Research of Polyvinyl Chloride (PVC) and Its Modification

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Abstract. Polyvinyl chloride (PVC) is a general-purpose plastic with excellent comprehensive properties, and it is also the second largest resin variety after polyethylene. As one of the most commonly used plastics, PVC is used in many fields, but there are still some defects such as poor toughness, poor heat resistance, and so on. Therefore, the modification of PVC materials is the main research direction in the field of materials. This paper introduces two modification approaches in the modification of PVC, chemical modification and physical modification. Chemical modification includes graft modification and cross-linking modification, and cross-linking modification can be divided into radiation cross-linking and chemical cross-linking. Physical modification includes elastomer modification. In the study of modification methods introduced in this paper, grafting modification can improve the plasticity of the material, and can also give the material special properties such as antibacterial properties. Crosslinking modification can improve the strength of materials, such as tensile strength and compressive strength. Physical modification can improve the impact strength of materials. This paper provides an overview of PVC modification and insight into improvements in common polymeric materials.

Keywords: Polyvinyl Chloride, chemical modification, physical modification.

1. Introduction

Polyvinyl chloride is a non-toxic and odorless polymer material with a moderate price. It has advantages such as oil resistance, acid and alkali resistance, and good light transmittance. It is widely used in fields such as construction, transportation, packaging, electrical, and healthcare [1, 2]. Global consumption is widespread and production capacity continues to increase. According to statistics, by 2030, the world's PVC production is expected to reach 59.72 million tons/year [3, 4]. But due to its poor toughness, poor heat resistance, low notch impact strength, poor processing rheological behavior, and unstable plasticization, its development in areas with high-performance requirements is restricted. In order to expand the application field and make PVC resin with higher performance, research on modification methods for PVC is very active, which are mainly divided into chemical modification and physical modification [5]. Chemical modification mainly involves altering the physical and chemical properties of polymers through chemical reactions and introducing flexible segments onto the molecular chains of PVC through molecular design grafting or copolymerization, thereby achieving the goal of toughening. Physical modification refers to the addition of plasticizers, lubricants, stabilizers, cross-linking agents, foaming agents, and other fillers to improve their performance through blending. The premise of blending modification is that the polymer must have a certain degree of compatibility. However, different modification methods have different drawbacks for polyvinyl chloride [6].

This paper systematically summarizes the advantages of specific methods under the two modification methods. The selection of different modification methods for different application fields is very meaningful in practical applications. Based on the existing advantages of excellent physical properties and economy, PVC has greatly overcome its shortcomings.

2. Chemical modification

Chemical modification mainly changes the physical and chemical properties of polymers through chemical reactions and changes the internal structure of polyvinyl chloride through chemical methods.
to meet the modification requirements. This paper mainly introduces graft modification and cross-linking modification.

### 2.1. Graft modification

The graft modification of polyvinyl chloride is to use the polyvinyl chloride molecular chain as the main chain and connect branch chains to the main chain through chemical reactions to change its linear structure.

Li et al.'s experiment is based on the nucleophilic substitution of chlorine atoms on PVC by amine long-chain structure compounds, introducing aliphatic chains into PVC molecular chains, and using the large-volume structure of long-branched chains to increase the distance between PVC chains and reduce the distance between molecular chains [7]. The interaction force can improve the plasticity of PVC material. Li et al. selected long-chain methyl stearate containing a flexible ester group and used propylene diamine as the active bridging functional group. First, they prepared amino-terminated methyl stearate (AMS) as a plasticizer modifier and then used the amino-terminated group (NH$_2$) of alms to nucleophilic replace the chlorine of PVC to prepare long-chain fatty acid ester grafted modified PVC (PVC-AMS) According to the test results, the glass transition temperature of the prepared inner plasticized PVC-AMS is significantly lowered. When the amount of AMS added is 1:30, the Tg can be reduced to 42.66°C, and the elongation at break reaches 323.52%, which shows a good plastic effect. The chemically modified internally plasticized PVC material has good stability and low migration and has broad application prospects in the fields of food packaging, toys, and medical equipment.

Yang et al. grafted unsaturated quaternary ammonium salts to PVC side chains to prepare a modified PVC resin (PVC-g-C) containing quaternary ammonium salt side chains, and then cross-linked polyethylene glycol diacrylate (PEGDA) in the resin to form a quaternary ammonium salt cross-linked resin (PVC-g-C–A), which not only imparts antibacterial properties but also improves hydrophilicity. [8] As can be seen from Figure 1, compared with PVC resin, the contact angles of PVC-g-C and PVC-g-C–A resins are all reduced, and the modified resin has better hydrophilicity and can be used in construction plastics. The antibacterial performance of the modified resin film was quantitatively investigated with Staphylococcus aureus, and the antibacterial activity (R) was used to describe the antibacterial effect. The quantitative antibacterial test results are listed in Table 1. The unmodified PVC resin film has almost no antibacterial activity as the control substance, and the antibacterial effects of PVC-g-C and PVC-g-C–A films are all very good, and the antimicrobial rate is above 97%. The antibacterial properties can be widely used in pipes, home textiles, clothing for the elderly and infants, masks, bed sheets for preventing decubitus patients, clothing for medical care and patients, clothing for special occasions, etc.

![Figure 1. The contact angle of PVC, PVC-g-C, PVC-g-C–A and water absorption of the film](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>Viable count</th>
<th>Antibacterial activity</th>
<th>Antimicrobial rate/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>1780</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC-g-C</td>
<td>13</td>
<td>2.1</td>
<td>&gt;99</td>
</tr>
<tr>
<td>PVC-g-C–A</td>
<td>60</td>
<td>1.5</td>
<td>97.07</td>
</tr>
</tbody>
</table>

Table 1. Test results of antibacterial properties of the film [8]
2.2. Cross-linking modification

Polyvinyl chloride cross-linking modification can be achieved through radiation and chemical approaches. Radiative cross-linking is to irradiate the polyvinyl chloride matrix under the condition of ultraviolet light to make the polyvinyl chloride generate free radicals and form C-C cross-linking bonds, while chemical cross-linking is to add a cross-linking agent to the polyvinyl chloride matrix to change the linear structure of polyvinyl chloride into a spatial network structure [5].

Xu et al. used radiation cross-linking technology to prepare a different PVC/epoxy resin (E-12)/Maleopimaric anhydride (MPA) composite foam [9]. Under normal temperature conditions, PVC, E-12, and MPA were placed in an internal mixer, followed by the addition of foaming agents and another pre-mechanical mixing, and mixed for 15 minutes at a temperature of 140°C. The blend was placed in a flat vulcanizer and molded at 140°C for 3-5 minutes. Then, the compressed sheet was irradiated and modified at a dose of 100 kGy using an electron accelerator. After irradiation, the PVC/E-12/MPA composite sheet was foamed at high temperature for 2 minutes at 220~240°C in a vertical foaming furnace, and then the foamed material was made into strips. The test results are shown in Figure 2. It was found that when the content of E-12/MPA (EM) curing was 10%, the degree and compression modulus increased by 23.4%, 26.7%, and 32.5%, respectively.

Figure 2. Mechanical properties of PVC/E-12/MPA composite foaming materials with different EM curing loadings [9]

Li et al. selected three different types of acid anhydrides including phthalic anhydride (PA), methylhexahydrophthalic anhydride (MHHPA), and pyromellitic dianhydride (PMDA) to prepare rigid cross-linked PVC foam materials with a semi-interpenetrating polymer network structure [10]. The key to crosslinking modification of PVC materials is the selection of crosslinking agents and the control of crosslinking networks. In cross-linking networks, the main factors affecting the cross-linking structure are cross-linking agents and process conditions. At present, mainstream commercial products use isocyanates and anhydride as crosslinking agents, and the crosslinking reaction is influenced by the type of anhydride compound under the same process conditions. It was found that when the acid anhydrides were PA and MHHPA, the rigid cross-linked PVC foam material had a faster foaming rate, better cell quality, and lower foam density. And because of the imide structure with good thermal stability, the thermal stability of the PMDA system is better than that of the anhydride-free system.

3. Physical modification

The main method of physical modification is blending. Yang et al. toughened and modified PVC resin with vinyl chloride butyl acrylate methyl methacrylate copolymer elastomer (VCE) to improve the impact resistance of PVC and compared it with PVC materials modified with traditional impact modifiers methyl methacrylate butadiene styrene copolymer (MBS), acrylate resin (ACR), and chlorinated polyethylene (CPE) [11]. The mechanical properties of PVC modified with different types of modifiers are shown in Figure 3. From Figure 3, it can be seen that as the content of the modifier increases, the tensile strength and bending strength of the PVC system gradually decrease, while the
elongation at break and notch impact strength gradually increase. When the same number of parts is added, PVC with VCE exhibits higher notch impact strength and elongation at break compared to PVC systems with CPE and ACR, reaching the level of PVC systems with MBS. This indicates that VCE has an impact modification effect on the PVC system, increasing its toughness and reducing its rigidity.

**Figure 3.** Influence of different modifiers on the mechanical properties of PVC [11]

By adding PVC-g-MAH to PVC/PTFE composites, Jiang et al. effectively improved the compatibility of PTFE and PVC and improved the mechanical properties of the composites [12]. As shown in Figure 4, the tensile strength and bending strength of the composite material increase with the increase of PVC-g-MAH content, while the impact strength first increases and then decreases with the increase of compatibilizer content. When the content of PVC-G-MAH is 5 wt%, the impact strength of the composite material is the highest.

**Figure 4.** Relationship between compatibilizer content and mechanical properties of composites [12]

4. Conclusion

This paper summarizes different approaches to PVC modification. Through research, the grafting modification of introducing fatty chains in chemical modification can improve the plasticity of materials, and the grafting of unsaturated quaternary ammonium salts to PVC side chains can improve the antibacterial properties of materials. The composite foam material modified by radiation crosslinking has improved tensile strength and compressive strength. In the crosslinking reaction of isocyanate and acid anhydride as the main crosslinking agent in chemical crosslinking, the material
with acid anhydride of PA and MHHPA has better heat resistance. In the physical modification, the impact modification effect of VCE on the PVC system is better than that of MBS, ACR, etc. Adding PVC-g-MAH to PVC/PTFE composites can effectively improve the compatibility of PVC, thereby improving the impact strength of composites.

However, since the modified PVC itself is stable, it is difficult to decompose and degrade after being discarded, which will destroy the negative feedback regulation of the ecology itself and pose hidden dangers to environmental protection. At present, the toxicity of PVC recycling and the remolding process is still relatively high, which has a great impact on the health of workers. Therefore, there is still a lot of room for exploration to maintain the stability of PVC during use and ensure the rapid natural degradation of PVC after being discarded. The cost of PVC material is not high, and the applicability is more comprehensive after improvement. It is a kind of material with relatively balanced practicability and economy. Using this kind of material with excellent properties can reduce costs and meet market demand. PVC material should further improve modification methods, reduce costs, enhance the economy and environmental protection, and have a bright prospect in close combination with related industries in the future development path.

References