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Study of the UV protective and antibacterial properties of aqueous polyurethane dispersions extended with low molecular weight chitosan

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ABSTRACT

A series of aqueous dispersions of polyurethane (PU) and low molecular weight chitosan ($CS_{(LMW)}$) has been prepared in two steps synthetic process. In first step PU prepolymer, with NCO termini were prepared by reacting isophrone diisocyanate (IPDI), poly (caprolactone) diol (CAPA, Mn 1000), and 2,2-dimethylol propionic acid (DMPA), followed by neutralization of PU prepolymer with triethylamine (TEA). In second step PU prepolymer chain was extended by low molecular weight chitosan followed by dispersion formation by adding calculated volume of water. Molecular characterization of $CS_{(LMW)}$-PU finishes was done by FTIR and application on poly-cotton blended fabric samples was confirmed by scanning electron microscopy (SEM). Antimicrobial and UV protective performance of treated fabrics was performed by AATCC 100 and AATCC TM183 methods respectively. Furthermore, it shows that the addition of chitosan remarkably increases antimicrobial and UV protective properties of PUs.

1. Introduction

In the past few decades, water born polyurethanes have emerged as a novel class of environment friendly alternatives to solvent based adhesives and coatings. Water based polyurethane dispersion (PUD) is a colloidal system of two components formed by dispersing thermoplastic polyurethane particles, incorporated with internal emulsifying groups in polymer chains, in aqueous medium. The main application areas of PUDs include adhesives, floor coatings and textile coatings [1,2]. Conventionally, PUDs are prepared by one of two processes: the ionic PU, polymerized in solvent, is dispersed in water, or ionic PU pre-polymer with an isocyanate (—NCO) terminals is prepared in an aprotic solvent or in the melt, neutralized with tertiary amine and reacted with a chain extender in aqueous medium. Non-ionic polyurethane dispersions are also prepared by incorporating polyoxyethylene as side chains. We have synthesized anionic aqueous carboxy-functional PU dispersions extended with low molecular weight chitosan. The stability of anionic PUDs is reported to be higher due the fine particle size leading to formation of\ films having superior chemical and mechanical properties [3]. Exceptional properties PUDs have established them as ideal binders for adhesives, sealants, coatings, foams, fibers and elastomers [4]. Aqueous PU dispersions are mostly used as hard coatings for wood and metallic surfaces and as flexible coatings for textiles [5]. Aqueous PU dispersion have received added prominence due to their outstanding characteristics including quick drying time, transparency, glossiness, flexibility, non-flammability, abrasion resistance, impact resistance and adhesion with most surfaces [6].

Structural modification by incorporation of ionic group in PU main chain is a distinctive technique for dispersion of PU in water [4]. The overwhelming properties of PU dispersion include solvent-free or low solvent content, low odor, low temperature drying, low viscosity at high molecular weight, many options for one component applications and excellent performance.

Biomaterials are available from abundant natural sources and global sustainability is maintained through their use without consumption of threatened resources. The biomaterials are non-toxic, ecofriendly, biodegradable and comparatively easy to handle with no or less health-related issues. With the growing awareness about healthy life style and cleaner surroundings, there is an increasing global interest for the use of biomaterials. Because of environ-

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mental apprehensions and scarce petroleum resources, aqueous polyurethane dispersions based on materials from natural and renewable resources have attracted much attention in academic research and industrial applications over the past twenty years. A number of researchers have reported the synthesis of PU dispersion based on biomaterials as such or after chemical structural modifications for various applications as coatings, paints, adhesives, composites and resins [7,8]. Synthesis of polyurethanes extended with chitosan and application as biocompatible, antibacterial and blood compatible material has also been well documented [9–13].

In past two decades, natural antimicrobial materials have got preference over conventional antimicrobial agents because of their hazardous side effects. Based on vast research done and reported, chitosan has been accepted as a natural antimicrobial biopolymer exhibiting excellent antimicrobial activity against a diverse range of pathogenic and putrefaction fungi, and bacteria (Gram-positive and Gram-negative bacteria). The antimicrobial and antifungal activities of chitosan have been investigated by several researchers, with particular emphasis on their ability as a food preservative [14]. Chitosan can be applied to extend the storage life of different categories of food materials [15]. Chitosan, derived from chitin, is a hydrophilic polysaccharide having a broad antimicrobial spectrum. Chitin and chitosan have been studied, in vivo and in vitro, as an antimicrobial biopolymer against a broad array of microorganisms as fungi, algae, yeast, gram positive and gram negative bacteria in the form of composites, films and solutions [16]. Early investigations about antimicrobial potentials of chitin and chitosan, dates back to 1980–1990s. Generally, in these studies the chitosan is considered to be a bactericidal (kills the live bacteria or some fraction therein) or bacteriostatic (hinders the growth of bacteria but does not imply whether or not bacteria are killed), often with no distinction between activities. Recent data in literature has the tendency to characterize chitosan as bacteriostatic rather than bactericidal [17], although the exact mechanism is not fully understood and several other factors may contribute to the antibacterial action [18].

A number of models have been proposed for antibacterial action of chitosan among which the most accepted models are (I) penetration of oligomeric chitosan into the cells of microorganisms and inhibition of the growth of cells by preventing the transformation of DNA into RNA [19] and (II) the electrostatic interactions between the positive charge of amino group in chitosan molecule (at pH lower than 6.3; the pKa value of chitosan) and negative charges on the surface of bacterial cells. These electrostatic interaction consequences in dual interference: (a) by promoting the alterations in properties of bacterial membrane wall permeability: the binding of cationic chitosan to sialic acid present in phospholipids and subsequently restricting the passage of microbial substances, thus provoking the internal osmotic imbalances thereby inhibiting the growth of microorganisms [20,21] and [b] by the hydrolysis of the peptidoglycans in the microbial cell wall, resultantly causing leakage of intracellular electrolytes like potassium ions (K^+) and other low-molecular weight proteinaceous constituents like nucleic acids, proteins, glucose and lactate dehydrogenase enzymes [22–24]. Supporting this proposal, it has recently been demonstrated that only the soluble protonated glucosamine parts, released from the solid chitosan film, have antimicrobial activity [25]. The relationship between the antibacterial action of chitosan and the characteristics of the bacterial cell wall of Gram-positive and Gram-negative bacteria has been investigated and explained that gram negative bacteria are more susceptible to chitosan due to negatively charged cell surfaces [26]. In a study, data analysis of transcriptional response has revealed that antibacterial action of chitosan involves a number of events which ultimately may cause killing of bacterial cell. Chitosan treatment leads to multiple changes in the expression profiles of *Staphylococcus aureus* SG511 genes involved in the regulation of stress and autolysis, as well as gene associated with energy metabolism [18]. Public health consciousness about the stains formation, pathogenic effects and malodors produced by micro-organisms has increased the need for antibacterial finishes in many areas like textiles, water purification systems, food packaging and storage, hygienic application, health care, medical devices, hospitals and dental surgery apparatus [27]. There is an increased pressure for safety of health care providing personnel with functional clothing due to the spreading of hepatitis viruses and HIV through contaminated materials by contact. Home textiles and apparels in daily use including socks, sport wear and working clothes as well as mattresses, floor coverings, and shoe linings are also highly susceptible to hygienic problems.

A very little fraction of the solar spectrum is constituted of ultraviolet rays but still these UVR can affect all the living beings and their metabolisms. Starting from 17th century, research on properties and effects of ultraviolet radiation (UVR) on living things spans on three centuries [28–32]. Approximately 5–6% of total incident spectrum of radiations is ultra violet radiations having same quantum energy as that of bond energies of organic molecules. Based on properties of UVR, physicists have devised the terms near UV (290–400 nm), far UV (180–290 nm) and vacuum UV (below 180 nm). UVR band consists of three regions; UVA (320–400 nm), UV B (290–320 nm) and UVC (100–290 nm) with the order of potency as UVC > UVB > UVA > [28–30,33–35]. Because of filtration of solar radiations through the upper environment and indigenous conditions (altitude, latitude, clouds etc), different amount of UV rays, composed of UV-A (400–320 nm), UV-B (320–290 nm) and UV-C (290–100 nm), reach the terrestrial environment. Almost all of the high energy UV-C and most of UV-B are filtered by the natural protective "ozone layer". UV-As reaching the earth, however, cause transformation of melanin in dermal layer resulting in sun tanning due to fast pigmentation within few hours of exposure. These short exposures cause no immediate harm. However, on recurring short exposures, these UV-As penetrate into human skin deeply and reduces the skin elasticity leading to premature ageing, lines and wrinkling of skin. UV-B, being higher in energy, can penetrate a few millimeters deep into the skin and cause acute and chronic damaging reactions like skin redness and sunburn. The UV -A and UV-B which are not filtered by ozone layer are necessary for synthesis of vitamin D and therefore are equally advantageous and detrimental for human well-being [36]. Prolonged exposure and absorption of excessive UVR causes scabs/burns on skin resulting in cell damage and inflammation of skin that may lead to erythema or sunburn [37]. Three useful protective means to avoid the damaging effects of UVR are reduction in the exposure time to sun light, use of sunscreens and wearing the protective clothing with good UPF/SPF [29,30,33,35,37–41]. Hence, textile materials need to be made UV resistant to reduce the skin exposure and to be used in durable technical applications. UV protective textiles comprise numerous apparels and accessories like shoes, hats, canopies, umbrellas, baby carrier covers and textile fabrics used to produce this stuff.

Considering the economic and ecological issues in the modern coating industries and need for protection against harmful pathogens and detrimental UV radiations, synthesis of polymer dispersion based on natural resources could be an obvious choice. In current project, a series of IPDI, CAPA and chitosan based aqueous polyurethane dispersions have been synthesized for use as antibacterial and UV protective textile finishing agent. Synthesized $CS_{(LMW)}$-CPUI dispersions were characterized through FTIR spectroscopic analysis and then these finishes were applied onto dyed and printed poly-cotton fabric samples to impart antibacterial and UV blocking sunscreen attributes and their application on fabrics was evaluated by SEM analysis of finished and unfinished fabric samples.