SOME STUDIES ON CHEMICAL MODIFICATION OF POLYAMIDE-6 (NYLON-6) FIBERS

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AIM OF THE WORK

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The present work aims at increasing the rate of grafting of 2-dimethylaminoethylmethacrylate onto polyamide-6 fibers without homopolymer formation as an attempt for carrying out grafting during the finishing process on the production line of polyamide-6 staple fibers. To achieve this grafting of 2-dimethylaminoethylmethacrylate was carried out onto modified polyamide-6 fibers, containing chemically bonded quaternary ammonium groups, using $K_2S_2O_8$ - Cu^{2+} redox system as initiator, instead of those containing quaternary ammonium salt in the form of physical mixture with the fibers.

ABSTEACT

Some studies on chemical modifications of polyamide-6 (Nylon-6) fibers

Nasser Hassan Abdella - Synthetic and proteinic fibres department, Textile research division, National research center (2005).

In recent years, chemical modification of polyamide fibers by graft copolymerization has received considerable interest, since preformed polymers are incapable of diffusing into the internal structure of the polymer. With the wide variety of vinyl and other monomers available, grafting promises to be a potentially powerful method for producing substantial modification of properties.

Among various types of monomers used for grafting onto polyamide fibers 2-dimethylaminoethylmethacrylate (DMAEMA) has an important place because of its specific properties which can be imparted to fibers. During the last decades this monomer has been grafted onto polyamide -6 fibers containing a small concentration of quaternary ammonium groups (QAG). These groups were introduced by impregenation of fibers with an aqueous solution of quaternary ammonium salt (QAS). It was stated that graft copolymerization reaction initiated in this case with $K_2S_2O_8$ proceeded with a small amount of homopolymer formation. Although the rate of reaction in the above mentioned case was higher than that obtained when other traditional method of grafting were used , it is still lower than the rate required for carrying out grafting of DMAEMA during the finishing process on the production line of polyamide staple fibers .

The present work aims at increasing the rate of grafting of 2-dimethylaminoethylmethacrylate onto polyamide-6 fibers without homopolymer formation as an attempt for carrying out grafting during the finishing process on the production line of polyamide-6 staple fibers. To achieve this grafting of 2-dimethylaminoethylmethacrylate was carried out onto modified polyamide-6 fibers, containing chemically bonded quaternary ammonium groups, using $K_2S_2O_8$ - Cu^{2+} redox system as initiator, instead of those containing quaternary ammonium salt in the form of physical mixture with the fibers.

The general kinetic of the graft copolymerization reaction induced by a above mentioned system was investigated. The rate of grafting has been determined by varying the concentration of DMAEMA, K2S2O8, metallic ions, polydiallyldimethylammonium chloride (PDADMAC), and the reaction temperature. The apparent activation energy was calculated and the reaction mechanism was suggested.

The effect of polymerization of PDADMAC and PDMAEMA with nylon-6 fibers on some properties of the latter was investigated. Properties examined include internal structure (by x-ray), fiber surface topography (by SEM), moisture regain, dyeing properties, mechanical properties, and thermal properties (by DSC-TGA).

Key Words

- **Grafting**
- **DADMAC**
- **PDADMAC**
- **DMAEMA**
- **PDMAEMA**
- **Initiating system**
- **Reaction order**
- **X-ray**
- **Surface topography (SEM)**
- **Moisture regain**
- **Dyeing properties**
- **Mechanical properties**
- **Thermal properties (DSC – TGA)**
- **Potassium persulphate**
- **Copper sulphate**
- **Nylon-6 fibers**

PREFACE

The global volume of fiber production in the year 2003 rose to 56.12 million tons (excluding Rame, flaxe, hemp, jute and sisal). With a world population of 6.23 billion, this corresponds to an average per capita consumption of 9.0 kg.

Man- made fibers have come to occupy a very important position in textile field. In 2003 these fibers have accounted for 33.66 million tons, comprising a 60% market share. The highest growth comes from polyester fibers which expanded in 2003 by almost 6%to a new record level of 22.1 million tons. As opposed to this, production of polyamide fibers (filament, yarns, and staple fibers) rose by only 0.4% to 3.93 million tons.

With regard to the future outlook for polyamide fibers the global fiber demand could pick up from the current estimate of 4 million tons and grow at an average rate of between 2 to 3%.This forecast scenario is based on some premises. China will experience very healthy polyamide fibers growth rate as its nylon textile industry continues to boom. Russia represents a further large potential. The polyamide fibers and textile industries are still very under developed. India has a very developed polyester fiber industry, but so far not installed polyamide fibers capacity to meet strong polyamide fibers demand for apparel and industrial yarn. In south America, Brazil will also experience strong polyamide fibers demand.

The fact remains that nylon fiber per capita consumption in the above region is only 0.4 kg versus over 1.0 kg / capita in the US and Western Europe, leaving room for strong growth. This means that there will be continued transfer of polyamide fibers industries to Asia from US and Europe.

Other factors which will positively affect future growth in polyamide fibers include:

- Very strong demand in airbag and tire yarn applications

- A move to polyamide carpet in Asia as the standard of living increases
- Nylon will continue to be used in blends with other fiber
- Advances in technology, cost improvement and application development.

Polyamide fibers have a set of unique, intrinsic characteristic, such as:

i) high breaking resistance ;
ii) high abrasion resistance and high durability, and
iii) good resistance to biological influences.

However, polyamide fibers have some inherent drawbacks, which limit their fields of usage, and thereby directed the attention, towards improving their properties. These drawbacks can be briefly formulated as follows:

a) poor moisture content;
b) high static build up;
c) high pilling tendency;
d) poor heat and thermal resistance;
e) low inflammability; and
f) poor resistance to light, weather, alkalis and concentrated acids.

Nowadays it is possible to construct the properties of polyamide fibers .By making physical or chemical modification, the fiber can directly be adjusted to the intended end –use field.

In recent years, chemical modification of polyamide fibers by graft copolymerization has received considerable interest, since preformed polymers are incapable of diffusing into the internal structure of the polymer. With the wide variety of vinyl and other monomers available, grafting promises to be a potentially powerful method for producing substantial modification of properties.

A variety of property changes can be imparted to polyamide through grafting. Some of the most important change in properties which have been brought about by grafting to polyamide fibers are viscoelasticity, stereoregularity, hygroscopicity, water repellency, improved adhesion to a variety of substances, improved dyeability, settability and soil resistance, bacteriocidal properties, antistatic properties and thermal stability.

Various methods have been used for grafting vinyl monomers onto polyamide fibers. However, most of these methods used have limited usefulness due to:

a) long time to achieve the required graft yield;
b) monomer wastage though undesired homopolymerization;
c) irregular reproducibility in graft yield; and
d) unapplicable on industrial scale.

Needless to say that the chemical modification of polyamide fibers via grafting with vinyl monomers could be applicable on industrial scale, only when the grafting processes proceed with higher rate and without homopolymer formation.

Recently, a novel method for grafting of acrylamide and methacrylic acid to nylon-6 fibers was developed. The method is based on modification of nylon-6 fibers by creation of quaternary ammonium groups (QAG) in polyamide macromolecules, complexation with initiator and finally grafting with choused vinyl monomer. The salient feature of this method it that grafting occurs with high rate and almost without homopolymer formation.

Among various types of monomers used for grafting onto polyamide fibers 2-dimethylaminoethylmethacrylate (DMAEMA) has an important place because of its specific properties which can be imparted to fibers.

During the last decades this monomer has been grafted onto polyamide -6 fibers containing a small concentration of quaternary ammonium groups (QAG). These groups were introduced by impregenation of fibers with an aqueous solution of quaternary ammonium salt (QAS). It was stated that graft copolymerization reaction initiated in this case with $K_2S_2O_8$ proceeded with a small amount of homopolymer formation.

Although the rate of reaction in the above mentioned case was higher than that obtained when other traditional method of grafting were used , it is still lower than the rate required for carrying out grafting of DMAEMA during the finishing process on the production line of polyamide staple fibers .

In an attempt for increasing the rate of grafting of DMAEMA onto polyamide-6 fibers using $K_2S_2O_8$ - Cu^{2+} initiating system without homopolymer formation we started, in the present work, with fibers containing chemically bonded QAG instead of those containing QAS in the form of physical mixture with the fibers .

The present thesis subdivided into two main parts; namely general part and special part. Both parts contain 4 chapters.

A general part deals with literature survey.

Chapter I: modification of polyamide-6 fibers properties by graft copolymerization

A special part deals with the experimental work, results and discussion

Chapter II: Experimental work.

The results and discussion of the thesis are given in

Chapter III: Grafting of 2-dimethylaminoethylmethacrylate to nylon-6 fibers containing chemically bonded quaternary ammonium groups.

Chapter IV: Characterization of modified nylon-6 fibers

Summaries in English and Arabic as well as a list of references are also given.

CHAPTER I

MODIFICATION OF NYLON-6 FIBERS PROPERTIES BY GRAFTING WITH VINYL MONOMERS

1- Introduction

Recently, most advances in research made in textile fibers have been aimed at giving some desirable properties and introduced new functionalities onto polymer surface .The new functionalities and properties introduced include improved surface hydrophilicity, hydrophobicity, biocompatibility, conductivity, anti-fouling, surface hardness, surface roughness, dyeability, thermal stability, water repellency, solvent and chemical resistance, soiling resistance and adhesion to rubber, etc..**[Uyama, Y.; et al. (1998)]**[149]**[Rao, B. V.; et al. (1987)]**[120]**.**

By making physical and /or chemical modification the fibers can directly be adjusted to the intended end – use field. To achieve the improvement of the polyamide -6 fibers, the physical and / or chemical structure may be changed. The physical structure of polyamide can be changed by means of physical modification, whereas change in its chemical structure can be achieved via chemical modification.

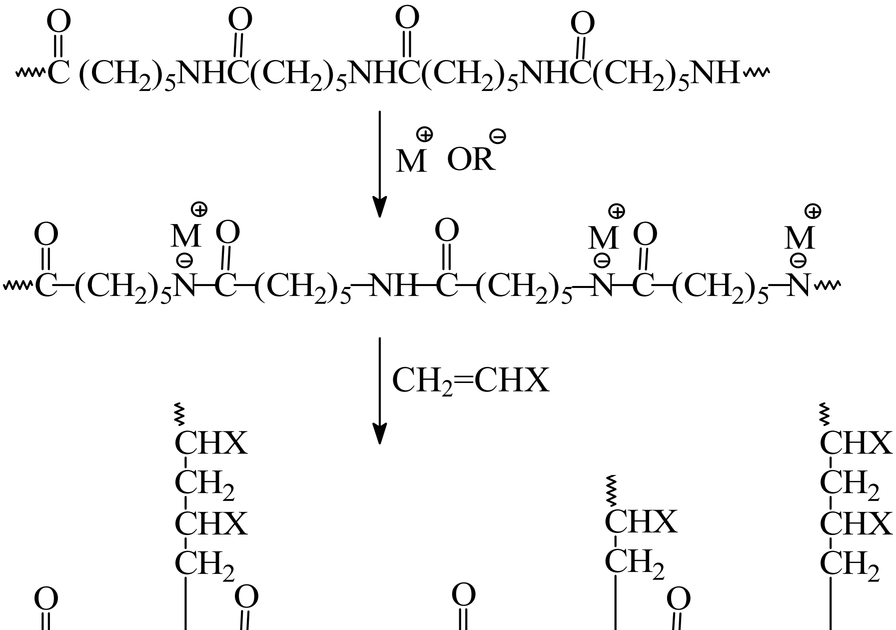
Although a variety of technologies have been proposed for improving surface characteristics, surface modification of polymer by grafting is rather new technology. It offers versatile means for incorporating new functionalities into existing polymers. However, in spite of the potentially wide applications of such surface grafting technology, this has been applied only to a few cases in industry, probably because the basic studies required for the application are still in their infancies. Another reason may have been that such a grafted polymer surface is relatively expensive to produce.

2- METHODS USED FOR GRAFTING VINYL MONOMERS ONTO NYLON-6 FIBERS

Various methods have been used for grafting vinyl monomers onto nylon-6 fibers. The most important methods which have attracted attention in recent years are anionic graft copolymerization and free radical graft copolymerization **[Nayak, P. L. (1979)[106]. Bhattacharya, A.; et al. (2004)[9]]** .

2-1. Anionic Graft Copolymerization

In anionic graft copolymerization nylon-6 is treated with alkali metal oxides such as sodium methoxide, potassium methoxide, potassium ethoxide **[Ikeda, I.; et al. (1980)[68]].** The metal plated nylon-6 is then treated with vinyl monomers in a polar aprotic solvent such as THF, DMSO, etc. The mechanism of anionic graft copolymerization is as follows:



Graft copolymer of Nylon-6

2-2.Free Radical Graft copolymerization

In the radical graft copolymerization the formation of initiating radical on the backbone of nylon-6 can be achieved by the following methods:

a) Radiation Initiation
b) Photo Initiation
c) Plasma
d) Chemical Initiation

2-2-1. Radiation Initiation

Radiation graft copolymers may be initiated by two techniques.

1- Pre-irradiation technique.
2- Simultaneous or mutual radiation grafting.

With the pre-irradiation technique the substrate is irradiated before being brought into contact with the monomer. In the case of the mutual radiation method the substrate is placed in a monomer solution or vapor and the whole system is irradiated. In general, the later method suffers from the disadvantage that high amount of homopolymers are formed which depend on the radiation sensitivity of the monomer. On the other hand, homopolymers formed by the first technique are quite small as compared with that of graft add – on.

Radiant energy is usually applied to the substrate in the form of high energy protons (γ rays) from radioactive isotope source or as high energy electrons (β rays) . Cobalt – 60 is convenient source of γ rays.

When polyamides are subjected to high energy radiation, the most obvious change is the production of a transient color whose nature is dependent on the chemical composition of the polyamide **[Zemmerman, J. (1959)[162]].** This color is indicative of an unpaired electron, generally on the α–carbon atom adjacent to the amide group. In the radiolysis of polyamides the predominant free radical species is formed by removed of hydrogen atom from the α–carbon adjacent to the amide group **[Zemmerman, J. (1959)][162] [Rogers, M. T.; et al. (1969)][121].** It has been observed that the free radical decay rate decreases with increasing dose up to about 25to30 Mrad and then levels off **[Shinohara, Y.; et al. (1962)][133].**

A major usefulness associated with the irradiation of polyamides has been in the area of grafting .A large number of vinyl monomers have been grafted to nylon-6 fibers.

The radiation–induced grafting of acrylic acid to nylon-6 in solution was extensively studied by using heterogeneous and homogeneous systems. In studies with the heterogeneous systems, the authors **[Huglin, M. B.; et al. (1969)[64],(1971)[65], (1972)[67], (1973)[66]]** have reported on the main feature of radiation grafting of acrylic acid in an aqueous solution to a nylon-6 film .Cupric chloride was incorporated in the aqueous solution to suppress homopolymerization .

Dziedziela, W. D. and Coworkers (1975)[42] have reported the radiation–induced grafting of acrylic acid to nylon-6 in homogeneous medium. The homogeneity of the reactants and products was achieved by the use of the mixed solvent, O-chlorophenol – methanol.

Liquid- and vapor phase grafting of acrylic acid onto nylon-6 by the mutual irradiation technique has been reported by **[EL-Azmirly, M. A. et al. (1975)][44] [Malcom and Ronda (1980)][91] .**

Radiation – induced graft copolymerization of methyl methacrylate onto nylon-6 was studied **[Nayak, P.L., et al. (1988)][103] .** The effects of monomer, dose rate, and of solvents on the grafting rate were investigated.

Factors affecting the radiation grafting of 2-dimethylaminoethyl methacrylate onto polyamide (nylon-6) fabric have been studied by **[ElGndy, E.; et al. (2000)][45].**

Nylon was modified by various workers **[Neil, T. (1972)[111]; Schambrg, E; et al. (1976)[123]]** using γ- rays to carry out radiation – induced graft copolymerization of styrene and acrylonitrile. The kinetic of the process was studied.