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Graft Polymerization of 1,1-Dihydroperfluorobutyl Acrylate onto Cellulose Fabric

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Synopsis

1,1-Dihydroperfluorobutyl acrylate was prepared and grafted onto cellulose fabric by means of γ-ray preirradiation to produce oil and water repellency. A 2% grafting was sufficient to impart oil and water repellency to cellulose fabric. In the case of 19.1% or 29.4% grafted fabrics, the grafting decreased rapidly with laundering, and the laundered fabric which possessed no oil and water repellency still had about 10% grafting of the perfluoro compound. Thus, the apparent graft polymerization takes place both on the surface and in the inner structure of the cellulose fiber; the polymer grafted onto the surface imparts oil and water repellency and is easily removed by laundering, whereas the polymer grafted onto the inner structure is hardly eliminated but does not impart oil and water repellency to the fabric.

INTRODUCTION

It has been well known that fluorochemicals impart oil and water repellency to textiles.[1,2] Although the general method of treatment is to deposit the fluoropolymer on the fabric, the investigation of graft polymerization of fluoromonomers has not been reported. In the present study, 1,1-dihydroperfluorobutyl acrylate (FBA), $CH_2{=}CH{-}COOCH_2C_3F_7$, was prepared and grafted onto cellulose fabric by means of γ-ray preirradiation and durability of oil and water repellency of the fabric was investigated.

EXPERIMENTAL

FBA Grafting onto Cellulose Fabric

Perfluoroacetic acid was prepared from fluorination of butylic acid by electrochemical fluorination[3] and then reacted with acrylic acid chloride to give FBA.[4]

The fabric used was a 5 × 10 cm^2 desized, scoured and bleached rayon cloth were immersed in 0.5% H_2O_2-water solution and irradiated in air from Co^{60} 1000-Curie source. Following the irradiation the samples were washed with water and centrifuged. The preirradiated fabrics were immersed in FBA-water-methanol solution in nitrogen atmosphere at different temperature. The fabrics were removed from the solution after various periods, thoroughly washed with benzene and dried at 50°C for over night in vacuum to constant weight. Graft per cent were calculated by quantitative analysis of fluorine by titration method of 0.01-N thorium nitrate solution with alizarine red-S as an indicator.[5]

A steel ball agitator type washing machine was operated for laundering test of grafted fabrics using 0.1% Marseille soap solution in water at 60°C, and 30 min is a period of one operation.

Test Method for Oil and Water Repellency

Oil and water repellency test is based on the period of penetrating or wetting of nujol/n-heptane in 50/50 mixture of water on the tested fabrics. One drop of test liquid is placed on the fabric and allowed to stand undisturbed, and the penetrating time is counted as second.

RESULTS

Before grafting, γ-ray-induced and azobisisobutyronitrile (AIBN)-catalyzed polymerizations of FBA were studied, and results were compared with those of butyl acrylate. Figure 1 shows radiation-induced polymerization, and AIBN-catalyzed polymerization is shown in Figure 2. The rate of polymerization, thus the radical polymerizability of FBA, is lower than that of butyl acrylate in the case of radiation-induced as well as AIBN-catalyzed polymerization. Poly-FBA, the resulting polymer, is a white, tough elastic material which does not dissolve in the common organic solvents.

Preirradiation was carried out for grafting. The mutual solubility of FBA–water–methanol at 25°C is presented in Figure 3, and the effect of water on grafting is shown in Figure 4. The degree of grafting increases with increasing water contents until the mutual solubility is broken.

The influence of preirradiation dose rate and total dose on grafting was studied, and the results are shown in Figures 5 and 6, respectively. Graft-

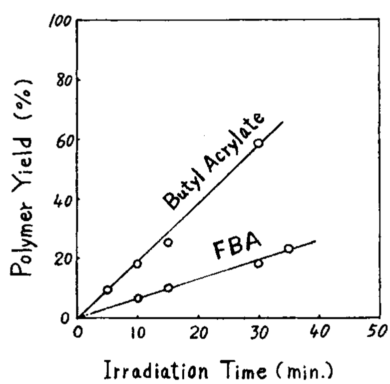

Fig. 1. Radiation-induced polymerization of FBA and butyl acrylate. Temperature 16°C, 9 × 10[4] rads/hr, in vacuo.

ing is proportional to total dose and is not influenced by a dose rate below 5×10^4 rads/hr. The influence of temperature on the rate of grafting was also studied, and the results are shown in Figure 7. The apparent activation energy for the grafting was found to be 22 kcal/mole.

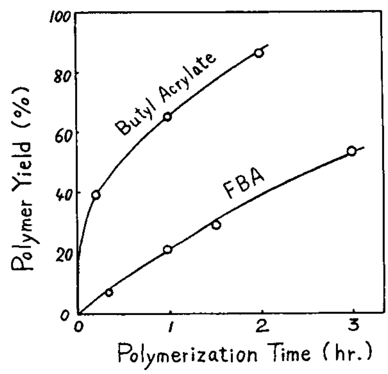

Fig. 2. AIBN-catalyzed polymerization of FBA and butyl acrylate. Monomer 0.75 mole/l., AIBN 5×10^{-2} mole/l., in benzene, 71°C, nitrogen atmosphere.

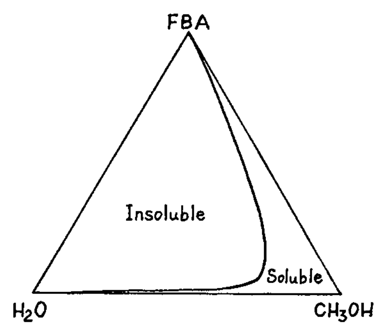

Fig. 3. Mutual solubility of FBA-water-methanol (25°C, vol.-%).

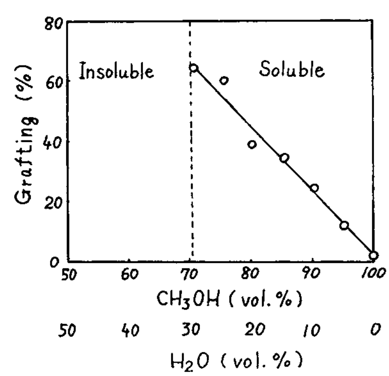

Fig. 4. Influence of water/methanol ratio on FBA grafting onto cellulose. Preirradiation: 5×10^4 rads/hr $\times$ 1.5 hr, 25°C, in 0.5% H_2O_2 solution. Grafting: 55°C, 22 hr, FBA 4% nitrogen atmosphere.

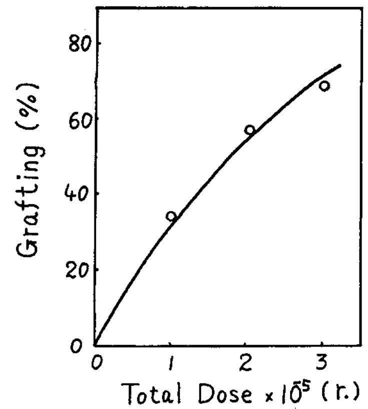

Fig. 5. Influence of preirradiation total dose on FBA grafting onto cellulose. Preirradiation: 9×10^4 rads/hr. Grafting: FBA 5%, methanol/water = 75/25, 50°C, 22 hr, nitrogen atmosphere.

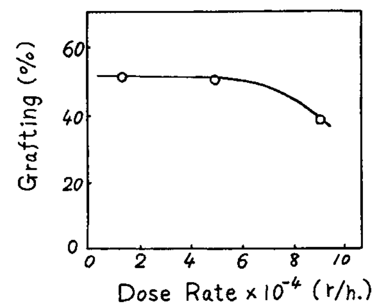

Fig. 6. The influence of preirradiation dose rate on FBA grafting onto cellulose. Preirradiation; 1.8×10^5 rads. Grafting: FBA 5%, methanol/water = 75/25, 50°C, 22 hr, nitrogen atmosphere.

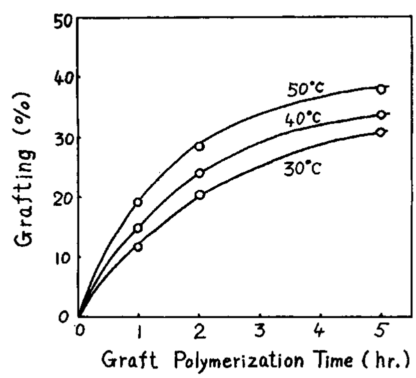

Fig. 7. Relationship between FBA grafting rate and temperature. Preirradiation; 8.5×10^5 rads, in 0.5% H_2O_2. Grafting: FBA 5%, methanol/water = 80/20, nitrogen atmosphere.

The oil and water repellency of FBA- and butyl acrylate-grafted cellulose fabric is shown in Figures 8 and 9, respectively. More than 20% of butyl acrylate grafting imparts water repellency to cellulose fabric, but oil affinity also appears. On the other hand, 2% of FBA grafting is sufficient to give oil and water repellency to the fabric.

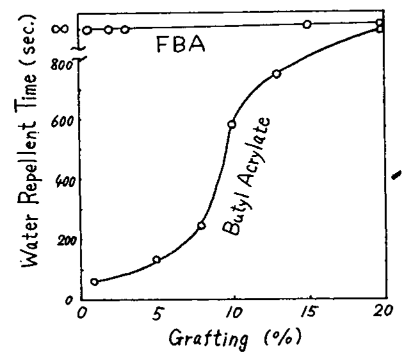

Fig. 8. Relationship between grafting and water-repellent time of FBA- and butyl acrylate-grafted cellulose fabrics.

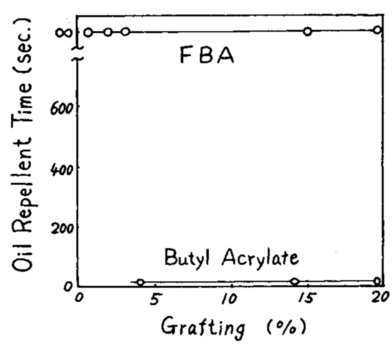

Fig. 9. Relationship between grafting and oil-repellent time of FBA- and butyl acrylate-grafted cellulose fabrics.

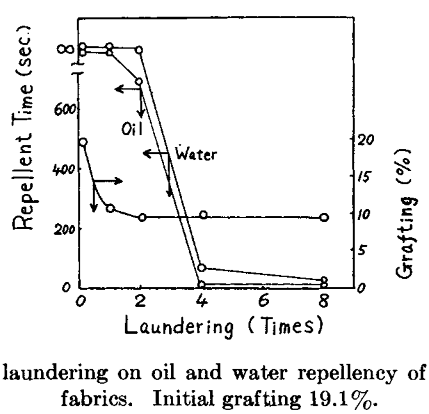

Fig. 10. Influence of laundering on oil and water repellency of FBA-grafted cellulose fabrics. Initial grafting 19.1%.

The dry-cleaning fastness of FBA-grafted fabric is excellent, but wash fastness is incomplete. Oil and water repellency decreases rapidly with subsequent repeated laundering tests. Results are shown in Figures 10 and 11, which are examples of initial grafting of 19.1% and 29.4%, respectively. As shown in Figure 10, an initial grafting of 19.1% decreases to 10.3% at a

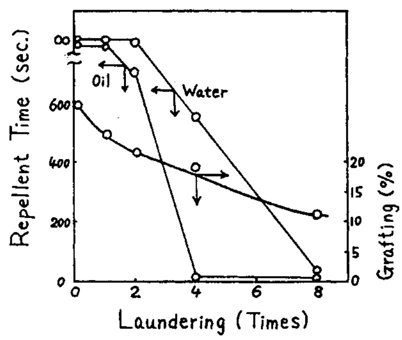

Fig. 11. Influence of laundering on oil and water repellency of FBA-grafted cellulose fabrics. Initial grafting 29.4%.

first laundering test, while oil and water repellency still holds. After four laundering tests, the fabric still holds 9.7% of grafting but retains no oil and water repellency. Similar results are obtained in the case of 29.4% FBA-grafted fabric, as shown in Figure 11.

DISCUSSION

Radiation-induced graft polymerization of FBA onto cellulose fabric imparts oil and water repellency. Because of the lack of adequate solvent[6] for extraction of homopolymerized FBA on the fabric, the grafted samples are not free from homopolymer, and the calculated per cent graft includes homopolymer and graft polymer. At the very initial stage of the grafting process, the polymerization proceeds on the surface of the fabric, so that 2% of FBA grafted onto the fabric exhibits oil and water repellency. In the case of 19.1% and 29.4% FBA grafted onto the fabric, grafting decreases rapidly following several times of laundering, and the laundered fabric which still hold about 10% of FBA grafting retains no oil and water repellency.

In view of the above facts, the most reasonable conclusions to be drawn from the available data are that the calculated graft per cent consists of a large portion of homopolymer and a small amount of real graft polymer, and that more than 2% of polymer which polymerized on the surface of the fiber imparts oil and water repellency but is removed by laundering. On the other hand, the polymer which polymerized in the inner structure of the fiber is hardly eliminated by laundering, while, although about 10% of FBA polymerized in the fiber, it makes no contribution to oil and water repellency.

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