

## Adhesion Behavior of Nylon Tire Cord/Adhesive/Rubber Systems

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### Synopsis

In static and dynamic adhesion tests, the behavior of nylon tire cord/resorcinol-formaldehyde-latex (RFL) adhesive/rubber systems was shown to be strongly influenced by the dipping and curing conditions, cord size, and the thickness of rubber layer adjacent to cords. The nature and extent of these effects were different in three types of adhesion tests which differed in stress concentrations they induced at the cord-rubber interface. The influence of stress concentration due to increased cord size was clearly seen in dynamic adhesion tests where the peel strengths of two-ply cord/rubber samples were measured after flexing them under tension over a pulley for predetermined periods at 230°F. In these tests, the adhesion of samples with large cords weakened more rapidly than that of small cords. The static adhesion level attained with nylons 6 and 66 and other polyamide fibers was strongly dependent on the conditions (time, temperature) under which the RFL adhesive was applied and cured. At any given exposure, adhesion initially increased rapidly with the RFL curing temperature and attained a maximum above a temperature which is characteristic of the polyamide. For nylon 66, optimum adhesion was attained with different combinations of RFL curing temperatures (390-460°F) and times (20-120 sec). Finally the adhesion of nylons 6 and 66 is discussed from thermodynamic considerations based on entropy change.

### INTRODUCTION

Several factors can influence the adhesion behavior of tire cord/adhesive/rubber systems. The effect of rubber characteristics on tire cord adhesion and the development of optimum resorcinol-formaldehyde-latex (RFL) adhesives for nylon and rayon tire cords have been well documented in the literature.<sup>1,2</sup> Although cords of widely different sizes are being used in passenger, truck, and off-the-road tires, little has been published on the effect of cord size on cord/rubber adhesion except for the very limited information in Kenyon's<sup>3</sup> recent work dealing mainly with processing and mechanical properties of large cords. The object of this paper was to examine the effects of cord size and other related factors on the static and dynamic adhesion of some polyamide tire cord/RFL adhesive/rubber systems

### ADHESIVE, RUBBER, AND ADHESION TESTS

Uncatalyzed and base-catalyzed resorcinol-formaldehyde-latex adhesives described in Table I were used to bond the polyamide tire cords to rubber.

TABLE I  
Composition of RLF Adhesives

Polyamide	No. of RFL adhesive	Solids, %	Solids, parts/100 parts rubber latex <sup>a</sup>				R/F mole ratio	Rubber (R+F) wt ratio
			R <sup>b</sup>	F <sup>b</sup>	NaOH	NH <sub>4</sub> OH		
6, 66								
Nomex	1	15-20	11	6	0.30	3.18	0.5	5.9
Nomex	2	25	37.5	7.5	0	0	1.35	2.2

<sup>a</sup> Butadiene-styrene-vinylpyridine (Gen-Tac).

<sup>b</sup> R = resorcinol, F = formaldehyde.

In all the experiments with nylons 6 and 66, the dip solids were adjusted to get a dip pick-up of about 5% by weight of the cord.

The rubber stock was based on a 75/25 blend of natural and styrene-butadiene rubbers and contained 35 phr of a conventional FEF furnace black. The vulcanizing system was based on sulfur, N-oxydiethylene benzothiazole-2-sulfenamide (NOBS) and benzothiazole disulfide (MBTS). The rubber stock had the following characteristics: Mooney scorch time (5 point rise/270°F.), 17 min; 300% modulus, 1940 psi; tensile, 3340 psi; elongation, 460% (all for 40 min cure at 300°F). All cord/rubber samples were cured at 300°F for 45 min.

Static adhesion was measured by three different types of tests. The first was the well known cord pull-through test, the H-pull test (ASTM D2138-62T), with the use of a  $\frac{1}{4} \times \frac{1}{4}$  in. H-block. In the second test, single cords cured onto the surface of the rubber block were stripped at 5 in./min. at 180° angle and the pulling force for about 1½ in. length of the cord was measured and averaged. This test is referred to henceforth as single end strip adhesion or SESA test. The final test involved the measurement of peel adhesion of  $1 \times 4\frac{1}{4}$  in. samples containing two parallel plies of cords. The samples were pulled at 5 in./min at 180° angle and the peel force averaged for 1½ in. length of peel. To eliminate the variable effects of rubber strike-through between the cords, the plies were built with the closest possible spacing of the cords. The thickness of rubber between plies was varied in this test from 30 to 72 mils. All the static adhesion tests were done at 25 and 140°C.

Dynamic adhesion of cords was characterized by peel strengths on 2-ply cord/rubber samples (5 × 1 in.) flexed for predetermined periods over 0.75 in. diameter pulleys on the Scott flexing machine.<sup>4</sup> The conditions of flexing were: temperature, 230°F; flexing rate, 15000/hr; tension on sample = 150 lb. Peel adhesion of the center region (2½ in.) of the flexing sample was plotted as a function of flexing time or flex cycles. This represents the influence of flexing and heat. The contribution of heat aging alone can be obtained from the peel adhesion values of the unflexed shoulder regions of the samples.

## STATIC ADHESION AND CORD SIZE

### H-Pull and SESA

Figures 1 and 2 illustrate the influence of cord size on the H-pull and SESA of 66 nylon tire cords. The cords used for these tests covered a wide range of sizes (1680–10080 den) and included two- and three-ply cords, all of the same twist multiplier. Since both these tests involved single cords, the adhesion of "large" cords was calculated relative to the observed adhesion of the cords of lowest denier (840/1/2) by the following relationship based on the fact that cord surface area is proportional to (denier)<sup>1/2</sup>:

$$A_L = A_S(D_L/D_S)^{1/2} \quad (1)$$

where  $A_L$  is the calculated adhesion of large cord,  $A_S$  is the measured adhesion of 840/1/2 cord,  $D_L$  is the denier of large cords, and  $D_S$  is the denier of 840/1/2 cord.

The calculated adhesion values are represented by dashed lines in Figures 1 and 2. The observed H-pulls match the calculated values for cords up to about 3000 den, above which the measured adhesion lags increasingly behind that anticipated on the basis of cord surface area. This behavior is obviously related to the increased stress concentrations arising from high pulling forces (>45/lb) involved with large cords. Since the H blocks have a fixed thickness, larger cords have thinner layers of rubber available for

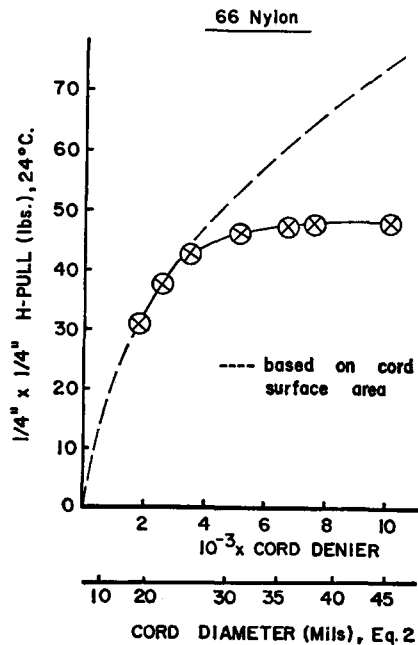


Fig. 1. Effect of cord size on H-pull adhesion for nylon 66.

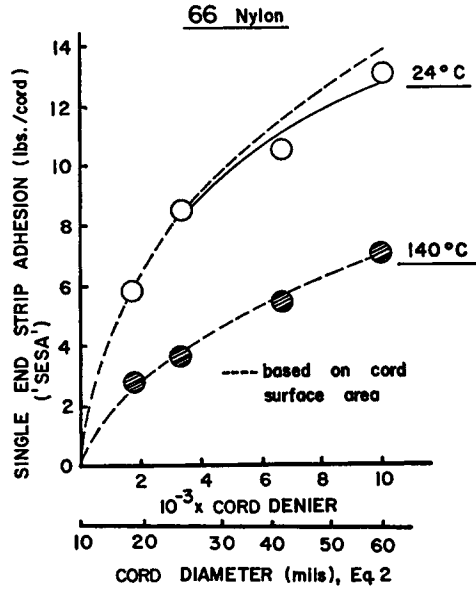


Fig. 2. Effect of cord size on SESA for nylon 66.

relieving their stresses. The SESA (Fig. 2), on the other hand, increased in proportion to the surface area. Apparently, high stress concentrations are unlikely in this test since the pulling force for any given cord is only about 20–25% of that in the H-pull test.

In Figures 1 and 2 cord diameter has been included as an additional ordinate. Cord diameter  $d$  (in centimeters) was calculated from the cord denier  $D$  from the relationship:

$$d = (4D/9000 \times 10^2 \pi \rho_c)^{1/2} \quad (2)$$

where  $\rho$  is the specific gravity of the cord.

When  $d$  is in mils, eq. (2) becomes

$$d = (10^3/2.54)(4D/9 \times 10^5 \pi \rho_c)^{1/2} = (D/4.55 \rho_c)^{1/2} \quad (3)$$

Since  $\rho_c = \rho_p K$ , where  $\rho_p$  is the specific gravity of polymer (=1.14 for nylon) and  $K$  is cord packing factor, eq. (3) for nylon cords becomes

$$d = (D/5.2K)^{1/2} \quad (4)$$

Kenyon's<sup>3</sup> expression,  $d = (D/4)^{1/2}$ , for nylon suggests that he has assumed a cord packing factor of 0.77.

### Two-Ply Peel Test

In preliminary tests, two-ply peel adhesion of samples containing nylon cord decreased as the cord denier increased, although the plies from cords of different sizes were similarly built with the closest possible cord spacing.

These samples had been made with the same thickness (30 mil) of rubber stock between the two plies. Since large cords were expected to increase stress concentrations, the adhesion of two-ply samples was examined in relation to the interply rubber thickness across which stresses would be relieved during the peeling of the samples. Table II summarizes information on the construction of samples designed to test the influence of cord size and interply rubber thickness on peel adhesion.

TABLE II  
Two-Ply Peel Adhesion Samples<sup>a</sup>

Cord	Twist	Cords per inch in ply ( <i>n</i> )	$nD^{1/2b}$	Rubber thickness between cord plies, mils
840/1/2	12 × 12	44	1800	30, 42
840/2/2	8.5 × 8.5	32	1840	30, 42
840/4/2	6 × 6	22	1800	30, 42, 52, 62
840/6/2	4.9 × 4.9	18	1800	30, 42, 52, 62, 74

<sup>a</sup> Nylon 66 cords, RFL dip 1, 4.3% (solid basis).

<sup>b</sup>  $D$  = cord denier;  $n(D)^{1/2}$  is directly proportional to the total width occupied by cords/inch.

Note that the cords of different sizes occupy the same width per inch of the samples as shown by the product of (denier)<sup>1/2</sup> and ends per inch. Peel adhesion of these cord rubber samples increased directly with rubber thickness and decreased inversely with the square root of cord denier ( $D^{1/2}$ ) as shown by the plot of adhesion versus  $t/(D)^{1/2}$  in Figure 3. From such master plots it is possible to predict for a given fiber substrate/adhesive/rubber system the two-ply peel adhesion for any desired combination of cord size and rubber thickness.

### DYNAMIC ADHESION AND CORD SIZE

In preliminary tests made with cords of relatively low denier (e.g., 1680 den), the adhesion of cord/rubber samples weakened only after a relatively long time (>30 hr) of exercising on the Scott flexing machine. Data in Figure 4 illustrate how the use of larger cords progressively reduced the time needed to weaken the initial cord/rubber adhesion. All the three samples had the same total cord width/inch as shown by the  $n(D)^{1/2}$  values in Table III.

TABLE III  
Construction of Samples for Dynamic Adhesion Tests

Cord	<i>n</i> , ends/in.	$nD^{1/2}$
840/1/2	35	1440
1260/1/2	28	1410
840/2/3	20	1420

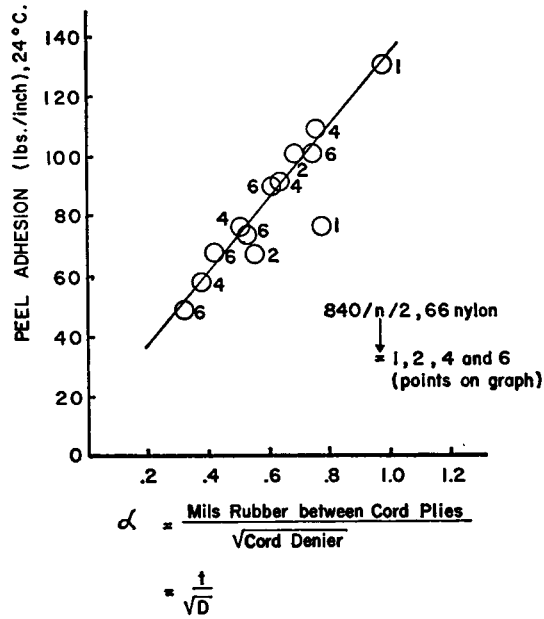


Fig. 3. Effect of cord size and interply rubber on two-ply peel adhesion.

The use of relatively large cords not only reduced the testing time but had the advantage of initiating interfacial (adhesive/rubber) types of failure. With small cords, the duration of the test was prolonged so much that rubber degradation set in before adhesion was reduced by the action of flexing and heat.

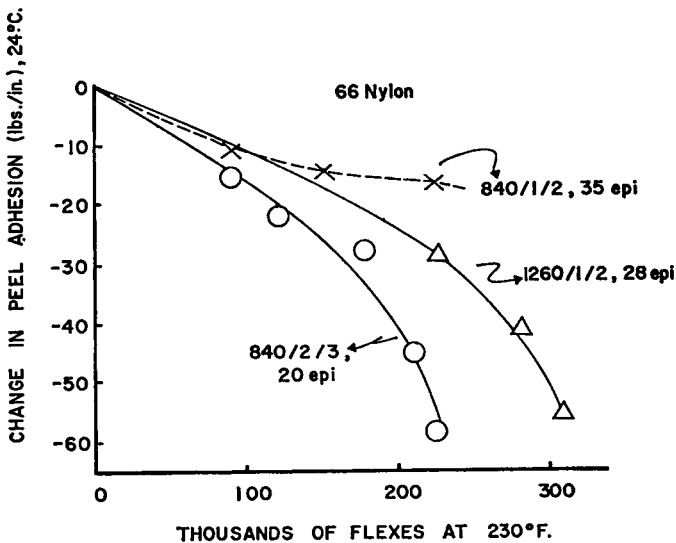


Fig. 4. Effect of cord size on dynamic adhesion for nylon 66.

## DEPENDENCE OF ADHESION ON RFL BONDING CONDITIONS

## Nylons 6 and 66

The adhesion development of polyamide cords was investigated in relation to the conditions (time, temperature) under which the RFL dip was cured on the cord after applying and drying the adhesive dispersion. Table IV summarizes the information on samples and cord processing conditions.

TABLE IV  
Adhesive Treatment of Polyamide Cords

Fiber	Cord denier	Drying step, °F/sec	Curing step, °F/sec
Nylon 6	3360-5040	300/90	270-410/80
Nylon 66	3360-5040	300/90	310-480/80
Nomex	2000	300/60	400-500/60-120

As shown in Figure 5, the static adhesion of nylon 6 and 66 cords was strongly dependent on the dip curing temperature at a given exposure (80 sec). Adhesion initially increased rapidly and attained a maximum above a temperature which is characteristic of the polyamide. This temperature is higher for nylon 66 compared to nylon 6. Consequently, the static adhesion of nylon 66 was poorer than nylon 6 at relatively low dip curing temperatures (e.g., 350°F/80 sec) but was fully equivalent to the latter when the dip was cured at a sufficiently high temperature (440°F). The trend for adhesion to drop off at very high dip curing temperatures (>470°F) is related to the overcuring of the dip under these severe conditions. Investigations of nylon 66 cords processed with adhesive at different combinations of time (5-240 sec) and temperature (310-460°F) indicated (Fig. 6)

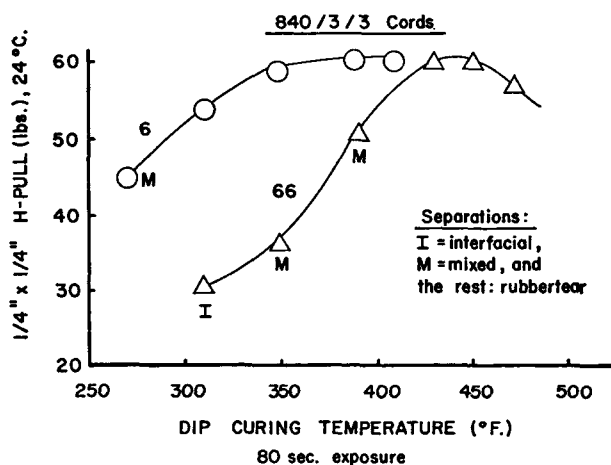


Fig. 5. Effect of dip curing temperature on adhesion of nylons 6 and 66, 840/3/3 cords.

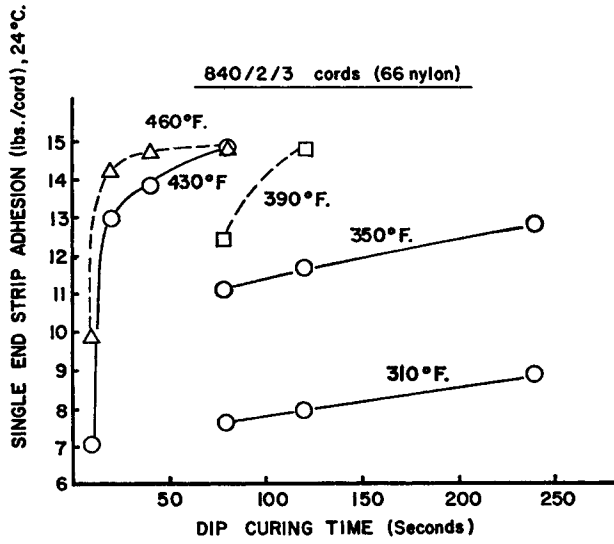


Fig. 6. SESA vs. dip curing time and temperature for nylon 66, 840/2/3 cords.

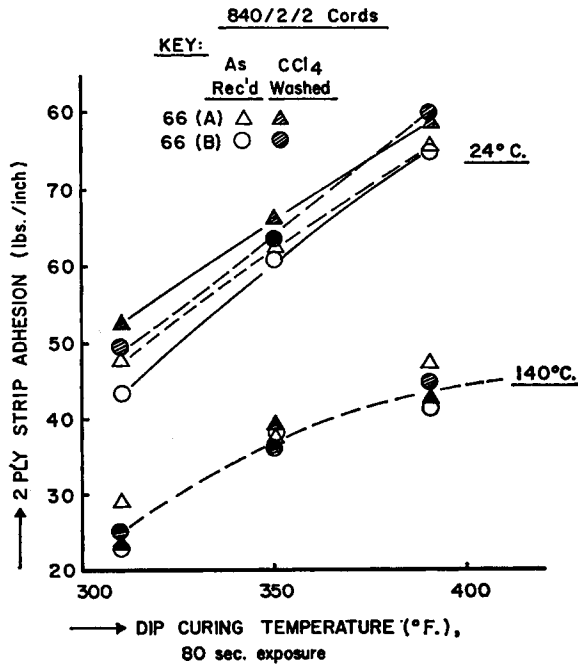


Fig. 7. Adhesion of as received and solvent-washed nylons, 66 840/2/2 cords.



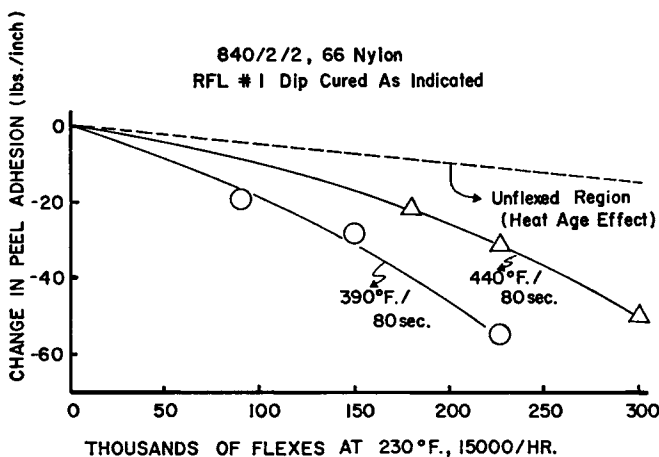


Fig. 8. Effect of dip curing temperature on dynamic adhesion of nylon 66, 840/2/2 cords; RFL dip 1, cured as indicated.

that optimum adhesion can be attained at practical levels of exposure (<120 sec) by using moderately low dip curing temperatures (390–430°F).

The observed adhesion effects are the characteristics of the polymers but are not likely to be associated with the finishes or other materials on the yarn surface as indicated by the insignificant change in adhesion of two different nylons 66 (A and B, Fig. 7) even after the yarns had been thoroughly washed with solvent ( $\text{CCl}_4$ ) prior to adhesive treatment. Similarly, the curve for nylon 6 in Figure 5 was unchanged when solvent-washed yarn was used.

Data in Figure 8 illustrate the importance of adhesive bonding conditions on the dynamic adhesion of nylon 66. Increasing the dip curing temperature from 390 to 440°F (80 sec exposure) significantly reduced the adhesion loss after dynamic flexing. Also shown in Figure 8 is the heat age effect on adhesion as measured by the peel adhesion of the unflexed shoulder region of the samples.

### Nomex

In the case of Nomex, a polyamide with a high glass transition temperature ( $T_g > 500^\circ\text{F}$ ), quite severe bonding conditions are needed to develop high adhesion levels. Data in Figure 9 show that Nomex adhesion increased with increase in dip curing temperature up to the highest value (500°F/60 sec). Higher levels of adhesion were developed with RFL dip 2, since this adhesive system has a high resorcinol content, providing increased OH sites for hydrogen bonding to the amide group of the substrate, and a low HCHO/resorcinol ratio, resulting in a less crosslinking and more diffusible RFL adhesive species.

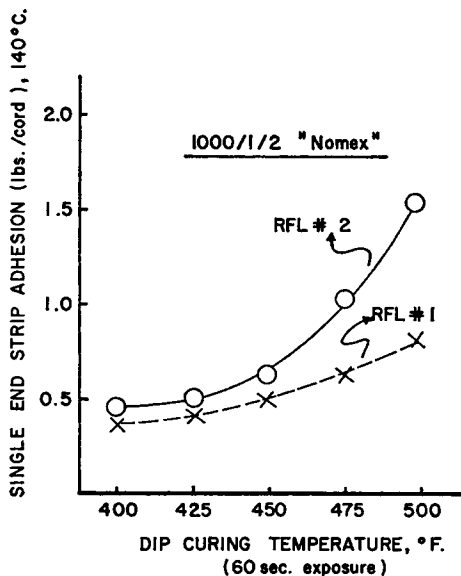


Fig. 9. Effect of dip curing temperature on adhesion of nomex cord, 1000/1/2 cord.

### NYLON 6 AND 66 ADHESION—ENTROPY CONSIDERATION

Thermodynamic considerations indicate that nylons 66 and 6 should show equivalent adhesion when bonded near their respective melting points. In a paper dealing with nylon 6, Nesty<sup>5</sup> pointed out that nylon 6 has a lower melting point than nylon 66 because its entropy of fusion ( $\Delta S_f$ ) is higher than that of the latter. The high  $\Delta S_f$  of nylon 6 has its origin in the low entropy of the solid polymer with its highly ordered inversion of chains not present in the nylon 66 structure. Since the heats of fusion ( $\Delta H_f$ ) of the two polymers are essentially equivalent,<sup>5</sup> the lower melting point ( $T_f$ ) of nylon 6 relative to nylon 66 is obvious by the relation:

$$T_f = \Delta H_f / \Delta S_f \quad (5)$$

remembering that  $\Delta S_f$  (nylon 6)  $>$   $\Delta S_f$  (nylon 66).

The information on  $\Delta S_f$  can now be applied to the adhesion concepts of Abere,<sup>6</sup> to obtain the relative bondability of nylons 6 and 66 near their melting points. According to Abere, the free energy change for creating a new interface is given by:

$$\Delta F = \Delta H_m - T \cdot \Delta S \quad (6)$$

where  $\Delta H_m$  is the heat of mixing determined by cohesive energy density considerations,  $T$  is the bonding temperature, and  $\Delta S$  is the entropy change at the interface. Since the cohesive energy density of RFL polymers based

on resorcinol matches that of nylon 6 and 66 polymers,<sup>7</sup>  $\Delta H_m = 0$ , and thus

$$\Delta F = -T \Delta S \quad (7)$$

For the situation at the melting point, eq. (7) becomes:

$$\Delta F_f = -T_f \Delta S_f \quad (8)$$

where the subscript f stands for the melting point (fusion).

Combining eqs. (8) and (5) yields

$$\Delta F_f = -\Delta H_f \quad (9)$$

Since the  $\Delta H_f$  for nylons 6 and 66 are the same, the change in free energy,  $\Delta F_f$  and hence the potential for bondability is the same for nylons 6 and 66 at their respective melting points.

The above discussion is limited to bondability at or near the melting point of the polymers. At temperature considerably lower than the polymer melting point, other factors become important, as shown by our data on the dependence of nylon 6 and 66 adhesion on adhesive curing conditions.

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