, effectively suffocating the fire. The water in the gel group can evaporate in batches, absorbing a significant amount of heat and providing a cooling effect. Polymer fire extinguishing gel also has good adhesion and can stay long even on vertical surfaces. A water-rich protective layer is formed on the surface of the tree's trunk, branches, and leaves, effectively preventing the spread of fire and sleeper fire. Therefore, the application of polymer fire-extinguishing gel to the ground fire is becoming increasingly popular.

5.3 Application in opening firebreaks In China, forest fire prevention often involves the use of opening firebreaks, which includes three main methods[8]. (i) Combustible removal method. Combustibles are the most controllable factor in the three elements of combustion. To prevent the spread of fire, it is important to regularly remove combustible objects from the surface and create channels of a certain length and width either mechanically or manually. (ii) Planned burning method. When using fire outside the fire prevention period, it is possible to prevent fire by creating a channel of a specific width and length. (iii) Water-soaking soil belt method. In the isolation zone, a flooding belt with a certain width can be laid in advance to allow the ground to absorb excess water. This helps to maintain a certain level of humidity and prevent fires.

These methods have limitations in practical application. The first one requires a significant amount of human and material resources during the opening process, resulting in low efficiency and a certain level of risk. The second option has more stringent requirements for determining ignition timing, which requires a higher level of experience from the commander. Improper use of this option may also result in casualties. The third method is the safest, simplest, and most feasible. However, due to the rapid evaporation rate of water under natural conditions, it is often inefficient when water resources are limited and can not effectively extinguish fires.

The drawbacks mentioned above can be effectively addressed by utilizing the benefits of polymer fire extinguishing gel. This gel can be rapidly deployed as a barrier without requiring extensive equipment or a large workforce. Polymer fire extinguishing gel is an effective solution for fighting fires without causing harm to the ecosystem and vegetation. The gel retains water and blocks the fire for an extended period of time. Additionally, it can be naturally degraded after firefighting, making it an environmentally friendly option.

5.4 Reduction of casualties in forest fire prevention Polymer fire extinguishing gel can be applied to the body surface of firefighters and trapped individuals in forest fires to provide valuable time for escape, without causing harm to the human body. After the danger has passed, it is important to rinse the affected area with a significant amount of water. This process can completely remove the protective gel, resulting in a decrease in the number of casualties during forest fires.

6 Conclusions

Due to its high water-absorbing capacity, rapid water-absorbing speed, water retention capacity, and non-toxic and tasteless properties, polymer fire extinguishing gel revolutionizes the traditional methods of relying solely on water, foam, and forest fire isolation belts in China's forest fire prevention and rescue efforts. It has introduced new forest fire prevention, fire resistance, and fire extinguishing techniques that will have a significant positive impact on forest fire prevention and fighting in China.

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