DIRECT FLUORINATION OF POLYAMIDE

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SUMMARY

Direct fluorination of polyamides imparts improved wetting property
to the surface of the polymer. The acid content and fluorine content are
compared to the wetting property of the treated polymer. The results
indicate there is a favorable ratio of acid content and fluorine content
that allows for best wetting property. The effect of added oxygen to
the fluorinating medium is to reduce the wetting property imparted to the
polymer.

INTRODUCTION

Recently, there has been several publications covering the fluori-
nation of polymers with elemental fluorine [1,2,3]. Most of the work
indicates that polymers such as polyethylene, polypropylene, and polyester
are not only fluorinated but are simultaneously oxidized. A trace
amount of oxygen is present in the fluorinating medium so that polymers
such as polyethylene and polypropylene can readily be oxidized. However,
for polymers such as polyester, the need for elemental oxygen to cause
oxidation does not exist [4].

Therefore, it was of interest to determine if in fact oxidation of
other polymers already containing oxygen as part of the polymer backbone
would also be oxidized during the fluorination step. The polymer chosen
was a polyamide since it not only has oxygen atoms as part of its back-
bone, but it also does not have aromatic groups as part of its backbone
as does polyester.

TABLE 1

Acidity measurements for fluorinated polyamide

Reaction Condition		Milliequivalents per Gram of Polymer	Grams of Methylene Blue per Gram of Polymer	% F Incorp.
F_2 Conc. (M)	Time (min)			
0	0	0.053	3.04×10^{-4}	-
1.78×10^{-3}	1	0.060	5.17×10^{-4}	0.31
1.78×10^{-3}	3	0.101	6.35×10^{-4}	0.17
1.78×10^{-3}	6	0.088	5.11×10^{-4}	0.16
1.78×10^{-3}	11	0.085	5.29×10^{-4}	0.14
3.57×10^{-3}	1	0.089	-	1.57
3.57×10^{-3}	3	0.161	1.31×10^{-3}	1.32
3.57×10^{-3}	6	0.186	1.84×10^{-3}	2.13
3.57×10^{-3}	11	0.377	4.02×10^{-3}	3.45
4.46×10^{-3}	1	0.151	-	2.63
4.46×10^{-3}	3	0.195	-	2.59

EXPERIMENTAL

Fluorination of nylon 6.6, Style 354A spun nylon 100% type 200
from Testfabrics, Inc., was fluorinated by placing the fabric in a
monel reactor. The reactor was then evacuated and purged with nitro-
gen four (4) times. Various mixtures of fluorine/nitrogen or fluorine/
nitrogen/oxygen were admitted to the reactor at ambient temperature for
varying reaction times.

The material was titrated using the procedure developed by Pohl [5].
In addition the acidity of the material was determined using methylene
blue [6]. The material was first dyed with aqueous methylene blue.
The excess methylene blue was then removed by continuously extracting
the product with acetone for forty-eight hours. This procedure should
remove not only excess surface methylene blue but also trapped methy-
lene blue. The material was then dissolved in acidic phenol and the
absorbance at 680 mμ was measured.

Wettability of the product was determined using the American Association of Textile Chemists and Colorists test method 39-1971 [7]. A second method used to measure wettability was by wicking height. A strip of fabric one inch wide was hung vertically with about one-fourth of an inch immersed in water. The height of the water as it wicked up the fabric was recorded versus the wicking time in minutes. The wicking height was measured over a fifty minute time span unless otherwise noted.
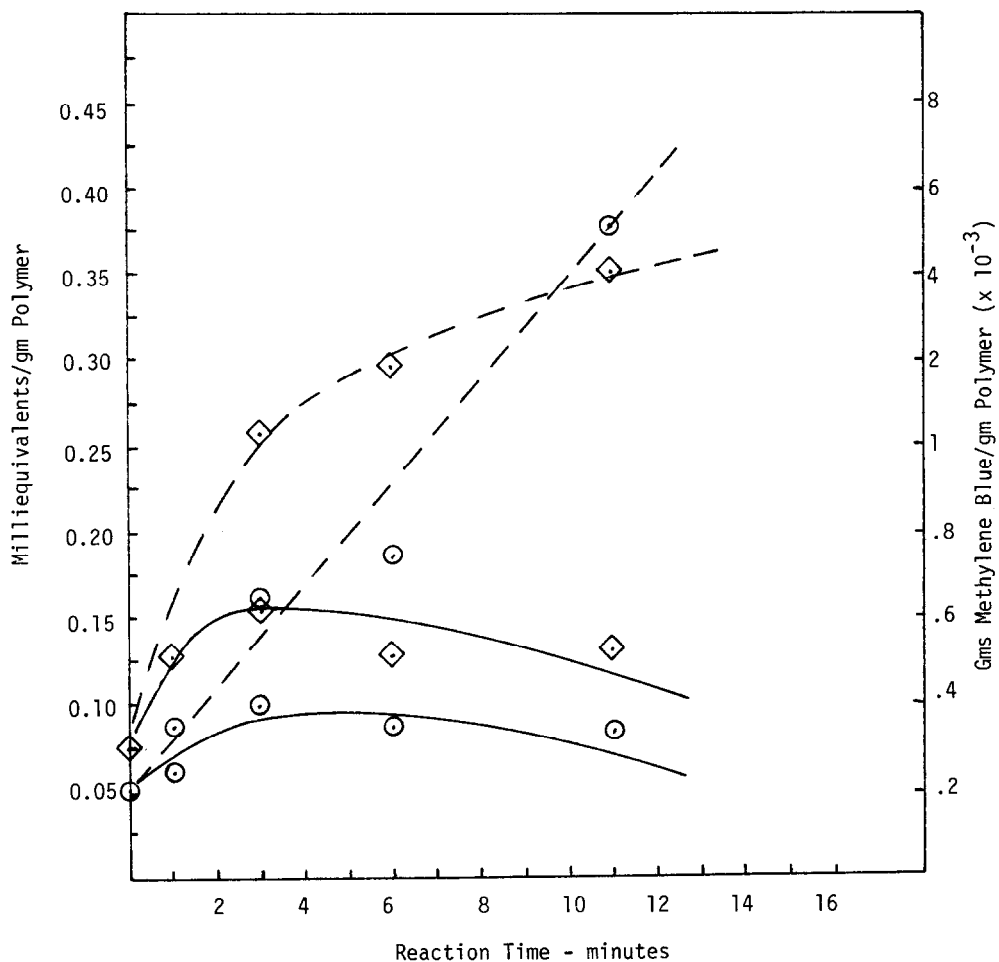

Figure 1. Acidity versus reaction condition. $(\bigcirc)$ - milliequivalents; $(\diamondsuit)$ - gms methylene blue; (———) - 1.78 x 10^{-3} M F_2; (---) - 3.57 x 10^{-3} M F_2.

RESULTS AND DISCUSSION

It has been found that the fluorination of polyamides causes not only fluorination to take place, but that oxidation also occurs. By oxidation is meant that the carboxyl group content (acid content) of the polymer has increased. This has been shown previously for polyester substrates [2]. Table 1 gives both the milliequivalents per gram of substrate and grams of methylene blue per gram of substrate for the various reaction conditions. As can be seen from Figure 1, both methods of measuring the acid content of the substrate are in general agreement.

An interesting correlation exists when the milliequivalents for the polymer is compared to the fluorine concentration in the reaction medium, Figure 2. As the fluorine concentration is increased, the rate of acid content increases only after a given fluorine concentration. That is at 1.78×10^{-3} M fluorine, the highest acid content material occurs at a reaction time of three minutes. At 3×10^{-3} M fluorine and above, the acid content increases with increasing reaction time. Over the fluorine concentration range studied, a three minute reaction gives a linear correlation between fluorine concentration and acid content.

The acid content of the treated material depends not only on the fluorine concentration but also on the length of the reaction time. As was found for polyester, the acid content usually levels off after a rather short reaction time. In fact the reaction time for polyamide is about one-third of that for polyester before the rate of acid content levels off at the lower fluorine concentration experiments.

Since acid groups are being formed during the fluorination reaction, it would be expected that the wettability of the fabric should increase. When the wettability was measured using the AATCC test method 39-1971, the material in fact did wet better, Table 2. Wettability was also measured by determining the wicking height for water after fifty minutes. In all cases, fluorination increases polyamide's hydrophilic property. At 1.78×10^{-3} M fluorine the best wetting property was found at six minutes reaction time. At 3.57×10^{-3} M fluorine maximum increase in wetting occurs below three minute reaction time. The maximum wetting property for the treated fabric does not occur at the highest acid content. This infers that wetting of the fluorinated polyamide relates
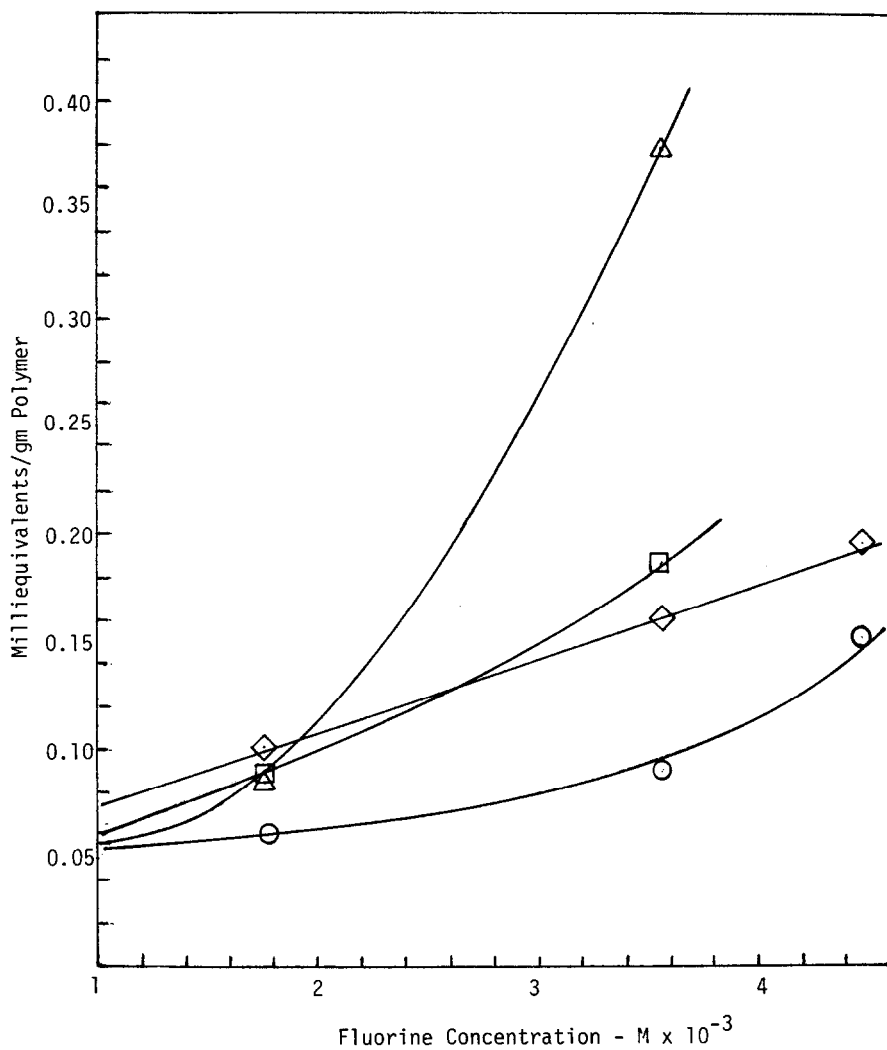
Figure 2. Acidity versus reaction condition. Reaction time (minutes):
(O) - 1; (◇) - 3; (□) - 6; (△) - 11.

to more than just the acid content of the fabric. Wicking height and
wettability are forms of measurement relating the ability of a fabric
to absorb or adsorb moisture from the body. This ability to wet is
considered a rough measure of comfort.

TABLE 2

Wettability of the treated polyamide

| Reaction Condition | | Wettability, | Wicking |
F_2 Concentration, M	Time, Minutes	Seconds[a]	Height, mm[b]
0	0	11,911	0
1.78×10^{-3}	1	231	140
1.78×10^{-3}	3	117	132
1.78×10^{-3}	6	92.5	151
1.78×10^{-3}	11	128.7	138
3.57×10^{-3}	3	193	87
3.57×10^{-3}	6	8,802	47
3.57×10^{-3}	11	3,866.2	57

a - see ref. 6

b - wicking height at 50 minutes

When the wicking height of the fabric is compared to the fluorine incorporation level, the wettability of the fabric decreases as fluorine incorporation increases, Figure 3. Also when the wettability of the fabric is compared to the ratio of milliequivalents per gram of polymer to % F incorporated, Figure 4, the maximum wettability occurs at a ratio of 0.2 or greater. This relates to the findings of Zisman [8,9] that show a partially fluorinated acid wets better than either a nonfluorinated acid or a perfluorinated acid. Thus, there seems to be a ratio between the fluorine content and the acid content that allows for maximum wetting property.

Nylon that was fluroinated at low fluorine concentration or short reaction times showed less loss of tensile strength than high fluorine concentrations or long reaction times, Table 3. Nylon that was fluorinated in the presence of small oxygen concentrations showed greater tensile strength loss than when oxygen was excluded from the reaction media, Table 4.
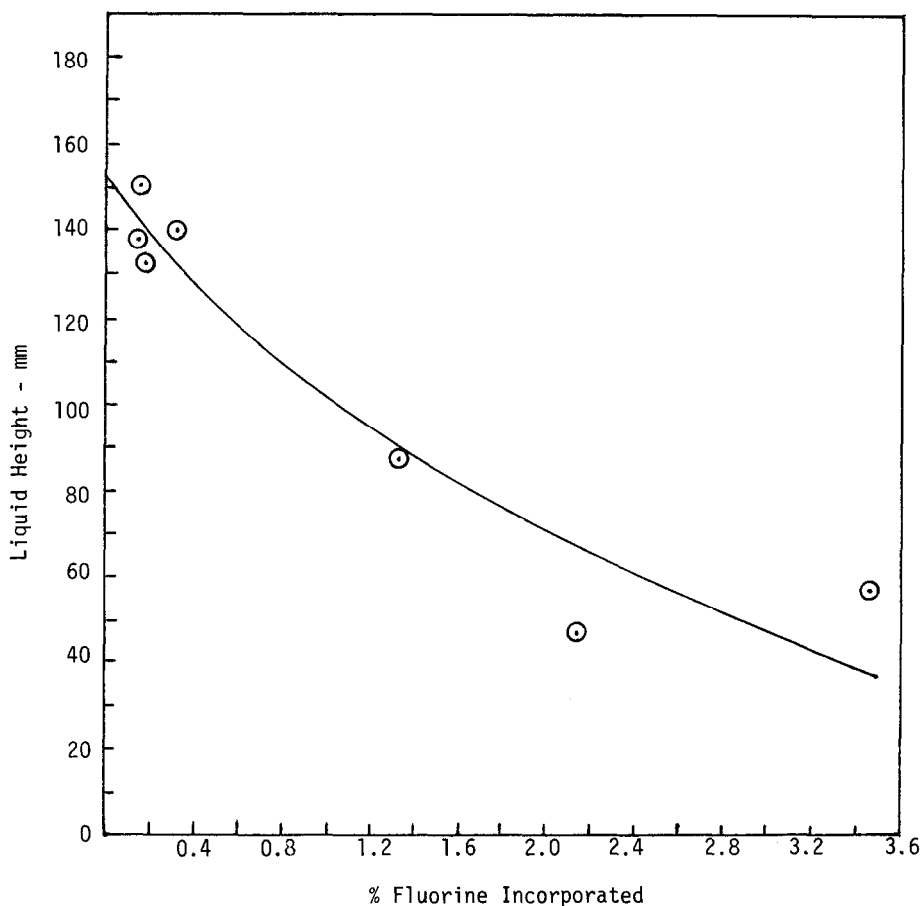
Figure 3. Wicking height versus fluorine incorporation.

Differential thermal analysis, DTA, of the nonfluorinated and fluorinated fabric showed no differences in Tg or Tm.

It has been previously shown that if a polymer is fluorinated in the presence of added oxygen, the wetting property towards water increases [1]. However, when the polyamide was fluorinated in the presence of oxygen, the wettability decreased, Table 5. This suggests that direct fluorination of polyamide does not directly cleave the carbonyl-nitrogen bond, but rather nonselectively fluorinates the entire molecule. At some point the molecules become hydrolytically unstable and decomposes to an acid group. The effect of added oxygen could be to reduce the amount of fluorination by radical inhibition and thus
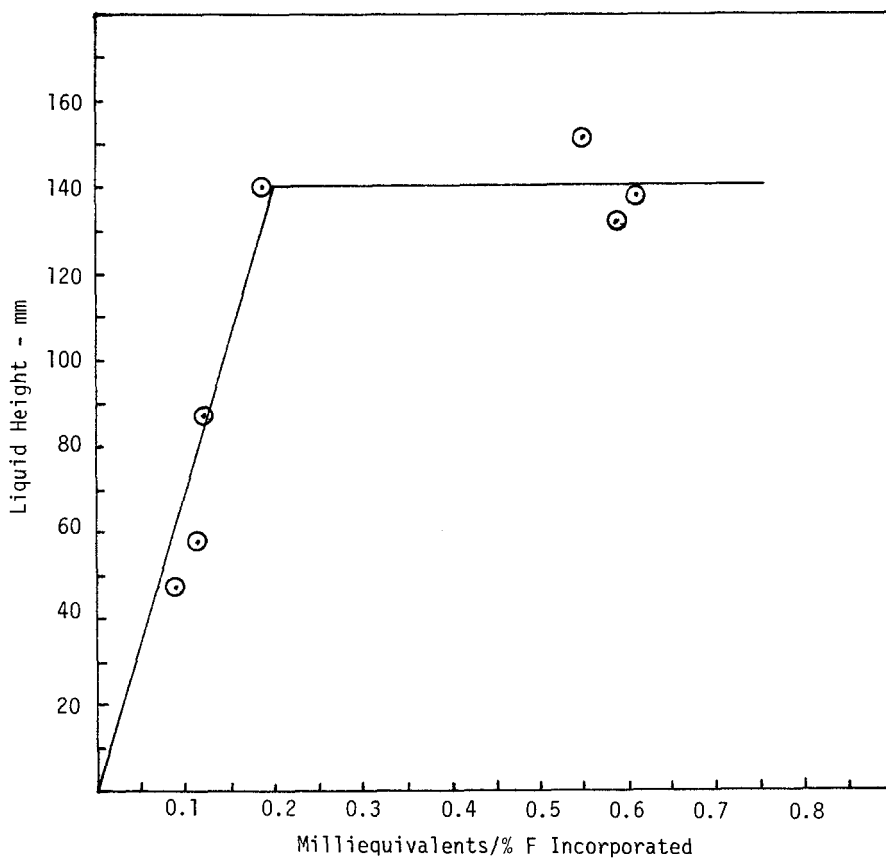
Figure 4. Wicking height versus the ratio milliequivalent per gram of polymer to % fluorine incorporated.

reduce the acid formation. Alternatively, oxygen could cause mass degradation of the surface molecules and thus the fluorinated material is easily washed off. In any case, the presence of oxygen in the fluorinating atmosphere for polymers containing oxygen in the polymer backbone, reduces the wetting property that can be imparted by direct fluorination.

Thus, it has been shown that direct fluorination of polymers whether they have oxygen as part of the backbone or not, can be converted to a more wettable substrate. If the polymer has oxygen atoms as part of the backbone, then the presence of added oxygen to the fluorinating medium is not desired.

TABLE 3

Tensile strength of fluorinated polyamide

Reaction Condition		
F_2 conc. (M)	Time (min)	Tensile Strength (lb/in)
-	-	59.1
1.78×10^{-3}	1	58.2
3.57×10^{-3}	1	48.6
4.46×10^{-3}	1	45.9
1.78×10^{-3}	11	58.6
3.57×10^{-3}	11	45.1
1.78×10^{-3}	25	49.9
3.57×10^{-3}	25	30.1

TABLE 4

Effect of oxygen on the tensile strength

Reaction Condition			
F_2 conc. (M)	O_2 Conc. (M)	Time (min)	Tensile Strength (lbs/in)
-	-	-	59
1.78×10^{-3}	-	6	56
1.78×10^{-3}	4.45×10^{-4}	6	43
1.78×10^{-3}	8.9×10^{-4}	6	45
1.78×10^{-3}	1.33×10^{-3}	6	39

TABLE 5

Effect of oxygen on wettability

Reaction Condition[a] O_2 Concentration, M	Wicking Height, mm[b]
-	113
4.45×10^{-4}	51
2.22×10^{-3}	71

a - F_2 concentration was 1.78×10^{-3} M

b - wicking height at 20 minutes

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