

Recent Approaches to Modify Poly(vinyl chloride) Chemical Structure

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Abstract

Since its first discovery in the nineteenth century, polymer researchers have continued to study poly(vinyl chloride). Its characteristics, such as its thermal instability, are delicate by its structural flaws that result from its containing chlorine atom which is sensitive to UV light as a good leaving group. Many researchers suggested adding various types of organic and inorganic additives as photo and/or thermal stabilizers of poly(vinyl chloride). Recently this work has been expanded by extensive ongoing research to modify the chemical structure of poly(vinyl chloride) by replacing part of the chlorine atoms with other molecules which could enhance its stability against weathering circumstances. The last was carried out not only for common chemical reactions but also to improve the characteristics of poly(vinyl chloride) in particular applications. Based on reports from the past ten years, this study outlines many of the chemical alterations of poly(vinyl chloride) as well as associated uses. These alterations are organized following the modification of poly(vinyl chloride) through Carbon-Carbon and Carbon-Nitrogen linkages.

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1. Introduction

Due to their useful features and affordable price, poly(vinyl chloride) and its modified compounds are one of the most widely used polymers [1-4]. Nearly one-third of all discarded plastic in the world is covered with this polymer [5-7]. In contrast to produced HCl gas and conjugated polyene [8, 9], PVC has low thermal stability and begins to break down at 120 °C [10]. Chemical alteration is a useful method for making materials that are less biodegradable and more sustainable [11-13]. Yousif et al. [2] investigated how modifications affected the photochemical characteristics of PVC. Polyvinyl chloride (PVC) is a substance that has significant commercial and technological value. PVC is regarded as the second-most-produced substance in the world, behind polyethylene.

Following polyethylene and polypropylene, which have been widely utilized in industrial applications, PVC comes in third [14]. All polymers may be divided into two main classes based on how they respond to heat processing (thermoset and thermoplastic). Thermoplastics are polymers that may be heated and softened to be processed into the required form; poly(vinyl chloride, or PVC), for example, falls under this category. The term "Thermoset" refers to materials that contain covalent bonds acting as chemical links between individual chains during polymerization [15]. One of its key issues is still autocatalytic de-hydro-chlorination, which results in the

formation of conjugated double bonds when they are heated up during molding or use [16].

Since polyvinyl chloride has a very low melting point and very poor thermal stability, it is crucial to add the right stabilizers to stop the breakdown of polyvinyl chloride during thermal treatment. The main categories of thermal stabilizers to date include lead salts [17], metal soaps [18], and tin(IV) complexes [19]. The usage of these thermal stabilizers has certain drawbacks, including toxicity, environmental contamination, and high cost. Focus is currently being placed on nontoxic, ecologically safe, and affordable thermal stabilizers as a result of the global surge in environmental consciousness. One of the top five plastics used globally, soft PVC is commonly found in toys for kids, baby gear, food packaging, and medical equipment. The applications for PVC are shown in Figure 1 [20], The polar carbon-chlorine bond causes interactions between the PVC chains [21], which limit the chain's mobility and give the material its hard and brittle features. Plasticizers are therefore often employed in the molding process to enhance the processing characteristics of PVC and increase its applications' scope. A plasticizer is a compound that is mixed to a substance to improve its plasticity, making it more flexible, when handling it during manufacture. In order to fulfill the needs of the market or to make it easier to handle the raw material during fabrication, plasticizers are frequently added to polymers like rubber and plastic. For

instance, polyvinyl chloride (PVC), which is normally hard and brittle, is frequently given plasticizers in order to make it soft and malleable. This makes PVC ideal for goods like garments, bags, hoses, and coatings for electrical wires. Clusters of tiny primary particles make up the PVC resin created by the suspension polymerization technique, which makes the substance porous [22].

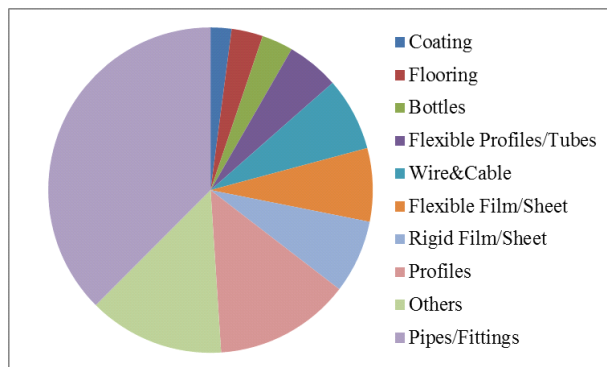


Figure 1. Applications uses of PVC [20].

Due to its impressive collection of qualities, including flexibility, simplicity, thermal and mechanical resistance, ease of production, porous, and cheap, plasticized (PVC) is the preferred material for disposable blood bags utilized for the collection, storage, and transfusion of human blood components [23].

Due to its unique qualities, such as its low cost, good process ability, processing capacity in rigid and flexible shapes, and strong synthetic resilience, PVC has drawn particular attention [24,25]. PVC is a solid plastic that is often utilized due to its low cost, quick manufacture, long-lasting qualities, and respectable mechanical and chemical capabilities [26]. It is used as a matrix for a variety of natural fibers, including kenaf [27], wood [28], sisal [29], and empty fruit bunch fibers from oil palms [30]. PVC is frequently regarded as a non-stable polymer when molded and used in high-temperature environments. Significant auto-catalytic dehydrochlorination of poly (vinyl chloride) results in the formation of conjugated double bonds [31]. In practice, it causes the polymer to discolor in an unfavorable way and alters its mechanical and physical characteristics [32], as well as causing chain scission or crosslinking to lower or raise the polymer's average molecular weight. Thermal dehydrochlorination is generally thought to be the result of structural flaws such as allylic chlorine accompanied by unsaturated fragments [33], tertiary hydrogen and chlorine atoms associated with branches [34], reactive terminal groups like double bonds [33], oxygen-containing units [34], or peroxide fragments [35,36]. Pipes and sidings are the main applications for poly (vinyl chloride), whereas pipes and window frames are more prevalent in Europe and Asia. PVC windows are now being used more often by builders in Japan, in part due to the better insulation they provide, which lowers heating and cooling costs. PVC is increasingly in demand in China for both consumer items and building materials. Soft PVC is

used for floor coverings, artificial leather products, insulating wire and cable, and film and sheeting. Figure 2 depicts the global PVC usage in 2016.

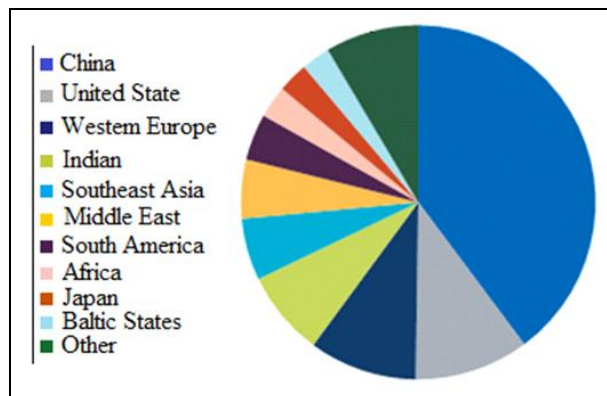
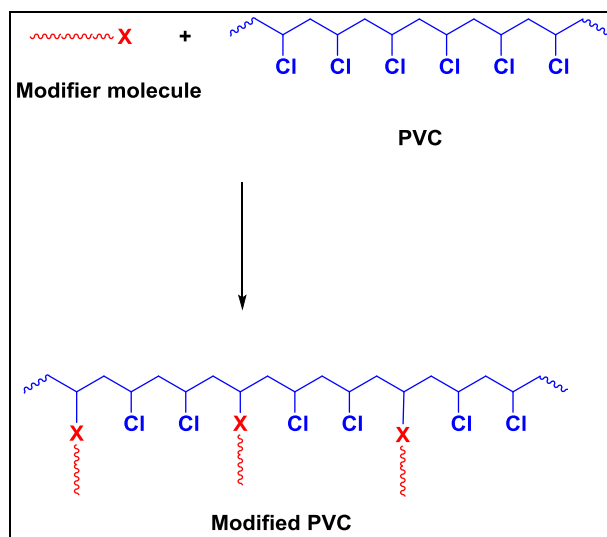


Figure 2. World consumption of poly (vinyl chloride) in 2016.

2. Modification of PVC

An overview of the most recent PVC chemical alteration trends recorded over the last twenty years is given below. Conferring to the bond established between the carbon atom of PVC chemical structure and various atoms from the modifier side such as (X=N, O, S, or Hal) [37], as shown in Scheme 1, modifications are handled accordingly. The nucleophilic alteration of PVC and its associated uses are first highlighted before these changes are shown. Scheme 1 shows the general substitution reaction to obtained modified PVC chemical structure.



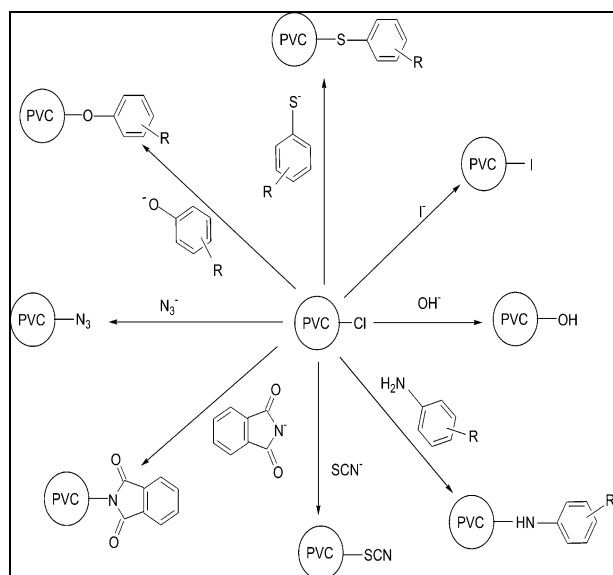
Scheme 1. General reaction of PVC modification.

2.1 Nucleophilic modification of PVC:

According to Frye-Horst research on PVC "reversible blocking mechanism" idea [38], a great deal of study has been put into showing that chlorine atoms exist *via* performing various alterations on PVC chemical structure. The dechlorination of PVC was aided by all chemical modifications; typical chemical reaction pathways for

example elimination, substitution, and cross-linking were used. The reaction that has been the most thoroughly researched is nucleophilic substitution. But when the nucleophile's basicity (Nu) outweighs its nucleophilicity, the removal of HCl may fiercely contend with the substitution. Phase transfer catalysts, photo-reaction, and ultrasonic methods have all been used to study the modification of PVC under a variety of circumstances.

In Scheme 2, a few nucleophile substitutions on PVC are compiled, for the sake of succinctness, the azidated PVC [12] is a good example of a later and useful chemistry on the chemically modified PVC. By reacting azidated PVC with salicylaldehyde, for instance, a PVC containing imine groups as chelating units that may react to form complex molecules. It should be mentioned that PVC linked to NH₂ group can be made in two ways first reducing azidated with LiAlH₄ second by reacting imino side with NH₄OH; to create PVC-NH₂ linkage.



Scheme 2. Examples of nucleophile substitutions on PVC.

2.2 PVC substitution based on stereo-chemistry:

The study projects have not only revealed that there are abnormally Cl atoms within PVC chemical structure, thus it has also revealed other unexpected characteristics. The predominance of substitution in some areas of the PVC film, particularly on the isotactic and heterotactic microstructures, is one noteworthy example; the syndiotactic portions, though, are not susceptible to the reaction. Thus, obvious result of region selectivity substitution was a modification in several of the physical characteristics of PVC, specifically the T_g for the glass transition. For over 20 years, the polymer school (ICTP) has been a leader in studying the chemical alteration aspects of PVC. Investigators on PVC have learned more about a variety of difficulties as a result of that school. The effect of the nucleophile's polarity, electronegativity, and size on the modification of PVC microstructure was thoroughly evaluated in two papers [40,41]. It was discovered that these

traits improved molecular microstructure-based processes. In actuality, the isotactic and heterotactic contents of PVC in a cyclohexanone decreased as a result of the nucleophilic substitution reactions, while the syndiotactic level increased. These changes in microstructure were conversion-dependent. The stereoselective increase of the substitution was caused by the steric hindrance and moderate reactivity of 2-mercaptobenzothiazolate. Overall, the findings dispersed across the literature obviously show that the numerous chemical endeavors have really produced highly valuable features in the modified PVCs and have made it possible to better understand the inherent qualities of PVC itself. Figure 3 shows the main three stereo structures of PVC which are syndiotactic, atactic, and isotactic.

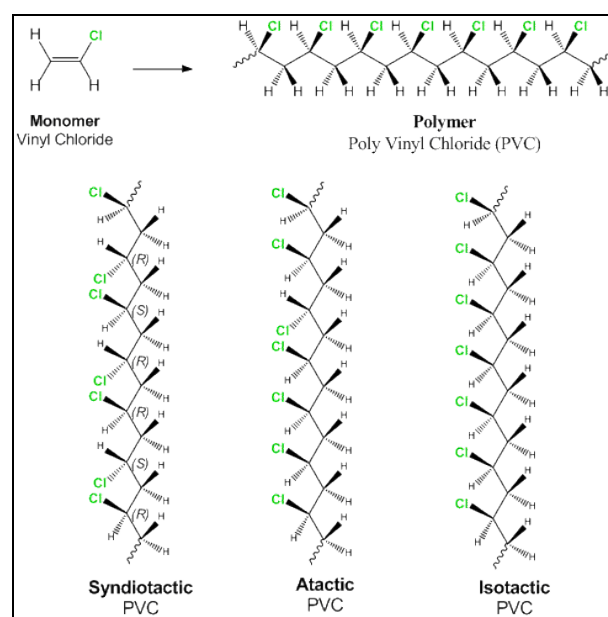
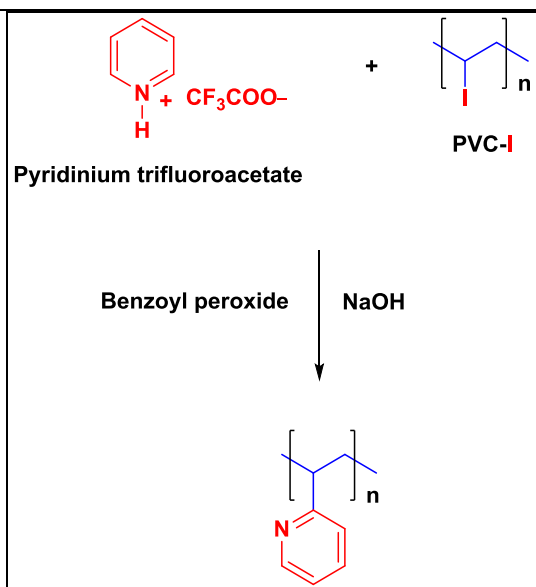


Figure 3. The stereochemistry of PVC chemical structure.

It is challenging for the chains to lay close together in polyvinyl chloride (PVC) due to the chlorine atoms' random protrusion from the chain and their huge size. The majority of polyvinyl chloride is amorphous, with only a few spots crystallizing.

2.3 Modified PVC through C-C linkage:

Through a variety of chemical processes, organic segments for example fullerene, acrylate, pyridine, etc. groups were bonded to the PVC backbone by a carbon-carbon link. Pyridine's introduction into polymer matrices has generated a lot of attention. Typically, the pyridinic unit has been directly or indirectly bonded to PVC using the nitrogen atom or an element other than carbon. In fact, Moulay and Zeffouni [42] used Minisci's homolytic alkylation of heteroaromatic bases, to modify PVC via pyridine. In this experiment, PVC was first iodinated to produce PVC linked to iodine, that was then given a homolytic reaction with pyridinium trifluoroacetate to produce Py-PVC as shown in Scheme 3.

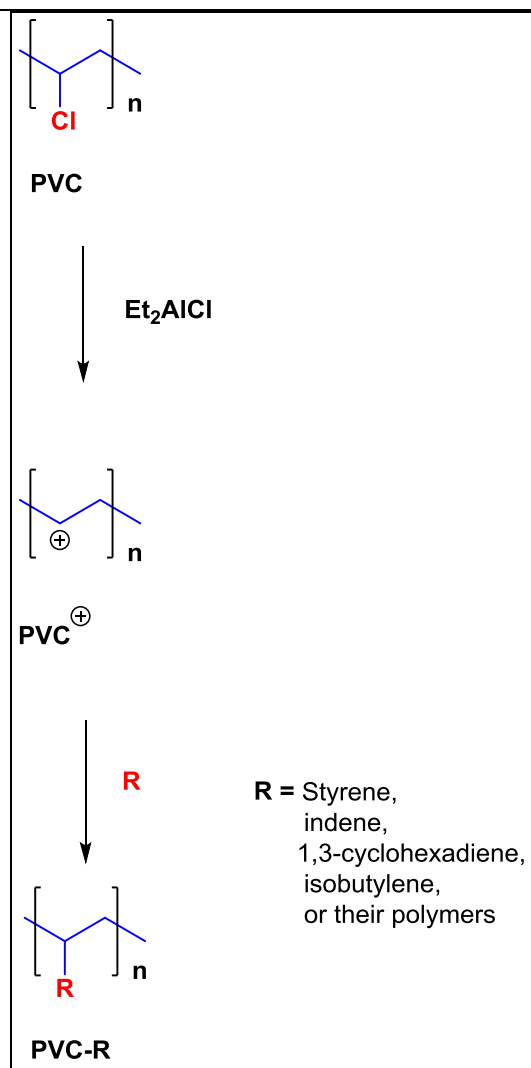


Scheme 3. Modification of PVC carbon-carbon bond.

C-C bonding was used to connect pyridine to the PVC backbone. In PVC-I with a 30% iodine content and under ideal reaction circumstances, it was discovered that the total substitution degree did not surpass 3%. The T_g of PVC-pyridine was measured to be 106 °C, as opposed to that of the unmodified PVC which is 81 °C, and I-PVC 111 °C due to the non-negligible influence of this minor amount of pyridination. Through the use of carbon-carbon bonds and a radical replacement of the chlorine atom, Martnez et al. [43] fullerene to the PVC chains. Kennedy and Pi [44, 45] were the first to patent their work on allylating PVC (PVC-All), utilizing allyltrialkylsilane in the existence of $AlEt_2Cl$ catalyst. There were about three allyl groups inserted within each PVC chain. Thermal research of PVC-All demonstrated a significant increase in thermal stability. By treating the defect-free PVC with 2-allyloxyethanol [46]. It shows the reaction being carried out in DMSO at 75 °C and using sodium dithionite and sodium bicarbonate as catalysts.

2.4 Grafting of PVC using a cationic process:

Grafting polymerization of several common monomers has been another component of PVC modification. A number of PVC-based grafted copolymers have been published by Kennedy, a pioneer in this field of study, and his colleagues [47–49] using a cationic process, see Scheme 4. On the course of the grafting polymerization, the impact of temperature changes between 50 °C and 20 °C was evaluated. Geff made the general observation that grafting efficiency increased with decreasing temperature.



Scheme 4. Using a carbocationic process to modify the PVC chemical structures.

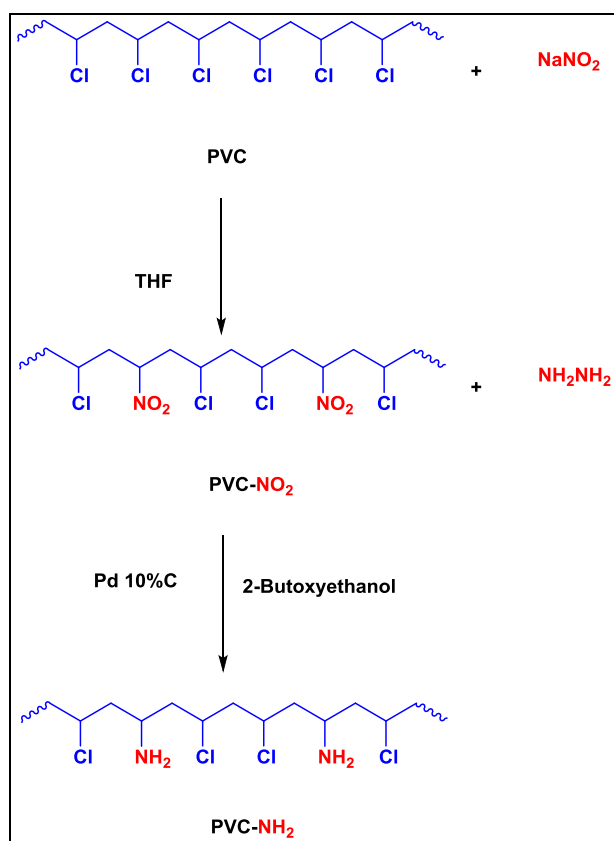
When grafting acrylate derivatives with PVC, Bicak and his colleagues [50,51] used copper atom as polymerization catalyst, as common polymerization techniques. High grafting yields of 61.8 and 51.2 percent, respectively, were achieved in 7.5 hours.

Grafting polymerization of PEHA-PVC that are well dissolved in THF, DMSO, and DMF organic solvents were produced as a result of ATRP co-polymer of EHA, which substituted with chlorines of PVC chains. In order to achieve the grafting, -methylcellulose was used as a suspending agent in an aqueous solution. The amount of grafting varied with time, reaching 26% for 16 hours and 46% for 24 hours of reaction time. Approximately 170,000 and 2.24–2.29, respectively, were the molecular weights M_w and polydispersity indices PDI. The plasticizing influence of PEHA ($T_g = 84$ °C) and its suitable to PVC were confirmed when the T_g of PVC, which was originally at 90 °C, changed to 60 °C for a grafting percentage 16%. (one T_g was observed for PEHAPVC). The grafted

polyacrylate side chains so enable an internal plasticization of PVC [52].

2.5 Modified PVC via C–N linkage:

By reacting PVC with sodium nitrate in a suitable solvent, the PVC linkage to NO₂ and NH₂ groups, was created with a high modification degree (73%) and a molecular weight that was around one-sixth that of started PVC, most likely as a result of chain cleavage. The PVC-NO₂ was insoluble in water but can be dissolved in few organic solvents such as ethyl acetate, and DMF. About 9.9% of the brownish PVC-NO₂ had unsaturation that was produced in-situ. In ambient settings, this PVC-NO₂, while having a lot of nitro starting compound, did not exhibit extensive characteristics. According to the authors, the process of nitration does not entail the direct replacement of chlorine by nitro. Thus, the releasing of hydrochlorides molecules happens first, then the addition of nitro group (S_N2 mechanism). Reacting the product (PVC-NO₂) with hydrazine using Pd-10%C catalyst and 2-butoxyethanol as solvent gives PVC-NH₂ modified polymer as shown in Scheme 5.



Scheme 5. Modification of PVC chemical structure with nitro and amino groups.

The plasticized PVC is recognized to have various drawbacks, which restrict its applicability. These negatives include the poor mechanical, chemical, and thermal resistance qualities as well as the plasticizer migration phenomena; keep in mind that the plasticizers used are not always non-toxic. In an effort to overcome this

disadvantage, Jimenez and colleagues [53] used rheological and thermogravimetric analyses to investigate the linkage of isophoron diamine to PVC chains from two sides. The findings showed that isophoron diamine was an effective cross-linker for PVC plastisol, and that the cross-link density enhanced with increasing curing time. According to the thermal study of PVC-isophoron diamine as shown in Figure 4, the isophoron diamine cross-linker caused PVC to thermally degrade, which was catalyzed by evolved HCl and resulted in a significant weight loss during heat treatment.

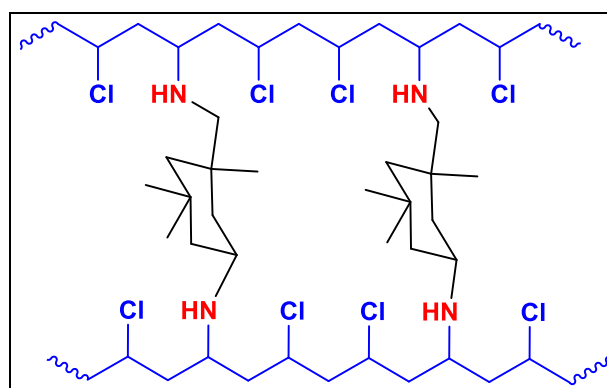
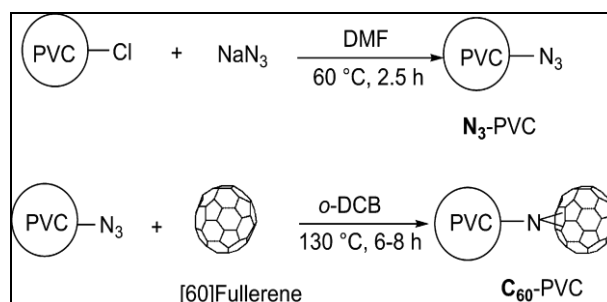


Figure 4. Using isophoron diamine moiety to cross-link PVC chains.

2.6 Azidation to modify PVC:

Typically, the azide function of fullerene C₆₀ is used to link it to polymer matrices [54,55]. For instance, Rusen and his coworkers' [56] azidation of PVC in DMF, as shown in Scheme 6 using sodium azide is an example. After 2.5 hours of response time at 60 °C, a 20 percent azidation extent was attained. In order to create PVC-C₆₀, the azidated PVC-N₃ was exposed to a reaction with C₆₀ in o-DCB. For response durations of 6 and 8 hours, respectively, the fullereneation degree was about 1.5 percent.



Scheme 6. Using azide group to link fullerene C₆₀ to polymer matrices.

As a result of the molecular weight increase, no degradation was seen during the fullereneation process. Following the same method, poly(vinyl alcohol) fullereneation resulted in a modification degree of less than 2 percent [57]. In a different study, Martnez [58] used the azide group to graft polystyrene onto PVC in order to use the stereoselective nucleophilic substitution of PVC.

3. Conclusions

To conclude, researchers have been studying polymers ever since they were first discovered in the eighteenth century (vinyl chloride). Because it contains a chlorine atom, which is vulnerable to UV radiation and serves as an excellent leaving group, it has structural faults that make some of its features, such as its thermal instability, delicate. Numerous studies recommended using different organic and inorganic compounds as polymer photo- and/or thermal stabilizers (vinyl chloride). This work has since been enhanced by intensive continuing research to alter the molecular structure of poly(vinyl chloride) by substituting other molecules for some of the chlorine atoms, which might improve its durability under weathering conditions. The previous was done not only for typical chemical reactions but also to enhance poly(vinyl chloride) features for specific uses. This research lists several chemical changes made to poly(vinyl chloride) as well as related applications, based on reports from the previous 10 years.

4. Future Perspective

We think that the process of PVC modification has not ended yet so it could be possible to modify the PVC with some naturally extracted molecules and use them in medicine as drug-releasing agents, and CO₂ storage. Moreover, it is possible to use modified PVC as a stereo-selective organic reagent (stereo-catalyst) for different organic reactions. Since it has a chiral molecule center.

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