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The role of polymer compatibility in the adhesion between surfaces saturated with modified dextrans

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Abstract

Wet and dry adhesion between dextran-coated surfaces were measured aiming to understand the influence of polymer compatibility. The wet adhesion measurements were performed using the atomic force microscope (AFM) colloidal probe technique whereas the dry adhesion measurements were performed using the micro adhesion measurement apparatus (MAMA). Two types of dextrans were used, one cationically modified dextran (DEX) and one that was both cationically and hydrophobically modified (HDEX), leading to three different combinations of polymer-coated surfaces; (1) DEX:DEX, (2) HDEX:DEX, and (3) HDEX:HDEX. DEX increased dry adhesion more than HDEX did, which likely is due to differences in the ability to form specific interactions, especially hydrogen bonding. HDEX gave strong wet adhesion, probably due to its poorer solvency, while DEX contributed to reducing the wet adhesion due to its hydrophilicity. All combinations showed a steric repulsion on approach in aqueous media. Furthermore, when HDEX was adsorbed on either or both surfaces a long range attractive force between the surfaces was detected outside this steric regime.

Keywords: Adhesion; Interaction forces; Polymer; Adsorption; Incompatible; Asymmetric; Cationic dextran; Hydrophobic; Hydrophilic; AFM; Colloidal probe technique; JKR

1. Introduction

When two polymeric surfaces come into contact polymer chains from one surface can penetrate the second surface, ultimately leading to a welded joint [1]. The French polymer physics school has published extensively on theoretical aspects of mixing at the interface upon contact [2]. Welded joints are stronger because energy is consumed, pulling out the interdigitated polymer chains [3,4]. The fundamental requirements for interdigitation are the presence of mobile chain ends and time for interdiffusion. It was recently demonstrated that chain ends contribute to adhesion between glassy polymers [5]. Furthermore, surface force apparatus (SFA) measurements showed that upon approaching the glass transition temperature, adhesion increases due to entanglement formation across the interface [6]. With longer contact times, the surface molecules have more time for rearrangement and interdigitation across the opposing surfaces. Adhesion also depends on the rate of surface separation. If welded surfaces are very slowly separated, entanglements across the interface will spontaneously disengage, whereas higher separation rates will result in visco-elastic losses and chain rupture that will contribute to the measured adhesion energies [7–9]. Finally, the relative humidity and the presence of plasticizing agents during joint formation and joint separation highly influence the joint strength [6,10]. Solvents can promote chain mobility in brittle polymers and thereby speed up the diffusion rate.

There are numerous technologies, including surface coating with latex paints and papermaking, where adhesive joints form by removing water from suspension of surfaces coated with

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hydrophilic polymers. One example of this type of process is film formation from the coalescence of latex paint. Upon drying, the exterior polymers in the latex particles inter-diffuse to form a continuous film, a process which has been characterized by fluorescent energy transfer experiments [11]. In the case of papermaking, cellulose fibers coated with hemicellulose, starch or synthetic polymers are pressed together and the water is removed. Although the glass transition temperatures of the surface carbohydrates on dry cellulose fibers are above 200 °C [12], the presence of plasticizing water during joint formation suggests that interdigitation of surface polymers might contribute to the remarkable adhesive strength of fiber–fiber joints in paper. This was first suggested by McKenzie in 1984 [13]. McKenzie emphasizes the role of hemicelluloses as surface polymers, which mix to form bonds between the fibers. However, in most modern papermaking suspensions, the fibers are at least partially coated with an adsorbed layer of water-borne polymers added to enhance the fiber–fiber joint strength, to retain fines, fillers or pitch, and to make the fibers water repellant. Thus, the capability of these polymers to participate in interdiffusion should also be considered.

If contacting polymer surfaces are not identical, polymer compatibility is also important because, by definition, incompatible polymers do not mix. The role of compatibility was demonstrated by Iyengar and Erickson, who showed that nearly matched solubility parameters were required for development of strong adhesion between polymer films [14]. If interdigitation is important for adhesion between fibers in paper, the strength of paper should be sensitive to the compatibility of polymers in the fiber–fiber joint. This hypothesis was tested by making paper from a mixture of two separate batches of cellulose fibers—one coated with dextran and the other coated with a hydrophobically modified dextran [15]. Both dextran polymers were water soluble, however, when mixed at concentrations of ∼10% (w/w), the dextran polymer solutions phase separated [16], similar to the extensively studied dextran/polyethylene glycol mixtures [17] and dextran/polyethylene oxide mixtures [18]. Such aqueous biphase systems are good examples of polymer incompatibility. Thus, the hypothesis suggests that paper with many joints containing incompatible polymers in the fiber–fiber joints would be weaker [15]. The results were inconclusive, perhaps because paper is a complex and poorly defined material for fundamental adhesion studies.

In this work, an attempt is made, to access the role of polymer compatibility for development of adhesive joints between surfaces coated with hydrophilic polymers using AFM with the colloidal probe technique and continuum contact mechanics applied to the JKR (Johnsson, Kendall and Roberts) theory [19]. Specifically, three cases are compared: (1) both surfaces coated with dextran (DEX); (2) both surfaces coated with hydrophobically modified dextran (HDEX); and (3) the asymmetric case where one surface is coated with DEX and the other with HDEX. It was also anticipated that all interactions would be repulsive in water and that the asymmetric HDEX:DEX would give the weakest adhesion for both wet and dry surfaces.

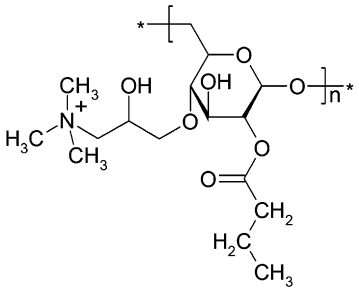

Fig. 1. A HDEX repeat unit showing the cationic and the hydrophobic modification. On average there is about one hydrophobic butyric ester on every other carbohydrate ring, whereas there are about 30 rings per quaternary ammonium group.

2. Materials

2.1. Modification of dextran

Chemicals: 3-epoxypropyl-trimethylammonium chloride (ETAC) was purchased from FLUKA. 1.4-pyrrolidinopyridine (PYP), 1,3-dicyclohexylcarbodiimide (DCC), dichloromethane and butyric acid were purchased from Aldrich. Formamide was from BDH and *N*,*N*-dimethylformamide (DMF) was from Caledon Laboratories Ltd. Dextran with a molecular weight (M_w) of 513 kDa was purchased from Sigma.

Cationic dextrans (DEX) were prepared according to a previously described method [20,21]. In the present study, dextran was dissolved in water to a final content of 20% (w/w) and pH was adjusted to 13–13.5 with 5% (w/w) NaOH solution. 70% (w/w) ETAC was added and the temperature was raised to 45 °C. After 5–6 h, the mixture was allowed to cool at room temperature and HCl was added to bring the pH to approximately 6–7. The samples were purified using dialysis (3400–1400M_w cut-off) for at least ten days. Finally, the sample was freeze dried using a Heto Drywinner, Model DW3, and then stored at 5 °C until use.

Hydrophobically modified cationic dextran (HDEX) was prepared by esterification of the cationic dextran, using butyric acid, according to a method presented elsewhere [16,22]. In the present research, dried cationic dextran was dissolved in formamide/DMF (33/67) to get an anhydroglucose concentration of 0.65 M. Butyric acid (0.45 M) and PYP (0.025 M) were added to the reaction mixture. The mixture was stirred to form a homogeneous solution, where after DCC, dissolved in dichloromethane 50% (w/w), was added to get a DCC concentration of 0.45 M in the reaction mixture. The reaction was performed at 30 °C under nitrogen for 24 h. The sample was filtrated to remove dicyclourea and then precipitated in acetone, dissolved in water, centrifuged (using a Beckman L7-55 ultracentrifuge; 30,000 rpm, 25 °C, 30 min), dialyzed for two days, centrifuged, filtrated, and freeze dried. The products were stored at 5 °C before use. Fig. 1 presents the HDEX repeat unit showing the cationic and the hydrophobic modification.

2.2. Substrates

Silicon wafers (150 mm, *p*-type) were purchased from Memc Electronics Materials, Novara, Italy. They were washed