5. Summary and Conclusion

Summary

Clothing is one of the basic necessities for the survival of modern man and its primary objective is to provide protection to humans from the environment. But due to changes in environmental conditions and increased consumer awareness, demand for fabrics with functional properties, apart from basic objective of protection, has increased rapidly, particularly for fabrics with functional properties like antimicrobial, UV protection and self-cleaning. Multifunctional fabrics, i.e., a single fabric exhibiting multiple properties gained more attraction. Inorganic compounds such as metal oxide become materials of choice, because of their high stability compared to organic compounds. These materials in their nano form are very active and exhibit higher efficiency.

A study on “Synergistic Effect of Plasma and Cationic Pretreated Polyester/Cotton Fabrics Finished with Metal Oxide Nanocomposites on Multifunctional Properties” was carried out with the following objectives:

- To synthesis and characterize TiO$_2$, ZnO, CuO, Fe$_2$O$_3$, MgO and Al$_2$O$_3$ nanoparticles, using hydrothermal method,
- To optimize the preparation of nanocomposites by Box-Behnken design,
- To optimize the process parameters of DC air plasma and cationization for the pretreatment of polyester/cotton fabric by Box-Behnken design,
- To impart multifunctional finish on pretreated fabrics, using metal oxide nanocomposites,
- To compare and validate the treated and untreated fabrics for their multifunctional properties, using standard test methods,
- To determine the skin irritation potential of the treated fabrics by HET CAM test, and
- To assess the wash durability and physical properties of the finished fabrics using standard test methods.

The above objectives were attained by conducting experiments in four phases.

Phase I

- A pilot study was carried out to check the feasibility of the research project. The fabric selected was polyester/cotton blended fabric (50/50), and six metal oxides (TiO$_2$, ZnO, CuO, Fe$_2$O$_3$, MgO and Al$_2$O$_3$) were also selected based on the literature studies,
All the six metal oxide nanoparticles were prepared by hydrothermal method in a teflon lined autoclave vessel at 180 °C for 12 hours. Then the metal oxides were subjected for optical, compositional, crystallographic and morphological analysis. Particle size analysis showed that all the metal oxides were below 65 nm, confirming that the particles were in nano regime. From the UV-Visible spectroscopy and XRD analysis, formation of each metal oxide was confirmed qualitatively. The EDAX analysis confirmed that the metal oxides were in their pure form and had no impurities. The morphological analysis revealed that all the metal oxide nanoparticles were in uniform shape and particle sizes were below 45 nm.

The metal oxide nanoparticles were then tested for their antimicrobial activity against *E. coli*, *S. aureus*, *A. niger* and *T. viride* using agar well diffusion method. TiO$_2$ and ZnO nanoparticles had the highest activity against all the microbes followed by Fe$_2$O$_3$ and CuO nanoparticles. The activity of the Fe$_2$O$_3$ and CuO nanoparticles were similar to the standard antibiotics (Ampicillin and Nystatin) used in the study. The Al$_2$O$_3$ and MgO nanoparticles had lesser antimicrobial activity compared to the other metal oxide nanoparticles, and

Based on the pilot study four (TiO$_2$, ZnO, CuO and Fe$_2$O$_3$) metal oxide nanoparticles were selected for preparation of nanocomposites in phase II.

**Phase II**

The four metal oxides selected from the pilot study were mixed in two different combinations, i.e., TZC (TiO$_2$, ZnO and CuO) and TZF (TiO$_2$, ZnO and Fe$_2$O$_3$) and made into two nanocomposites, using ball milling. The nanocomposites were milled in a tungsten carbide chamber employing zirconia balls (sample to ball ratio of 1:20) at a speed of 300 RPM for 10 hours.

For each nanocomposite, different ratios of the three constituent metal oxides were blended using ball milling. The optimum ratio of metal oxides was identified for each nanocomposite by response surface methodology using design expert software. A total of 17 different combinations were chosen in random order according to BBD (Box-Behnken design) configuration for three factors. All the 17 combinations were tested for their antibacterial activity against *E. coli* and the combination with the highest antibacterial activity was selected as the optimum composition, and

Optimum composition for TZC nanocomposite was 3.7, 3.3 and 2.8 grams of TiO$_2$, ZnO and CuO respectively. This combination exhibited an antibacterial activity of 28.5 mm. Optimum composition of TZF nanocomposite was 4.1, 3.6 and 2.2 grams of TiO$_2$, ZnO and Fe$_2$O$_3$ respectively. This combination exhibited an antibacterial activity of 27.2 mm. The compositions were also confirmed using
EDAX analysis and no traces of impurities were found. XRD and FESEM analysis also confirmed the formation of nanocomposites. Further, the optimized nanocomposites exhibited higher antimicrobial activity than the individual metal oxide nanoparticles as well as standard antibiotics against *E.coli*, *S.aureus*, *A.niger* and *T.viride*.

**Phase III**

- Polyester/cotton blended fabrics were subjected to pretreatment procedures, to enhance the affinity of the nanocomposites to the fabric. Polyester fibers hydrophobic in nature, whereas, cotton fibers usually contain impurities such as pectins, waxes, protein and sugars in the cuticle layer which are responsible for poor hydrophilicity of the fabric. This consequently reduce the material uptake. To overcome the problems, the fabrics were pretreated using DC air plasma technology (P), a cationic agent 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (C) and both (PC),
- Various independent parameters involved in the plasma treatment were optimized using BBD (Box-Behnken design). 29 trials were carried out at different pressure, current, exposure time and inter-electrode distance, and the optimum parameters were identified by measuring the wickability of the fabric. The maximum wickability obtained was 5.8 cm. Similarly, the cationization process was optimized by carrying out 29 trials under different volume of CHPTAC, NaOH, batching time and drying temperature. The maximum absorption obtained was 47.3%. The optimum parameters were identified by absorption studies using UV-visible spectroscopy, and
- The pretreated fabrics were characterized using FTIR and AFM. The FTIR analysis revealed that the intensity of the hydrophilic bonds like O-H, C-H and C=O were increased in the pretreated fabrics with PC fabric exhibiting highest increase in the intensity of hydrophilic bonds. AFM studies revealed that the pretreatment procedures altered the surface roughness of the fabrics and thus will increase the quantity of material uptake into the fabric.

**Phase IV**

- The pretreated fabrics were finished with the nanocomposites, using pad-dry-cure method, and the fabrics were characterized. The FTIR analysis showed additional peaks between 500 cm⁻¹ and 650 cm⁻¹ corresponding to the metal oxide bonding, confirming the presence of nanocomposites in the treated fabrics. The XRD analysis also showed peaks of both nanocomposites as well as polyester/cotton blended fabrics. In both FTIR and XRD intensity of nanocomposite peaks were high in the PC fabric, showing that higher material absorption happened in the
ratings of 45, while the control fabrics exhibited had UPF ratings of less than 5 only.

- Self-cleaning results also showed high dirt reduction of about 93% in PC+TZC and PC+TZF fabrics. Other pretreated fabrics finished with nanocomposites exhibited 80-90% dirt degradation, while the control fabrics showed only 10% decrease in K/S values after 48 hours exposure to sunlight.

- Functional property analysis results showed that the PC+TZC and PC+TZF fabrics had better functional properties when compared to all the other fabrics. So, both the fabrics subjected to wash durability analysis against all the three functional properties. Almost 80% of the functional properties were retained even after 20 washing cycles. While retaining more than 98%, 94% and 90% functional properties after 5, 10 and 15 washes respectively,

- The skin irritation potential of the test fabrics were analyzed by HET-CAM test. The CAM does not showed no sign of hemorrhage, vascular lysis and coagulation for the used concentration of nanocomposites treated fabrics,

- The selected fabrics PC+TZC and PC+TZF were compared to the untreated fabrics along with the pretreated fabric samples PC to evaluate the change in physical properties inferred on to the fabrics caused by the nanocomposite finishing,

- A slight increase in weight of around 1.5% and increase on thickness of around 6% were observed between the control and the finished fabrics,

- Nanocomposite finished fabrics PC+TZC and PC+TZF showed round 7% increase in tensile strength for both warp and weft direction with around 4.6% and 1.5% increase in elongation along the warp and weft directions respectively,

- Around 1.6% increase in tearing strength for both warp and weft direction were observed for the PC+TZC and PC+TZF fabric samples,

- The abrasion resistance analysis of PC+TZC and PC+TZF fabric samples showed around 1.5% loss in fabric weight,

- The stiffness in the warp and weft directions of the nanocomposite finished PC+TZC and PC+TZF fabrics increased around 5%, while the pilling resistance increased by 66%,

- Assessment of aesthetic properties revealed that around 3% increase in drape coefficient was observed, whereas, around 6% increase in crease recovery were observed in both warp and weft directions of the finished fabrics,

- Almost 80% increase in water absorbency was observed in drop test, while around 70% wicking height was recorded for the PC+TZC and PC+TZF fabric samples when compared to the untreated fabric samples,
• The air permeability of the nanocomposite finished PC samples were slightly decreased around 1.3% when compared to the untreated fabrics, and

• From the physical testing results, a substantial increase in the mechanical properties were observed in the combinatorial pretreated fabrics finished with nanocomposites, without any significant negative effects on the aesthetic and comfort properties of the fabrics.

Conclusion

This research concentrates on producing multifunctional fabrics with antimicrobial, UV protection and self-cleaning properties without altering the comfort and hand value properties. Two different combinations of metal oxide nanocomposites were prepared and finished on the fabrics pretreated with plasma and cationic agent. The experimental results revealed that the nanocomposites treated fabrics have excellent multifunctional properties. Specifically, the fabrics pretreated with both plasma and cationic agent, and then finished with the nanocomposites, exhibited comparably higher efficiencies. The quantity of the nanocomposites absorbed onto the fabric were more when treated with plasma followed by treatment with cationic agent. The plasma treatment increased the hydrophilicity of the fabric by introducing oxygen containing functional groups, while the pretreatment with cationic agent imparted a positive charge on the fabric surface. Increase in the wettability and introduction of positive charges on the fabric surface synergistically improved the uptake of the nanocomposites into the fabric.

Nanocomposites were more active against the microbes than their individual metal oxides, this was due to the synergistic effect of the three metal oxides combined together. Each metal oxide nanoparticles had their absorption in different regions of the spectrum, but when they were combined together to make the nanocomposite, it collectively absorbed more radiation, thus leading to higher performance. The ability of the nanocomposite to absorb light and take part in the microbicidal and self-cleaning activity were much higher than the individual metal oxides. Also, the combinatorial pretreatment method increased the uptake of the quantity of nanocomposites, this increased concentration of the nanocomposite in the PC+TZC and PC+TZF fabric samples increased the antimicrobial activity of the fabrics significantly. Similarly, the combinatorial pretreated fabrics also exhibited a good self-cleaning effect.

The ultra-violet protection factor of the PC+TZC and PC+TZF fabrics were well high, due to the presence of two UV absorbing metal oxides in both the nanocomposite combinations. Both the titanium dioxide and zinc oxide have their bandgap energies falling in the UV range and due to their synergistic effect they absorbed more UV radiation and had an UPF value of 50+. The fabrics were also wash durable and does not show
any skin irritation potential at the fabricated concentrations. The physical testing of the fabrics revealed that there was only slight variations in the mechanical, aesthetic and comfort properties of the fabrics. Thus the usage of the nanocomposites to develop multifunctional fabrics will not downgrade the fabrics in terms of basic functions and quality. The findings of the research work opened up a new possibility of exploring the use of metal oxide nanocomposites for developing highly value added multifunctional textile with high commercialization potential. And also it can satisfy the consumer demands in various fields like apparel, healthcare, medical and technical textile.

**Recommendations**

- The studies can be extended to other types of natural, synthetic and regenerated fabrics like wool, jute, nylon, polypropylene, viscose, lyocell and their blends,
- The influence of the different fabric structures like knitted and non-woven on multifunctional properties can also be studied,
- The present research work is focused only on DC air plasma and CHPTAC cationic agent. It may be extended to other pretreatment methods,
- The efficiency of the functional properties can be further increased by controlling the particles size of the nanocomposites, and
- The effect of doped metal oxides nanoparticles on the functional properties of the textile can also be explored.