SYNTHESIS OF METHACRYLIC ACID-ETHYL ACRYLATE BASED THICKENERS AND THEIR APPLICATION IN PIGMENT PRINTING

By

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• • •*dedicated to my parents*

CERTIFICATE

This is to certify that the thesis entitled **"SYNTHESIS OF METHACRYLIC ACID-ETHYL ACRYLATE BASED THICKENERS AND THEIR APPLICATION IN PIGMENT PRINTING"** being submitted by **Miss Meenakshi Goyal,** to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy, in the Department of Textile Technology, is a record of bonafide research work carried out by her. Miss Meenakshi Goyal has worked under our guidance and supervision and fulfilled the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

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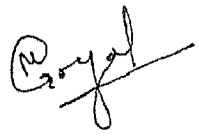

(Meenakshi Goyal)

ABSTRACT

The origin of this study lies in the development of a substitute of kerosene emulsion thickener used in pigment printing which has the disadvantages like, inadequate availability, risk of fire and air pollution. Generally, the copolymers of acrylic/methacrylic acid and alkyl acrylate and their crosslinked products are used as synthetic thickeners.

Methacrylic acid-ethyl acrylate copolymers of varying compositions (MAA 50.1-82.3 mol%) were synthesized using emulsion polymerization technique. Mechanism of polymerization which is not expected to be a true emulsion polymerization, because of the presence of higher amount of water soluble carboxylic acid monomer, was studied. From the partition behaviour of methacrylic acid in aqueous and ethyl acrylate phases, and reactivity ratios of methacrylic acid-ethyl acrylate pair, it was inferred that the system follows a two loci polymerization mechanism. Alongwith the emulsion polymerization, some water soluble polymer is also produced. IR and NMR techniques were employed to characterize the copolymers.

Thermal studies revealed a good correlation between the chemical structure and thermal behaviour of copolymers. An endothermic transition in DSC curves of methacrylic acid ethyl acrylate copolymers relates to the dehydration reaction of methacrylic acid units. Interestingly it has

been established that ethyl acrylate comonomer also participates in the dehydration reaction of methacrylic acid in methacrylic acid-ethyl acrylate copolymers. A decrease in the activation energy with increase in ethyl acrylate content of the copolymers was also observed. An increase in weight loss in the temperature range of 140-280°C with the increase in the ethyl acrylate content of the copolymer, further confirms the participation of ethyl acrylate in dehydration reaction. On the basis of detailed analysis of the degradation products of methacrylic acid-ethyl acrylate copolymers through mass spectroscopy, a comprehensive thermal degradation scheme has been proposed.

Brookfield viscosity of methacrylic acid-ethyl acrylate copolymers (at 5 rpm and pH 7.5 after adjusting with ammonia) was found to be very low, i.e., in the range of 5000-16000 cp at 10% solid contents. In order to accomplish the higher viscosity at lower solid content, the crosslinked polymers were synthesized by incorporating small amounts of crosslinking agent like, ethylene glycol dimethacrylate or N,N'-methylene bisacrylamide in conjunction with methacrylic acid and ethyl acrylate. A significant increase in the Brookfield viscosity was observed and the crosslinked polymers had a viscosity of 26000-70400 cp at a solid content of 4% only. Viscosity of these polymers was found to be dependent on pH and maxima was obtained in the pH range of 7.5-8. This behaviour has been related with the ionization of the carboxylic acid groups. Pseudoplastic

behaviour of these polymers confirmed their suitability for textile printing applications.

As the viscosity was very low in the linear copolymers, printing trials were confined to the crosslinked polymers only. The performance of these products in pigment printing of cotton was evaluated in terms of colour value, wash, rub and scrub fastness and handle, using four pigments. Though all other characteristics were quite comparable with the conventional and commercial (Alcoprint PTF) thickener, the feel of the fabric was stiffer which was improved by using a mixture of synthetic and kerosene emulsion thickener in the ratio of 80:20 and 60:40 (w/w).

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CHAPTER 2 SYNTHESIS AND CHARACTERIZATION OF METHACRYLIC ACID-ETHYL ACRYLATE COPOLYMERS