FACTORS AFFECTING TEXTILE CORD-RUBBER ADHESION

by

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THESIS

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1. INTRODUCTION

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In the rubber products, for example tires, belting and hoses, it is necessary to increase the strength of the rubber by incorporating a reinforcement, which is usually textile. In these products it is not enough to have the textile present, it is essential to have a good bond, high level of adhesion between textile and rubber. Therefore the development of a suitable adhesive systems was an important step.

It can be said that there are three main factors which affect the adhesion between the textile cord and the rubber compound :

- the reinforced rubber compound
- the quality and the structure of the textile cord
- the adhesive system

Adhesion is of great importance not only between rubber and textile but also in several fields of science and technology. The wide industrial application of textile-to-rubber adhesion has emphasized the need for a more detailed evaluation of the various parameters which directly influence and affect the adhesion strength.

The evaluation of adhesion is important for a variety of reasons:

(a) to optimize the methods and conditions which yield the required adhesion strength.

(b) to differentiate between systems with poor and good adhesion strength.

(c) to gain fundamental insight into the mechanism of adhesion.

Accordingly, the aim of the present work is to gain information on those factors which affect the adhesion between rubber and textile cords. Therefore we investigated the effect of heat treatment conditions (temperature and time) after dipping. The scope of this work is also to determine the optimum conditions which give the best adhesion. In this thesis we also discuss the effect of the textile cord quality, the type of the rubber compound and the heat treatment conditions on the tensile properties, the dip pick-up quantity, and the adhesion level. The results will help the rubber technologist to obtain a good balance of static and dynamic adhesion properties with nylon and polyester cords.

2. LITERATURE REVIEW

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2.1 Most Commonly Used Reinforcing Fibres.

In the rubber industry, in 1910, the first reinforcing material was cotton, but thereafter with increasing requirements it was replaced by Rayon in 1923. Du Pont (1) introduced high tenacity Rayon in 1933. Rayon (being regenerated cellulose fibre) is chemically very similar to cotton, but the various processes by which the yarn is produced introduce differences in properties between the two. Then new tougher materials were required for heavy duty applications. In 1947, the nylons, both 6,6 and 6, were the first of the truly synthetic fibres to be adopted for use by the rubber industry. They offer better tensile strength and fatigue resistance over the cellulosic fibres. Goodyear started to produce polyester as reinforcing material in 1962. Polyester, with tensile strength similar to nylon, has higher modulus rendering it more suitable for many applications, for example, passenger car tires and conveyor belts. Aramids, the aromatic polyamides, were introduced in the 1970s as rubber reinforcement materials. They have been engineered for the reinforcement of radial tires and mechanical goods, including hoses, conveyor belts, and power transmission belts.

Although not strictly textile fibres, glass and steel have found many applications as reinforcements in elastomers. In 1936, steel cords have been used extensively in radial tires and in the 1960s glass fibre cords are used for the belt ply or radial tires or belted bias tires.

2.1.1 Types of textile fibres and their physical properties.

Five main types of fibres are used in the reinforcement of elastomers. They are cotton, rayon, nylon, polyester, and aramid. The properties of each one of them are mentioned below (2).

Cotton

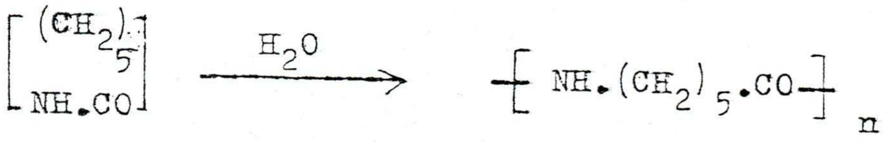
Cotton is a natural fibre, consisting of the seed hairs of a range of plant species in the Mallow Family. The plants are grown, mainly as an annual crop, in many countries around the world. Cotton is of only moderate strength. It has largely been replaced by the stronger man-made fibres, but it still finds application where the requirement is not primarily for high strength. The advantage possessed by cotton derives from its staple nature. This relates to its use as an adhesion contributor, since adhesion is obtained basically by the mechanical anchoring of the staple fibre ends in the elastomer matrix.

Rayon

Rayon is a man-made fibre, based on regenerated cellulose. The raw materials used are either cotton linters or wood pulp, both of which have a very high cellulose content. The rayons are much stronger than cotton. They also possess good modulus characteristics but with rather low ultimate elongation, which can be a disadvantage in some applications. One other disadvantage of the rayons lies in their sensitivity to moisture. They lose a significant proportion of their strength in moist conditions.

Nylon

Originally Nylon was a Du Pont trade name, which became the generic name for the linear aliphatic polyamides. Nylon 6 is the polyamide derived from ε-amino caproic acid (caprolactam) which contains six carbon atoms, hence giving the designation nylon 6.



$$\begin{bmatrix}(\mathrm{CH_2})_5 \\ \mathrm{NH.CO}\end{bmatrix} \xrightarrow{\mathrm{H_2O}} \left[\mathrm{NH.(CH_2)_5.CO}\right]_n \qquad [1]$$

Caprolactam

Nylon 6

Nylon 6,6 is the polyamide obtained from the polycondensation of hexamethylene diamine and adipic acid, each monomer containing six carbon atoms so giving the designation of nylon 6,6.

$$\underset{\text{Hexamethylene Diamine}}{n\,H_2N.(CH_2)_6.NH_2} + \underset{\text{Adipic Acid}}{n\,HOOC.(CH_2)_4.COOH} \longrightarrow$$

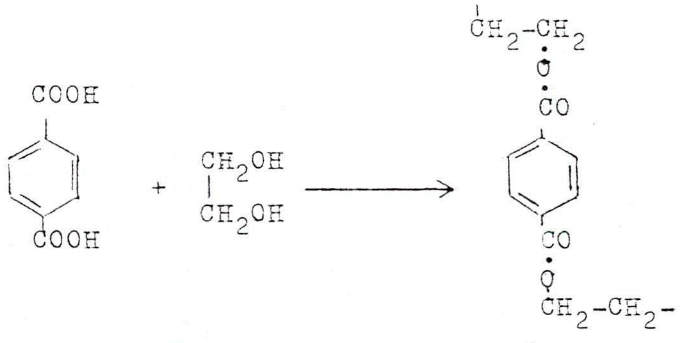
$$\underset{\text{Nylon 6,6}}{\left[NH.(CH_2)_6.NH{-}CO(CH_2)_4CO \right]_n} + 2n\,H_2O \qquad [2]$$

The nylons are of much higher strength if compared with cellulosics, and also give much higher ultimate elonga-tions. This latter property imparts to nylon fabrics a greatly improved impact resistance, higher work to rupture and much better tear resistance.

One characteristic of nylon, not possessed by the cellulosics, is the thermal shrinkage. Being a thermoplastic material, when heated, nylon tends to shrink, its elongation will increase and modulus will fall. By choosing suitable conditions of processing, it is possible to modify the shrinkage characteristics to suit more precisely the final parameters to be satisfied.

Polyester

In the textile industry, polyester is the general name given to the fibres from poly-ethylene terephthalate. It is prepared by the direct esterification of the terephthalic acid with ethylene glycol.



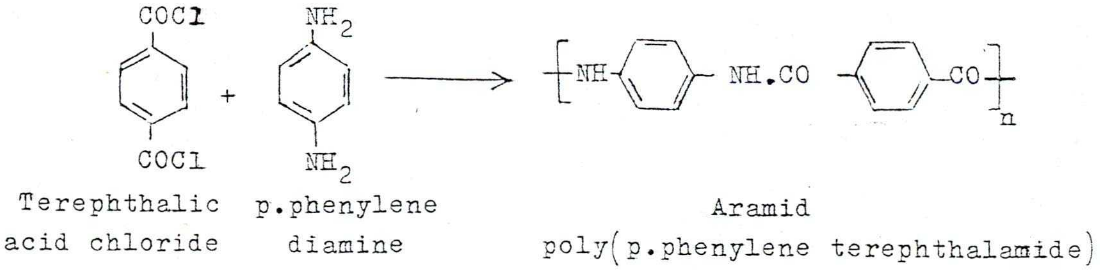
[3]

Terephthalic Acid Ethylene Glycol Poly(ethylene terephthalate)

The polyester combines the strength and elongation characteristics of the nylons with the modulus characteristics of the rayons. This combination of properties suits polyester for many applications, but there are two main areas where problems exist. The first concerns adhesion : being relatively inert chemically, it is somewhat more difficult to obtain adequate levels of adhesion with polyester than with nylon or rayon, but methods of treatment have been developed to overcome this. The second area relates to thermal shrinkage, which is even greater than with nylon, therefore processes were developed to modify the shrinkage characteristics of polyester.

Aramid

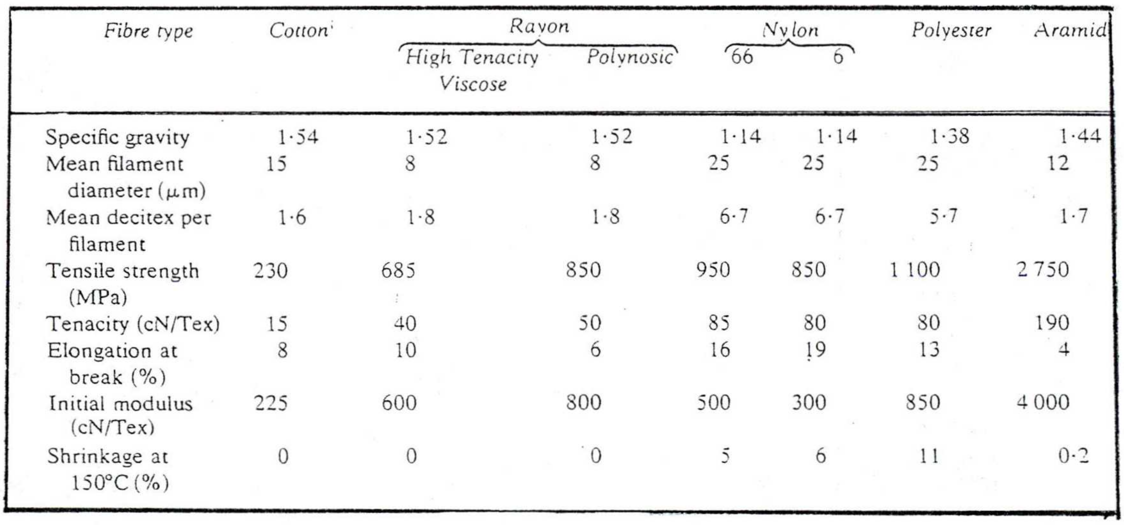
The aramids are aromatic polyamides, although they are closely related to the nylons (the aliphatic polyamides), the substitution of the aliphatic carbon backbone by aromatic groups brings about considerable changes in the properties of the resultant fibres. Aramid is formed by the reaction of terephthalic acid chloride with p.phenylene diamine.



[4]

The strength of aramid is exceptional. Also the modulus is very high, but this is coupled with a very low ultimate elongation which introduces some difficulties in applications. For example, when aramid is used in several layers; when flat, each layer of textile is able to contribute its own share of strength, but on bending, the low elongation of the outermost layer prevents this from accommodating to the curve, so that the neutral axis is raised to this layer, which places the other layers under compression. This directly reduces the contribution of the inner plies to the total strength. So under such conditions, premature failure of the inner plies is likely to occur since the dynamic fatigue resistance of aramid is not good.

The main physical properties of the textile fibres are given in the following table (2) :



Fibre type	*Cotton*	*Rayon*		*Nylon*		*Polyester*	*Aramid*
		High Tenacity Viscose	*Polynosic*	*66*	*6*		
Specific gravity	1·54	1·52	1·52	1·14	1·14	1·38	1·44
Mean filament diameter (μm)	15	8	8	25	25	25	12
Mean decitex per filament	1·6	1·8	1·8	6·7	6·7	5·7	1·7
Tensile strength (MPa)	230	685	850	950	850	1 100	2 750
Tenacity (cN/Tex)	15	40	50	85	80	80	190
Elongation at break (%)	8	10	6	16	19	13	4
Initial modulus (cN/Tex)	225	600	800	500	300	850	4 000
Shrinkage at 150°C (%)	0	0	0	5	6	11	0·2

The stress-strain characteristics of the above mentioned textile fibres is illustrated in figure 1.

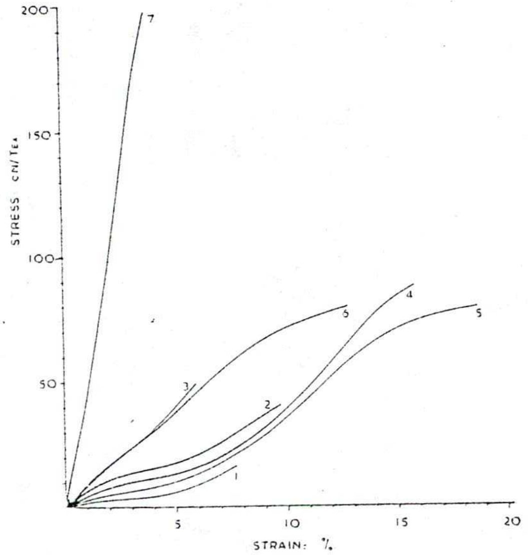


Fig. 1. Stress-strain characteristics of the textile fibres. 1. cotton: 2. H. T. rayon: 3. polynosic rayon: 4. nylon 66: 5. nylon 6: 6. polyester: 7. aramid.(2)

2.2 Adhesion Between Textile Cord And Rubber.

2.2.1 Physicochemical aspects of adhesion

The problem of bonding textile fibers to rubber is a very complex one because it involves the great difference between two types of surface. Many authors discussed the physicochemistry of polymer adhesion in detail, but a short account will be reviewed in this part.

(a) Types of interaction forces proceeding from polymer surfaces.

The interaction forces can be classified in the following types (3):

1. Chemical bonding

Chemical bonds can be subdivided into heteropolar, homopolar and metallic bonds. In the heteropolar bond (ionic bond) an atom donates electrons and another accepts them. The homopolar (atomic bond) is based on the exchange of valence electrons of the interacting atoms. Thus, one pair of electrons belongs to both atoms. The metallic bond is characterized by the lattice structure of the metals in which the lattice points are occupied by positively charged ions while the valence electrons are freely movable in the lattice and neutralize its charge.

2. Dipole interaction

Dipole forces are produced by the interaction of static dipoles of one interaction partner with static or induced dipoles of the other one. Induced dipoles are generated if a permanent dipole approaches a polarizable molecule.

The hydrogen bond, considered as an independent bond type, is based on the interaction of oriented dipoles. Fowkes (4) discusses the hydrogen bond as a form of the acid-base interaction.

3. Dispersion interaction

The dispersion interaction is based on the motion of the electrons in the electron shell of the molecules. This motion causes, in each molecule and at any instant, an electrical dipole moment which can correlate with the moment of a neighbouring molecule produced in the same way. This creates a force of attraction.

4. Electrostatic interaction

Electrostatic forces can occur between solids. An electrostatic interaction between two solids occurs when electrons are transferred from one to the other contact partner (electron donor and electron acceptor). Consequently, an electrical double-layer is formed at the interface.

5. Hydrophobic interactions (3)

The hydrophobic interaction is observed when surfactants from aqueous solutions are adsorbed on polymers and when proteins interact in aqueous solutions. All polymers, fillers, reinforcing materials adsorb water at the surface or in a swelling-layer at normal atmospheric humidity and at elevated temperatures. Therefore, in the presence of surfactants, the effect of hydrophobic interactions cannot be excluded in polymer processing or in studies of the properties of polymer composites.

6. Solvation forces

The solvation forces are repulsive forces effective up to distances of some nm between inorganic solids in aqueous solutions. They are interpreted by the hydration of the surface of the solid. With regard to polymers, the solvation forces can take place in the system polymer/inorganic filler (5).

7. Acid-base interactions

Bolger (6) stated that electrostatic interactions can occur between metals, metal oxides and hydroxides and organic acids or bases. Their energy is determined by the basicity or acidity of the participating components. Fowkes (4,7) extended the acid-base interaction to acids and bases in the sense of Lewis theory, according to which an electron transfer occurs when Lewis acid (electron acceptors) come into contact with Lewis bases (electron donors). The electron transfer causes electrostatic interaction between the partners.

Jacobasch (8) showed that the most important forces between fibers and other substances are electrostatic, dispersion and dipolar forces. These forces cause adhesion, wetting and adsorption of gases, vapors and surface active agents. He stated that the difference in adhesion of fibers against other substances is mainly caused by polar forces which can roughly be estimated from the surface free energy determined by contact angle measurements according to Fowkes (9), Wu (10) and Owens and Wendt (11).

(b) Methods of investigation

Different methods are used to characterize the interaction forces. These methods are classified into the following:

1. Direct determination of interaction forces

Many methods have been developed to determine the adhesive strength of composites. Generally, the force necessary to solve the adhesive joint is determined. The most important methods, e.g., weighing method; pendulum method and vibration method are discussed in detail in the literature (3).

2. Indirect methods

These methods include (3,8):

- Determination of Hamaker constant which characterizes the interaction between solids and other substances caused by dispersion forces.

- Wetting measurements in which the surface free energy is used for characterizing polymer surfaces. For this purpose, the surface free energy is mostly determined by contact-angle measurements (12).

- Electrokinetic measurements: the electrokinetic method of inorganic or organic particles dispersed in liquids has been used to describe the electrostatic interaction between particles. The description of electrokinetic phenomena is based on the model of the electric double-layer at the solid/liquid interface, as e.g., most textile fibers have a discrete surface layer containing an electrical double layer because of the uptake of water vapor in a normal atmosphere (8). Therefore, neglecting the contribution of the electrical double layer to adhesion of polymers may lead to completely incorrect results (13).

- Sorption measurements: with these measurements some information about thermodynamic data, the degree of coverage and the orientation of adsorption layers can be known. These follow from the interaction energy between adsorbent and adsorbate. Also some information can be obtained about the specific surface of the adsorbent and the diffusion of the adsorbate into the solid. Measurement of gas sorption and sorption of dissolved substances are the means applied to characterize the surface properties of polymers.

3. Surface spectroscopy

Spectroscopical methods and different procedures of instrumental analysis are applied to the surfaces of solids, e.g., electron spectroscopy for chemical analysis to give information about the surface structures and infrared spectroscopy to give information about chemical bonding (3). Different methods are combined in such a way that they complement each other concerning the information they yield.

Mittal (14) pointed out the differences between "fundamental" and "practical" adhesion. Fundamental adhesion signifies summation of all interfacial intermolecular interactions whereas practical adhesion is expressed as the force or the work required to remove the coating and that the practical adhesion depends on interfacial interactions plus a number of other factors. These other factors include stresses in the coating, technique used to measure practical adhesion and mode of applying external stresses. He also mentioned that there are many surface analytical tools used, e.g., ion scattering spectroscopy and electron spectroscopy for chemical analysis, to determine the locus of failure.

2.2.2 Factors affecting adhesion and methods of bonding

Some of the important factors which affect the adhesion between textile cords and rubber can be summarized as follows (15):

Mechanical interlocking.

Formation of primary bonds and hydrogen bonds.

Coating characteristics.

Interdiffusion.

Environmental effects (light, oxygen, ozone, sulphur dioxide, nitrogen oxides) (16-24).

Prevorsek and Sharma (25) and others (26) showed that the level of adhesion between rubber and textile cords decreases with time of cycling and that mechanical loss and dynamic modulus of cord-rubber composites depend on temperature, pretension, time of cycling and the presence and type of adhesive at the cord-rubber interface.

Strong adhesion is obtained through adhesive treatment of the textile or through addition of bonding agents to the rubber compound. Though several methods are available to bond textile to rubber, it is necessary to select an adequate method according to the raw materials and the application.

The method of rubber-to-textile bonding can be divided into the following groups (27):

Adhesion based on structural effects.

Adhesive treatment of textile material.

2.2.2.1 Adhesion based on structural effects.

Borroff (28), and Wake (29) investigated the function of staple fibre in adhesion. Fabrics were coated with a rubber solution and then vulcanized in an oven. Adhesion was measured by the direct tension method. It was found that bond strength is remarkably affected by amount of staple yarn as well as type of rubber solution and kind of textile material.

2.2.2.2 Adhesive treatment of textiles.

2.2.2.2.1 Rubber solution adhesives.

This method is used for the belt and coated fabric industries. These adhesives are based on rubber solution to which very reactive chemicals are added just prior to use, for example, diisocyanates or triisocyanates. Adhesion is obtained by immersing the textile material into rubber solution of low concentrations as used for cotton and rayon, or spreading with doughs of high concentrations as for nylon and polyester (30). The adhesive-treated textile is then dried in an oven, bonded to rubber and vulcanized. The use of this adhesive method is limited by the danger of fire and toxicity. Blocked isocyanates have been used instead of free isocanate in order to decrease toxicity.

2.2.2.2.2 Resorcinol-Formaldehyde-Latex (RFL) adhesives.

The techniques used for adhering textile cords to rubber have involved either treating the cord itself with a suitable dip system or the incorporation of bonding additives into the rubber compound or a combination of both are used if improved adhesion is required (31).

Resorcinol formaldehyde resin was selected to be used as an aqueous adhesive incorporated into latex because of its superior adhesion and ease of processing (32). The original RFL formulation was developed by Charch and Maney (33). The adhesive system was applied primarily to rayon fibres and later extended to nylon and glass fibres.

The RFL system did not give satisfactory adhesion in case of polyester fibres, this can be attributed to the nature and structure of the fibre (2,27) and lack of reactive hydrogen in the polyester molecule (34).

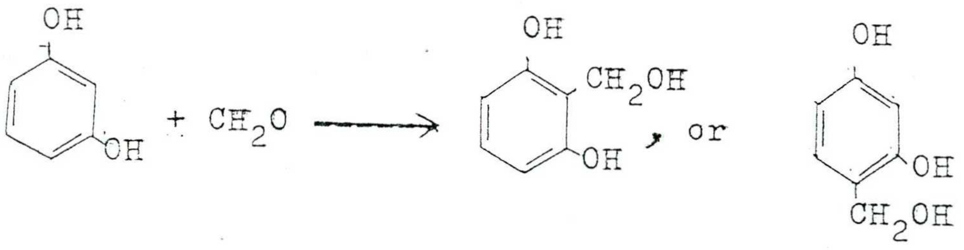
Many factors are known to affect the bond strength secured with RFL adhesives. For example, composition of RFL, method of RFL preparation, amounts of adhesive applied to cords, its distribution on the cord, heat treatment after dipping, method of storing dipped cord, composition of rubber compound, and vulcanization conditions may be factors affecting the cord-to-rubber bonding.

Textile cord or fabric is immersed in an RFL dip bath, and squeezed by passing through a squeeze roll unit, beater to adjust pick-up of adhesive. Then the cord is introduced into an oven where drying and baking of the RFL is accomplished. Widely accepted dipping machines for cord and fabric are illustrated in the literature (35). Water predip before RFL immersion is a widely used technique to improve physical properties of dipped cords (36).

I. Adhesive treatment of nylon, rayon, and aramid.

(a) Resorcinol Formaldehyde (RF).

RF resins are usually prepared by reacting resorcinol and formaldehyde under alkaline conditions prior to addition to latex. Resorcinol readily combines with formaldehyde to form methylol derivatives, with the methylol groups occupying either the positions ortho to both hydroxyl groups, or ortho to one and para to the other.



[5]

The reactivity of these methylol derivatives is so high, they continue to react under ambient, uncatalyzed conditions with formaldehyde, resorcinol or other methylol-containing molecules to form polymer chains of higher molecular size, with branched, as well as linear, configurations of great complexity. These reactions continue until steric considerations prevent further interaction. In these polymers the resorcinol nuclei are joined together through methylene linkages to give complex molecules.

The reaction rate of resorcinol with formaldehyde is dependent upon : the molar ratio of the two constituents, the concentration of the solution, pH, the presence of various catalysts, and the amount of alcohols used (37-40). The rate of the reaction is accelerated with increasing amount of formaldehyde. The reactivity is high in the presence of strong acid catalysts ($pH < 2$), but exceedingly low at a range of pH 3 to 5. As the pH increases to 7 or above, the rate increases again. Ethanol and other alcohols have a retarding effect on the rate of the reaction since they react with formaldehyde forming hemiformals which in turn reduces the rate of reaction because of the smaller concentration of free formaldehyde. In this resin master, the formaldehyde ratio vary from 1.5 to 5 moles per mole of resorcinol. By careful ageing of resin master, dispersed resole molecules are formed, which have composition depends upon time, temperature, pH, and concentration (41).

It was found that resorcinol to formaldehyde ratio has a great effect on adhesion, since the viscosity of matured RF solution varied with this ratio. Also the network structure of RF resin changes widely with resorcinol-formaldehyde ratio. Thus by putting the results of Miller and Robison (42), Dietrick (43), and Uzina and co-workers (44) together the preferred ratio in RF resin is found to be 2 to 5 mole formaldehyde per mole resorcinol for nylon and rayon. Also Solomon (45) stated that ,in order to obtain a high level of adhesion the formaldehyde-to-resorcinol molar ratio be in the range of 2:1 as illustrated in figure 2.

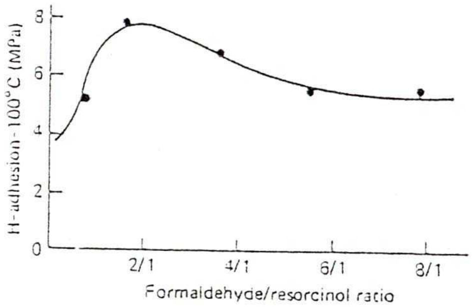
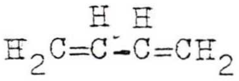


Fig. 2. Formaldehyde-to-resorcinol ratio of the adhesive dip—effect on adhesion.(45)

(b) Latex type (L).

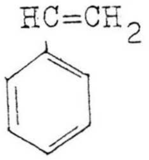
Natural and SBR latexes were used in RFL adhesive systems. However it was found that latexes containing vinyl pyridine terpolymer (B/S/VP) gave high levels of adhesion of fibres to rubber. The chemical composition of this latex is illustrated as follows :



$H_2C{=}\overset{H}{C}{-}\overset{H}{C}{=}CH_2$

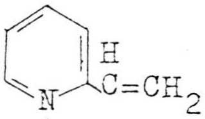
Butadiene

(70 Parts)



Styrene

(15 Parts)



Vinyl Pyridine

(15 Parts)

One explanation for this good adhesion is due to the exceptionally high strength of the vulcanized terpolymer itself. Another explanation attributes the superior adhesion to a direct dipole-dipole interaction between the more polar vinyl pyridine terpolymer and the textile fibre. A third view is that the pyridine nuclei facilitate the interaction of the resin and the rubber phase.

Sufficient latex is added to the resin with good stirring. It was found that adhesion increases with increasing amount of resin (27), as shown in figure 3. However, too much resin in the adhesive can result in stiff cords, while too much latex can give unsatisfactory film strength and low bonding strength.

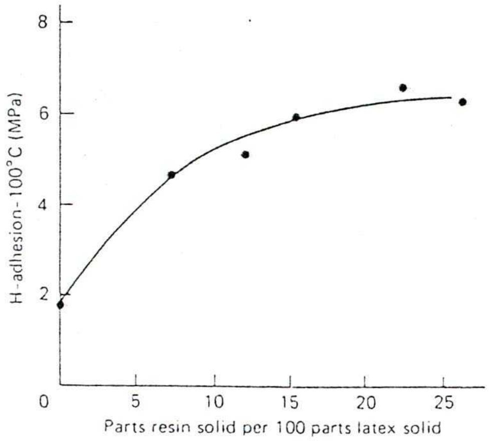


Fig. 3. RF-to-rubber solids in tire cord adhesives—effect on cord adhesion.(27)

The mixture is usually aged to obtain optimum adhesion (46). At this stage a reaction takes place between some of the methylol groups on the resin molecules with the unsaturated carbon of the rubber molecule to form crosslinks of chroman type (47), the chemistry of the reaction is shown in equation [10]. Then the resin-rubber molecules can combine with the functional groups on textile surfaces through residual methylol groups (48). Later on, when the treated cord is moulded into the rubber matrix, the remainder of the unsaturated groups in the elastomer portion of the particles are available for reaction with sulphur and combine with the surface of this substrate through direct covalent linkages (47,48). The mechanisms of adhesion will be discussed later.

In case of adhesion of resorcinol resins to fibre surface, the nature of the fibre plays an important role in the bonding of rubber to fibre. It was found that rayon cords are relatively easy, nylon and aramid cords are more difficult to bond.

The RFL recipe should be varied with the textile material. The following formulations (27) have been found to give optimum adhesion with rayon and nylon.

Fabric	Rayon	Nylon
Gentac latex, 41% *	52.5 g	428.0 g
SBR latex, 40%	215.0	-----
RF solution,6.5%	284.0	465.0
Water	487.8	107.0

* Butadiene/Styrene/Vinyl pyridine terpolymer latex.

The maturing condition for RFL mixtures is: 6 hrs. at 25°C

It has been suggested (49) that for a maximum adhesion with dipped nylon some adjustments of pH is necessary depending on the compound being bonded. The static adhesion levels obtained with nylon 6 and nylon 6,6 are strongly dependent on conditions (time,temperature) under which the RFL is applied and baked (50).

Iyengar (51) proposes a two-step adhesive system for aramid fibre adhesion to rubber. In the subcoat he uses epoxide as adhesion promoter. An RFL top coat is then used as second step dip. The subcoat is heat-set for one minute at 243°C while the top coat RFL is heat-set for one minute at 232°C. Another two coat adhesive system (52) uses a 2% solution of glycerol diglycidyl ether as the subcoat and the top coat consists of 1,3-butadiene-styrene-2-vinyl pyridine copolymer along with a heat reactive 2,6-bis(2,4-hydroxy phenyl methyl)-4-chlorophenol. An epichlorohydrin treated hydroxybenzoic acid resin (53) is also used to improve adhesion of aramid to rubber.

(c) Mechanisms of adhesion of RFL.

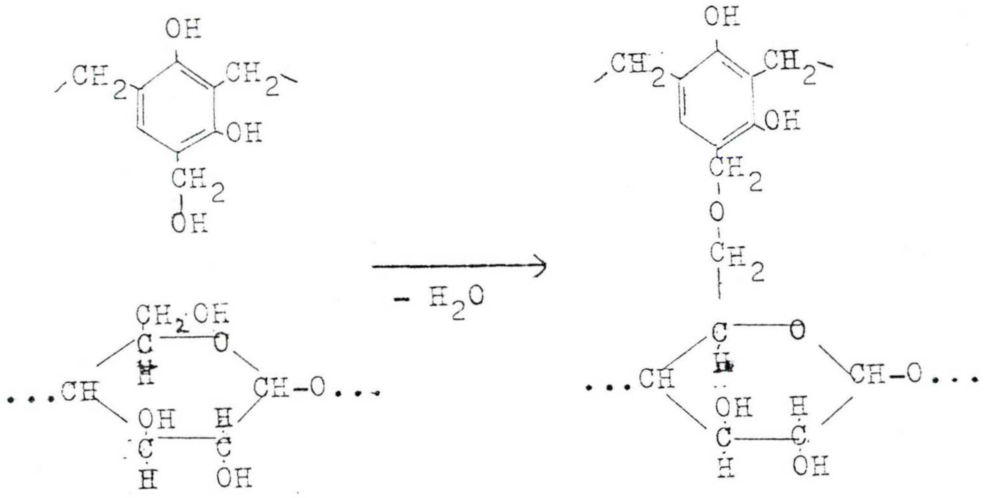
Iyengar (54) discusses in detail the mechanism of adhesion development. Adhesion can occur by primary bonds, H-bonds or diffusion between adhesive and substrate. The diffusion type bonding becomes important for substrates that have limited capacity for H-bonding. For such substrates, thermodynamic compatibility of the substrate and adhesive is attained when the solubility parameters of substrate and adhesive are matched.

To explain the mechanism of rubber-to-nylon and rayon cord bonding, it is very important to take into consideration the nature of RFL to fibre bond and the nature of RFL to rubber bond.

(i) RFL-to-textile adhesion.

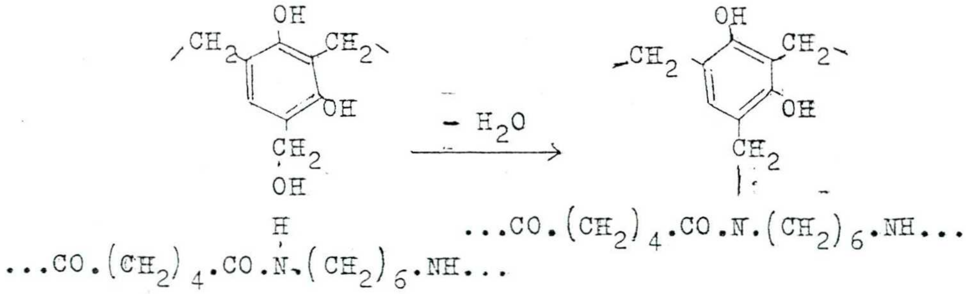
There are many opinions on how RFL functions with rayon and nylon : hydrogen bonding between phenolic hydroxyl groups in RFL resin and electronegative groups in fibres (55), condensation reaction between methylol groups of RF resin and active hydrogen in fibre (42,47).
The following mechanisms are illustrated for both rayon and nylon. The reactions of which are very similar, being condensation reactions between methoxy groups on the resin with active hydroxyl or amide groups in the fibre polymer chain.

(a) With Cellulosics



[6]

(b) With Polyamides

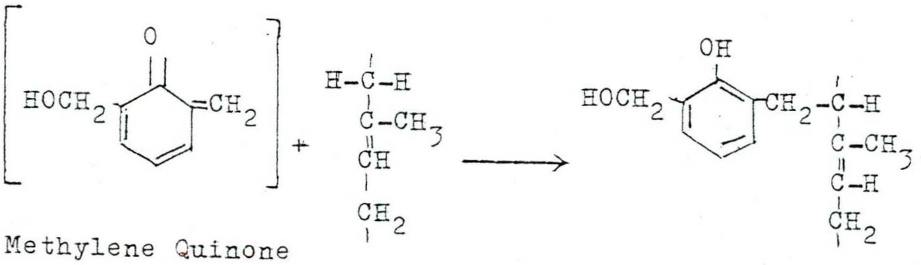


[7]

(ii) RFL-to-rubber adhesion.

Two basic types of mechanisms have been postulated for bonding RFL to rubber. The first associated with van der Meer (56) involves the formation of methylene quinone intermadiate which reacts with an active hydrogen atom such as allylic hydrogen of isoprene unit of natural rubber, as can be seen from equation [8], or the reaction with active hydrogen in the polymer chain giving a methylene linkage between the resin and the rubber (2). The latter mechanism seems to be very unlikely since the hydrogen atom is not active because it is vinylic and not allylic hydrogen.This mechanism is illustrated in equation [9] although we have to note that there is no direct evidence in support of it. The second type of mechanism, associated with Greth (57) and others (58,59), suggests the formation of chroman structure between benzene ring of resorcinol and the double bonds of butadiene units in the diene synthetic rubber.
The mechanisms are illustrated as follows :

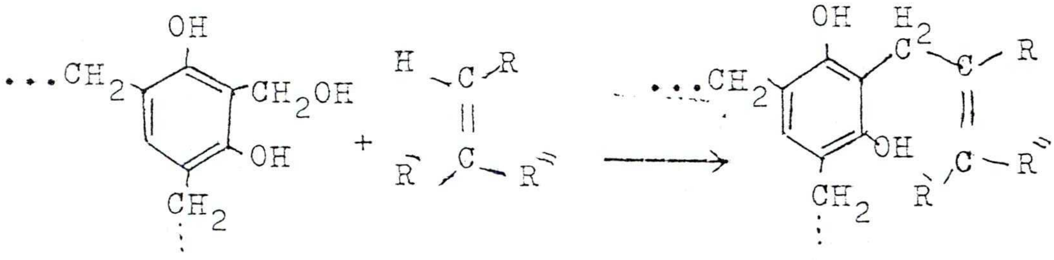
(a) With Active Hydrogen



Methylene Quinone Intermediate

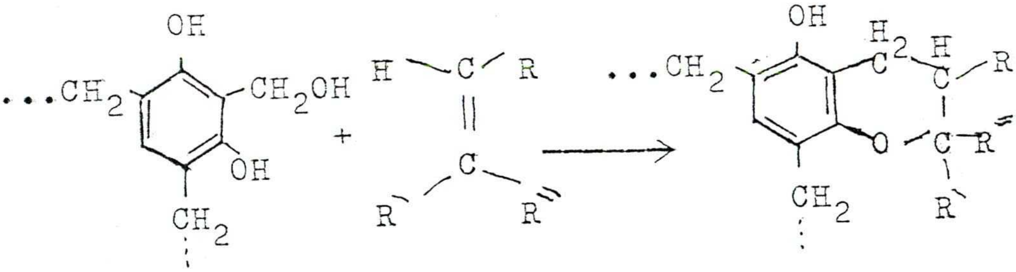
[8]

(b) With Vinylic Hydrogen



[9]

(c) Chroman Formation



[10]

Chroman structure

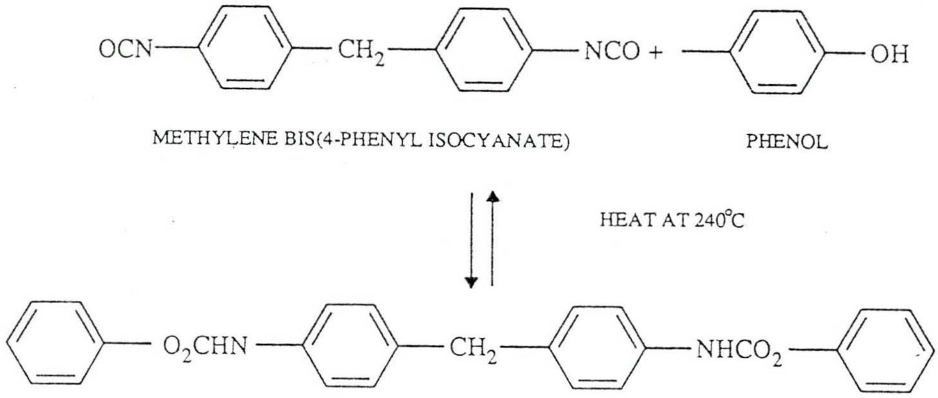
II. Adhesive treatment of polyester

Due to the lack of reactive hydrogen in the polyester molecule and its hydrophobic nature, ordinary RFL adhesive system would not bond to its surface. Therefore different methods are used to bond polyester to rubber, some of these methods are described as follows :

A/ Treatment with active isocyanate.

The first systems found to give good adhesion to polyester were based on very active isocyanate solution (2). Polyester was first treated with dilute organic solutions of an isocyanate, and after drying given a second treatment of a standard RFL. However, the isocyanate-in-solvent treatment of polyester cord was never commercialized, except for V-belt cords, because of the need for solvent recovery, ventilation, and toxicity.

Isocyanates form addition products reversibly with compounds which contain moderately reactive hydrogen such as phenol, oximes, and lactams. The following figure is an example of a typical blocking-unblocking reaction. These addition compounds, called "blocked isocyanates",are stable to water. They have been used in place of free isocyanate. The phenol-blocked isocyanates are the most common.



Typical blocking-unblocking reaction.

[11]

B/ Two-step adhesive system.

A two-step adhesive system was developed by Shoaf (60), based on blocked isocyanate. This process, called D-417,used phenol-blocked methylene-bis(4-phenyl isocyanate) and a water soluble epoxide. RFL is used as the topcoat or second step dip (45) :

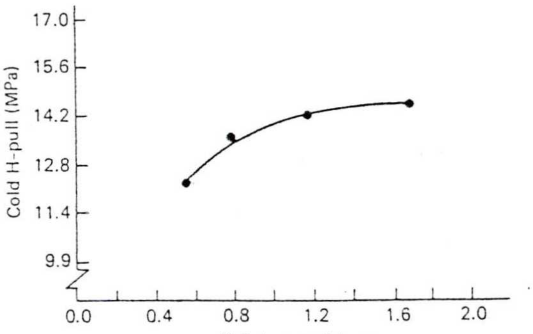
Hylene MP *	3.56 parts
Nagase 010A epoxide	1.34
Aerosol OT **	0.10
Water	95.00
	100.00 parts

* phenol blocked methylene-bis(4-phenylisocyanate) by DuPont.

** dioctyl sodium sulfosuccinate (wetting agent).

The major product of the reaction between isocyanate and epoxide is polyurethane. The polyurethane-polyester bond is pictured primarily as a physical interaction rather than a chemical one. Iyengar (61) reported that the cohesive energy density of polyurethane is 10.5, while that of polyester is 10.3. Therefore, the compatibility between these two substrates would be quite high and the probability exists for adhesion by the diffusion theory of Voyutskii (62). A heat-set for polyester cord for about one minute at 240°C, before application of the topcoat RFL dip, is necessary to develop good adhesion of polyester to rubber compounds. Somewhat lower temperatures of 210°C-220°C for one minute are required for RFL topcoat heat-set. Figure 4 shows the effect of subcoat pick-up on adhesion after a topcoat of RFL (45).

The author states that optimum subcoat pick-up for adhesion is about 1.0% although the curve does not show any optimum value. The figure only shows that there is an increase of adhesion with increasing % subcoat pick-up, and the adhesion approaches a limiting value asymptotically.



(45)

Fig. 4. Cold H-pull adhesion vs. subcoat pickup.

C/ Single-step adhesive dip for polyester.

One of the first single-step adhesive dips for polyester was developed by ICI (63). This adhesive, called Pexul or H-7 or Vulcabond E, was based on a co-resin of resorcinol and p-chlorophenol with formaldehyde (64-66). The actual dip recipe is given in the following table (45):

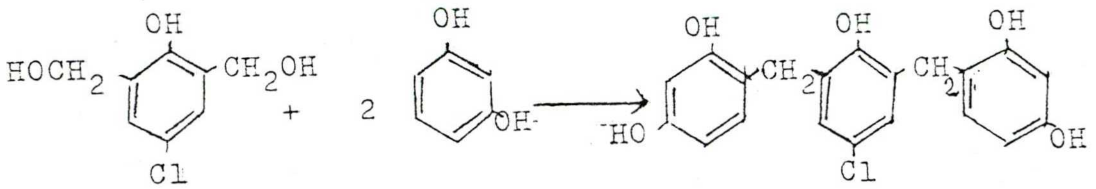
Component	Parts by weight
Koppers Penacolite R-2200 resin * (70%)	3.4
Sodium hydroxide	0.17
Water	18.8
Pexul (20%) **	30.0
Vinyl pyridine latex (38%)	31.8
Water	12.6
Formaldehyde (37%)	1.0
Water	1.0

	98.8

* Resorcinol-formaldehyde resin.

** Co-resin of resorcinol and p-chlorophenol with formaldehyde.

The reaction mechanism for resin formation is illustrated as follows :



[12]

Many other one-step adhesive dips for polyester fibres have been discussed (16). The adhesion activating agents in the RFL dip are usually based on isocyanates or cyanurates such as triallyl cyanurate, triphenyl cyanurate, etc. Other agents are also used, based on condensation polymers similar to that used in Pexul.

D/ Chemical activation of the polyester surface during fibre spinning.

Another adhesion improvement method utilizes surface-modified polyester yarns and standard RFL dips. This surface modification, generally referred to as adhesive activation, is achieved during the yarn manufacturing process (67). In order to activate the surface of polyester fibres during the spinning operation, many processes used epoxides and silanes in combination with other activating ingredients (68,69).

E/ Improvement of adhesion of polyester-to-rubber by carboxylated vinyl pyridine latex.

Hisaki and Suzuki (70) recently studied the possibilities of promoting the adhesion of polyester cords to rubber. It was postulated that the adhesion between polyester and rubber decreases during function due to hydrolysis of the ester bond of the polyester by amine compounds migrating from the rubber portion through the adhesive layer (61). Therefore, it was concluded that adhesion could be improved if the adhesive layer prevents amines from migration into the polyester. This was achieved by the development of a carboxylated vinyl pyridine latex which is effective in protecting the polyester from attack by amine compounds in the rubber compound (71), as can be seen from figure 5.

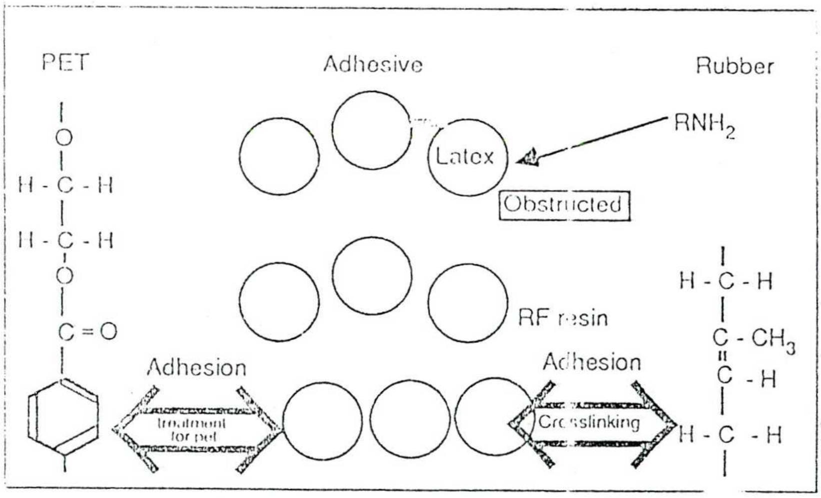
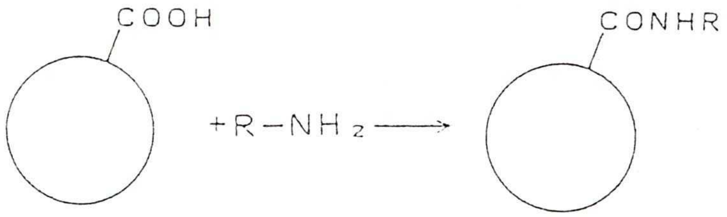


Fig.5. The mechanism of the improvement of polyester cord to rubber by carboxylated vinylpyridine latex (70).

This improved latex, the carboxylated vinylpyridine-butadiene-styrene terpolymer, contains both carboxylic and pyridyl groups which can form a network structure through H-bonding. Thus a physical obstruction of the amines by the network structure can occur or reaction of the carboxylic groups with the amines takes place, thus the amines being captured on the surface of the latex, preventing them from migrating to polyester cord. The mechanism of the penetration prevention of amines by carboxylated VP-latex is shown in figure 6.

A: Reaction with amines



B: Network structure by hydrogen bonds

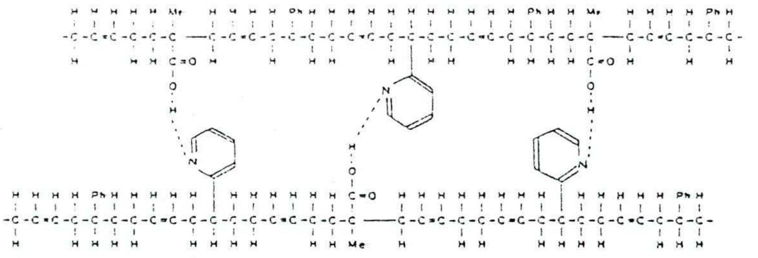


FIG. 6 — *Mechanism of the penetration prevention of amines by carboxylated VP-latex.* (71)

III. Methods to improve the dipping solution.

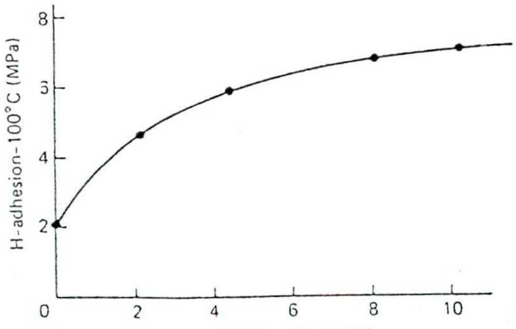
In order to minimize the effect of ozone exposure, several methods have been proposed. Encapsulation of the rubber latex particle by acrylic copolymers (72). This is done by adding for example acrylic acid or methyl methacrylate to RFL and used as cord dips for nylon, rayon, and polyester cords. While Adams (73) added N,N'-ethylene-bis-stearamide to cord adhesives, because it is likely that the bis-stearamide migrates to the surface of the cord adhesive and provides protection against atmospheric degradation. Microcrystalline waxes (24) are added to adhesive dip formulations to reduce the loss in adhesion to rubber which occurs when the cords are processed in fuel oil or kerosene-heated dryers, since exposure to both ozone and nitrogen oxide is likely. Calcium silicate, magnesium oxide, a formaldehyde donor, and a resorcinol derivative were added to rubber-based adhesive compositions to improve adhesion of rayon, nylon, and polyester cords to rubber (74). Rubber-reinforcement fibres can also be treated with compositions containing N-alkylalkanamide with C_6 alkyl and/or C_7 alkanamide groups (75) to improve the adhesion to rubber.

IV. Effect of dipping and heat treatment conditions on adhesion.

Adhesion is affected by conditions of dipping and of heat treatment after dipping.

(a) Effect and control of dip pick-up.

Pick-up of adhesive on a cord and penetration conditions of the adhesive into the cord interior affect adhesion. Penetration may be controlled by squeezing conditions (42), concentration of the adhesive, viscosity of the dip, cord tension in the dipping bath (76). Adhesion increases gradually with pick-up and reaches a saturation point. Too much pick-up should be avoided because the amount of adhesive affects stiffness of the cord (77). About 4-6% as shown in figure 7, is considered optimum for satisfactory adhesion of cord to rubber (45). The author gives an optimum value for the adhesive pick-up although the curve does not show an optimum value.



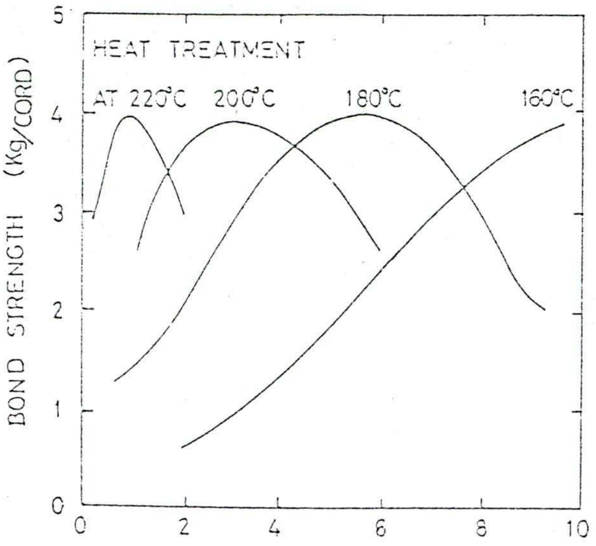
(45)

Fig.7. Effect of RFL pickup on cord to rubber adhesion.

Pick-up level is affected by the kind of textile material, textile lubricant, concentration and viscosity of the adhesive. Concentration of adhesive should be changed with the textile material to adjust the pick-up level. Even if the textile material is the same, different lubricants cause different pick-ups and different bond strengths (78). Petroleum sulfonate is often used as lubricant to enhance cord to rubber adhesion (79).

(b) Effect of heat treatment after dipping.

The heat treatment conditions (temperature and time) have important effect on the adhesion between rubber and cord. Lattimer et.al (80) showed the effect of the heat-setting temperatures on the adhesion. During heat treatment, a highly crosslinked structure is formed in the adhesive layer and strong interaction between adhesive and textile is achieved. Weak heat treatment causes the adhesive coating to have inferior tensile properties and there is lack of interaction with the textile. Strong treatment impairs compatibility with the rubber. In general, both over- and under-heat treatments are undesirable for adhesion. These features are shown in figure 8 taken from the publication of Takeyama (27). The figure does not give us enough information about the heat treatment time on the adhesion since there are no measured points on these curves, and the details of the experimental conditions are not given in the paper.



(27)

FIG. 8.—Variation of adhesion with heat treatment conditions.

2.3 Effect of Rubber Compounds on Adhesion.

2.3.1 Factors affecting rubber adhesion to rayon and nylon.

To obtain the highest level of adhesion, it is necessary to consider the effects exerted by the rubber substrate.

2.3.1.1 Effect of curing systems

It was shown that (66), in case of nylon the type of accelerator is not of great importance provided the stock is cured with sulphur. The effect of sulphur level appears to be important, in general, adhesion increases as the sulphur is increased.

Several authors (81,82) have stressed the importance of scorch-safety and cure-rate to obtain good adhesion. Adequate scorch-safety is thought to be necessary to allow proper wetting-out of the textile surfaces and penetration by the rubber compound before set-up. The vulcanization time should enable adequate diffusion of curatives to the interface between the rubber and dip coating. Other results (83) suggest that scorch safety up to a minimum value is required, and the chemical nature of the curing system has an influence. This has been demonstrated in semi-efficient vulcanization systems cured with DTM (N,N'- dithiomorpholine) and S-DTP [bis(diethyl dithiophosphoryl)sulphide]. The former compound is very safe, while the latter is quite scorchy and faster curing. However, the adhesion of the DTM compound is inferior to the S-DTP compound (31).

2.3.1.2 Effect of carbon black

Several studies (31,49,66) have shown that the type of carbon black used in the bonding stock does not have a pronounced effect on the adhesion, although a recent study published by Jain and Nando (84) discussed the effect of carbon black particle size on the adhesion levels. The authors stated that better adhesion levels can be achieved when carbon black with lower particle size (such as FEF black) is used.

2.3.1.3 Direct bonding systems

The use of direct bonding systems based on resorcinol/formaldehyde donor/silica (RFS) is the most common method for improving the adhesion of nylon and rayon to rubber (85). It is generally claimed that silica addition or substitution of some carbon black by silica improves the level of adhesion (31,66,84). Wake (86) suggested that the function of silica is to retard vulcanization until the formaldehyde donor has reacted with resorcinol. But Hewitt (87) suggested that the main purpose of silica is to improve the wetting-out characteristics of the compound, giving better cord adhesion. Shmurak's studies (88) of the mechanism of direct bonding systems have shown that resorcinol derivatives migrate into rayon and nylon.

2.3.2 Influence of rubber compounding ingredients on adhesion to polyester.

Under high temperature conditions losses in polyester cord strength and adhesion are observed. At High temperature degradation of polyester embedded into rubber is mainly due to amine catalyzed hydrolysis, and the loss in cord strength and retained adhesion to rubber are influenced by the constituents of the embedding rubber compounds (61,89,90).

The influence of rubber compounding ingredients on the adhesion of polyester is summarized as follows :

2.3.2.1 Effect of polymers

It was found that (66) the introduction of increasing proportions of SBR into a natural rubber-based stock, reduces degradation and improves bond levels to a marked degree.

2.3.2.2 Effect of accelerators

To reduce the degradation of polyester to a minimum, amine-based accelerators should be kept to a minimum or their use avoided (31). It was found (66) that thiazole accelerator give superior adhesion to the sulphenamide and the former degrades polyester to a smaller degree.

2.3.2.3 Effect of fillers

It was found that increased black loadings produce a useful improvement in bonding, and have beneficial effect on polyester degradation (66). Partial replacement of carbon black by silica can give high adhesion levels.

2.3.2.4 Effect of direct bonding system

Direct bonding systems are often used in conjunction with dip system to give improved levels of adhesion under operating conditions. The formaldehyde donor, hexamethylene tetramine, resorcinol, and silica system cause cord degradation problems with polyester due to the presence of amine. It is advisable therefore not to use a direct bonding system in an article reinforced with polyesters (31). However, another research suggests that addition of RF resins to rubber compound can give good adhesion if the polyester is pretreated with polyepoxide (91). Also addition of p-chlorobenzoquinone together with RF resin can be used to bond polyester (without pretreatment) to rubber (92).

2.4 Evaluation of Adhesion of Textile Cord-to-Rubber

There are a number of different test methods for evaluating textile cord adhesion to rubber (93). Some of them relate to static conditions (94-96) and others to dynamic conditions (97-99).

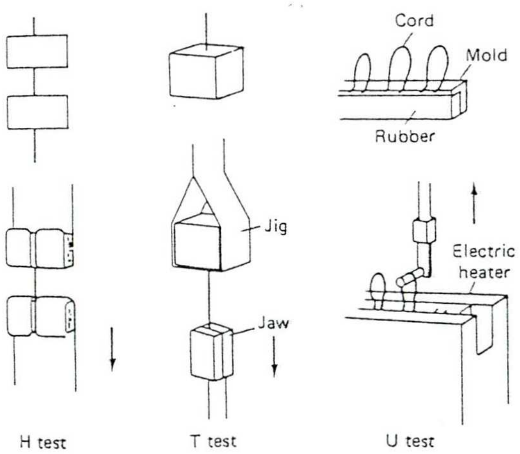
2.4.1 Static measurements

In the static tests the adhesion force between two layers of textile-rubber systems is measured. The force needed for peeling two bonded layers is characterized and measured in N/cm. The results might be highly affected by ruptures inside the rubber, because in this case the observed values of the adhesion strength will be smaller than that of the textile-rubber adhesion.

Generally, two methods are used for measuring the adhesion: the pull-out test and the peeling test.

2.4.1.1 Pull-out test

The pull-out method (100) is used to determine the force required to pull a cord from a block of vulcanized rubber. For measuring the adhesion of textile cords, different test specimens are prepared. They are called H-, T-, or U-tests (101,102) according to their shape. The most generally used one is the H-test (103,104). Figure 9 illustrates these pull-out tests. In these methods, the force needed to pull-out the cord from the bonded rubber is measured in N, or N/cm considering the embedded length. Different diameters of twisted cords can be compared by calculating the pull-out force in N/cm^2 on the basis of cord surface.



H test T test U test

Fig. 9. Test specimens and testing features of pull-through type tests.(27)

2.4.1.2 Peeling test

The peel test is used to separate a cord from a rubber sheet by stripping. This test can be used also to strip two plies of fabric bonded with rubber (96,105), or a rubber layer and a fabric ply bonded together. For the peeling method, the adhesion values are given for fabric in N/cm, for cords in N/cord.

With any method, the measurements indicate the level of the adhesion between textile and rubber if after peeling or pulling-out the cord or fabric is not covered with rubber. If the adhered rubber pieces are still on the surface of the textile cord or fabric, the adhesion is supposed to be greater than the strength of the rubber.

With any method, the measurement can be performed at high temperature also and thus data may be obtained about the dependence of adhesion on temperature. The results obtained by different methods are affected by the shape of the applied test specimen, the measuring arrangement, the quality and characteristics of the bonded rubber (106).

2.4.2 Dynamic tests

Under dynamic conditions, the fatigue of a cord-rubber composite may occur as cohesive failure in:

- rubber
- bonding material
- cord

or as adhesive failure on the interface:

- cord/bonding material
- bonding material/rubber

In dynamic tests under laboratory circumstances usually cyclic loads are applied and the fatigue resistance is expressed by the number of cycles. With increasing number of cycles, the adhesion decreases due to fatigue. The dynamic characteristics relate to hysteresis losses and consequently, rolling resistance and heat-build up (107).

Many methods of dynamic tests are known for cords. Some more important ones are described here.

2.4.2.1 The repeatedly applied compressing apparatus.(Compression Type).

This test can be done with two sorts of test specimens. Both of them are rubber cylinders. For one of them, the cord is placed in the middle of the cylinder's length perpendicular to the cylinder's axis as shown in figure 10.a. In the other one, the cord is placed along the cylinder's axis in the center line of the specimen. The tested cord is under tension by means of a weight. When the test specimen is compressed, the rubber to cord interface is subjected to shear force. Adhesion deteriorates with compression cycles and failure occurs when the bonding force becomes less than the suspended weight.In general, this apparatus is used with large frequency, with which overheating of the rubber can be the cause of damage. Therefore, it is said that (76) these methods are inadequate to examine adhesion.

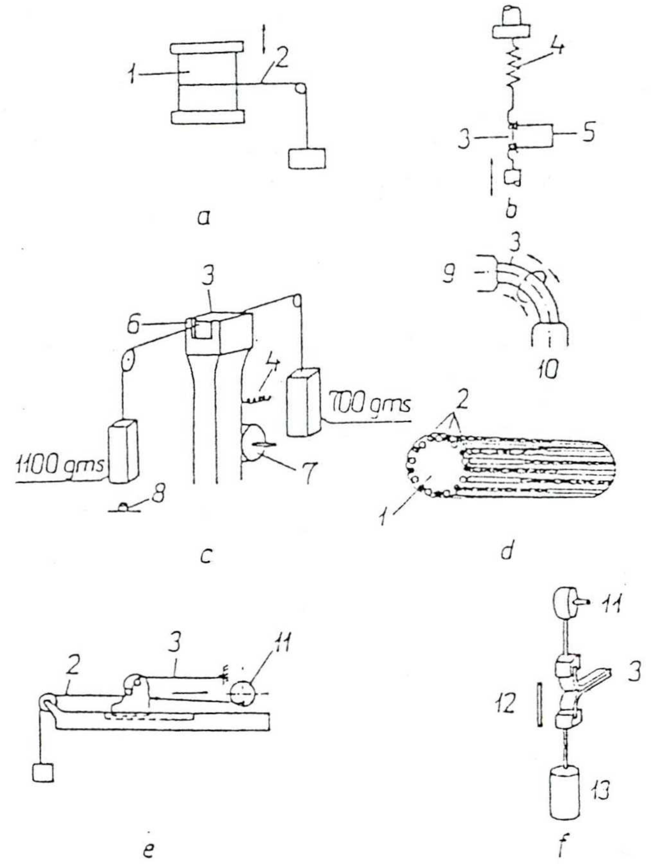


Fig.10.Methods used for dynamic tests(27,109)
1-rubber;2-cord;3-test specimen;4-spring;5-jaws;6-socket;7-eccentric drive;8-time cut-off;9-fixed end;10-rotating end;11-eccentric drive;12-heater;13-weight.

2.4.2.2 Dynamic Shear Adhesion (DSA) Tester.

In De Mattia apparatus, H- or T-shaped test specimens are fatigued. The test specimen is series-connected with a calibrated steel spring, and this system is put under the influence of repeated pulling as shown in figure 10.b. The induced force is practically constant during the fatigue time. Similar to this method many apparatus are used with another shaped-test specimens and in the up-to-date instruments electronic measured systems and data acquisition are used. The Bayer vibrator is working with two-directional shear for which its test specimen contains many cords, while in the Iyengar vibrator (108), its test specimen contains one cord only. Continuous vibration is applied to a rubber specimen as illustrated in figure 10.c. Adhesion is represented by cycles to failure of the cord-to-rubber bond and this is automatically recorded.

2.4.2.3 Bartha Tester (109).

In the Bartha tester, the test specimen is rod-shaped with dimensions 15-20 cm length and 2 cm diameter, see figure 10.d. The cords are embedded into the rubber cylinder at equal distance from each other. In the fatigue testing machine, the test specimen is bended and rotated around its axis. The twisted cord is put under the influence of alternative pulling-compression stress.

2.4.2.4 Apparatus operated with repeated flexing. (Flexing Type).

In this method, the cords are passing longitudinally through the middle of test strap. They are fixed at one end and from the other end a weight is suspended. The strap follows a sigmoidal path around movable rollers, see figure 10.e. Adhesion is evaluated by the comparison of the forces needed to pull the cord out from the specimens before and after flexing (110,111).

2.4.2.5 Dynamic strip adhesion tester. (Scott Tester).

This method is used for textile cords or fabrics. A two-ply strip test piece is subjected to continuous vertical vibration under a certain weight. Adhesion is expressed by the number of cycles required to strip a unit length. This type of equipment is known as Scott tester, see figure 10.f.

The field, related to adhesion between textile cords and rubber; adhesive systems; static and dynamic tests used to evaluate the adhesion, was reviewed recently by Renner and Langenthal (112) as well as by Darwish (113). We can conclude, that, despite of numerous test methods, there is little information in the open literature on the comparison of various methods with different textiles and rubber compounds.

3. EXPERIMENTAL

3. EXPERIMENTAL

All the experimental work was made in the Technical Institute of Taurus Hungarian Rubber-Works. The mixing of the rubber compounds, the dipping process of the textile cords, and the building of the test specimens were carried out in the technological laboratory. All the measurements were carried out in the chemical, physical, and textile laboratories of the Technical Institute in Taurus.

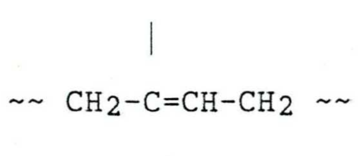
3.1 Tested Materials.

3.1.1 Types of rubber used.

Two kinds of rubber are used in this study, namely, natural rubber and chloroprene rubber (neoprene).

3.1.1.1 Natural Rubber-NR

The hydrocarbon component of NR is the cis-polyisoprene, which is fairly widespread in nature (114).



$$\sim\sim \mathrm{CH_2-\overset{\overset{\textstyle CH_3}{|}}{C}=CH-CH_2} \sim\sim$$

For the present experimental work, the Standard Malaysian Rubber (SMR 10) was used. Two similar rubber mix formulations R-1 and R-2 and the vulcanization conditions are given in table 1. The only difference between them is the addition of resorcinol/hexa methylene tetramine to the second mix in order to promote the adhesion of the textile cord-to-rubber.

Table 1 : NR mix formulations (parts by weight).

Mix	R-1	R-2
Ingredients		
Natural rubber	100	100
Carbon black	45	45
Zinc oxide	5	5
Oil	5	5
Vulcanizing system	4	3.4
Stabilizer	2	2
Stearic acid	2	2
Adhesion promoting material	---	3.2
Vulcanizing temperature,°C	155	155
Vulcanizing time,min.	6	8

Rubber compounds were prepared on Werner and Pfleiderer Banbury mixer (type D 700/A 161 and 2.5 liter capacity) at a friction ratio of 1.10 : 1. The rubber compounds were tested on a Monsanto Rheometer (Model ODR 2000E) at 155°C and the optimum cure times were found to be 6 and 8 minutes for R-1 and R-2 rubber mixes respectively. Their tensile properties were illustrated in table 2.

Table 2 : Tensile properties of the natural rubber mixes.

	R-1	R-2
Tensile strength,MPa	24.60±0.59	24.40±0.62
Elongation at break,%	510.00±21.22	512.00±15.45
M100,MPa *	2.67±0.21	2.57±0.23
M200,MPa *	7.33±0.33	6.56±0.35
M300,MPa *	13.24±0.46	12.23±0.43
Hardness,Shore A	59	58

* M100, M200, M300 are stresses at 100,200,and 300% elongation respectively.

3.1.1.2 Chloroprene Rubbers-CR

Neoprene vulcanizates show high levels of tensile strength like those from NR (115). Similarly to NR, Neoprene may crystallize when conditions are favourable. Crystallization can occur in raw polymers, in uncured compounds, and in vulcanizates too.

Neoprene WRT was selected for this research project together with NR aiming to give more light to this elastomer from the adhesion-point of view. From polychloroprene, two similar rubber mix formulations R-3 and R-4 were prepared and the vulcanization conditions are given in table 3.

Table 3 : CR mix formulations (parts by weight).

Mix	R-3	R-4
Ingredients		
Neoprene WRT/BR	95/5	95/5
Carbon black	45	45
Zinc oxide	5	5
Magnesium oxide	4	4
Oil	5	5
Vulcanizing system	4	4
Stabilizer	2	2
Stearic acid	1	1
Adhesion promoting material	---	2.8
Vulcanizing temperature,°C	155	155
Vulcanizing time,min.	20	20

Also, the difference between the mixes R-3 and R-4 is that the latter contains promoting material (resocinol/hexa methylene tetramine). The tensile properties of the two rubber mixes are given in table 4.

Table 4 : Tensile properties of chloroprene rubber mixes.

	R-3	R-4
Tensile strength,MPa	20.04±0.48	17.79±0.49
Elongation at break,%	290.00±17.79	294.67±13.85
M100,MPa	5.45±0.43	5.48±0.26
M200,MPa	13.93±0.47	11.95±0.59
Hardness, Shore A	72.00	73.00

3.1.2 Dipping solutions

The tested textile cords were treated with two types of dipping solutions generally used in the rubber industry.

3.1.2.1 Resorcinol Formaldehyde Latex (RFL-1).

The first type of the adhesive systems used, is the resorcinol-formaldehyde-latex (RFL), it will be given the symbol (RFL-1), in which the latex has been styrene/butadiene/vinyl pyridine terpolymer. The specifications of (RFL-1) dipping solution are given in table 5.

Table 5 : Specifications of RFL-1 dipping solution.

Specifications	Values
pH	8.25
Viscosity (cP)	1.7539
Density (g/cm^3)	1.0046
Dry material content(%)	15.72

This RFL-1 adhesive system is industrially used in Taurus for the dipping process of nylon cords.

3.1.2.2 (RFL-2) adhesive system

The second type of the adhesive systems, namely RFL-2, is used in Taurus for the dipping of the polyester cords. This adhesive is a one-step dipping process in which both the activating material,based on a co-resin of resorcinol and p-chlorophenol with formaldehyde, as well as the RFL are included in a single-step dip. The specifications of this adhesive system are given in table 6.

Table 6 : Specifications of (RFL-2) dipping solution.

Specifications	Values
pH	9.50
Viscosity (cP)	4.8580
Density (g/cm^3)	1.0068
Dry material content(%)	19.99

3.1.3 Textile cords

For the experimental work two kinds of textile cord were used, namely nylon 6,6 cords and polyester cords.

3.1.3.1 Nylon 6,6 cord.

Nylon 6,6 was chosen for this research because it has higher modulus and lower shrinkage than nylon 6 (116). For the experimental work the following types of nylon 6,6 were used and the data were given by the producing companies.

C_1: ICI 140/2 tex nylon 6,6 cord (390/395 Z/S twist)

C_2: ENKA 140/2 tex nylon 6,6 cord (394/394 Z/S twist)

C_3: ENKA 94/2 tex nylon 6,6 cord (490/500 Z/S twist)

For simplicity, they were given the symbols C_1, C_2, and C_3 respectively. Some data (measured values) for the three types of cord are given in table 7.

Table 7: Characteristic features (measured values) for the three types of undipped nylon 6,6 cords.

Features	C_1	C_2	C_3
linear density (dtex)	3034.6±29.83	3116.2±26.56	2117.4±13.34
diameter (mm)	0.775±0.02	0.756±0.02	0.629±0.02
twist number S	395.8±5.91	398.2±8.14	501.0±2.55
twist number Z	390.0±1.92	401.3±2.19	491.7±1.64
breaking strength (dN)	21.90±0.55	20.85±0.23	14.40±0.44
elongation at break (%)	26.9±0.45	29.0±0.53	30.1±0.99
elongation (%) at 45N	9.9±0.26	9.9±0.27	13.9±0.27
68N	12.5±0.25	12.5±0.0.28	17.0±0.32
90N	14.4±0.28	14.4±0.36	19.5±0.32
(LASE) at 5% (dN)	2.0±0.01	2.0±0.03	1.24±0.04
melting point (°C)	263.5±0.58	261.5±0.58	264.5±0.60
shrinkage force at 160°C(cN)			
after 4 min.	745±35	815±0	368±10.41
30 min.	780±34.6	840±0	382±7.64
free shrinkage at 160°C (%)			
after 4 min.	5.542±0.07	5.875±0.13	3.500±0
30 min.	6.083±0.07	6.292±0.07	3.875±0
free shrinkage after 10 min.			
relaxation (%)	3.500±0	3.667±0.07	1.417±0.07
tenacity (cN/tex)	72.2	66.9	68.0

3.1.3.2 Polyester cord

For this research three types for polyester cord were used and the data mentioned below were given by the producing companies.

P_1: ENKA 110/2 tex polyester (435/435) Z/S twist
P_2: Allied 110/2 tex polyester (370/370) Z/S twist
P_3: Allied 110/3 tex polyester (355/355) Z/S twist

They are given the symbols P_1, P_2, and P_3 respectively.
The characteristic features (measured values) for these three types of polyester cord are given in table 8.

Table 8: Characteristic features (measured values) of the three types of undipped polyester cord.

Features	P_1	P_2	P_3
linear density (dtex)	2487±12.98	2384±4.45	3663±16.23
diameter (mm)	0.555±0.04	0.585±0.05	0.706±0.02
twist number S	438±4.97	371±2.41	362±3.89
twist number Z	443±4.60	371±1.60	355±1.84
breaking strength (dN)	15.74±0.42	15.67±0.49	23.54±0.34
elongation at break (%)	15.4±0.41	20.8±0.71	22.9±0.53
elongation (%) at 45N	6.7±0.16	7.6±0.21	5.9±0.20
68N	8.7±0.19	10.1±0.23	8.8±0.19
90N	10.2±0.21	12.0±0.25	10.7±0.25
(LASE) at 5% (dN)	3.20±0.09	3.03±0.09	3.96±0.12
melting point (°C)	267±0.58	262±1.00	266±1.53
shrinkage force at 160°C (cN)			
after 4 min.	707±5.77	443±5.77	595±8.66
30 min.	727±5.77	460±10.00	620±10.00
free shrinkage at 160°C (%)			
after 4 min.	6.333±0.07	4.708±0.07	4.792±0.07
30 min.	6.792±0.14	5.167±0.07	5.292±0.07
free shrinkage after 10 min. relaxation (%)	6.458±0.07	4.958±0.07	5.000±0
tenacity (cN/tex)	63.3	65.7	64.3

3.2 Methods Used in the Experimental Work

3.2.1 Dipping process

The tested cords were treated with the dipping solution in a dip unit. Immediately after dipping, they were stretched on a suitable frame and entered a heated drying oven. The cords were dried at 160°C, 180°C, and 220°C for different durations.

3.2.2 Dip Pick-up measurements

From each cord 5 meters were weighed for both undipped and dipped cord at different temperatures and durations. The percentage dip pick-up was calculated from the following formula:

$$\text{\% dip pick-up} = \frac{G_1 - G_0}{G_0} \times 100$$

where G_0 and G_1 are the weights of the undipped and dipped cords respectively.

The pick-up mass per cord length, per cord outer surface, and per cord volume were also calculated.

3.2.3 Tensile tests and tensile properties

Tensile properties of the three types of nylon 6,6 and the three types of polyester cords were tested for both undipped and dipped cords at different temperatures and times. The tensile machine used for these measurements was Zwick 1441, the rate of elongation was 500 mm/20 sec according to the standard method (MSZ 10788/4-83).

3.2.4 Test method used for testing the adhesion between the textile cords and the rubber compounds. Static adhesion H-pull-out test.

Textile cords were bonded to rubber compounds using a mould capable of producing 60 H-type testpieces. The mould consists of twelve cavities 300 mm x 6.3 mm x 3.2 mm. Through the separating strips were a series of grooves to accommodate the cords. 6 mm wide rubber strips were placed in the mould cavities, and the treated cord placed in contact with the rubber. Further strips of the rubber were placed on the first strips, thus sandwiching the cords (117). The mould was closed and vulcanization then carried out in a press. After curing the pads were stored overnight before being cut and then tested in the Zwick 1441 tensile tester, the rate of elongation was 150 mm/min according to the standard method (MSZ 642-83). The force required to separate the cord from the rubber is determined at room temperature and at 90°C for the four rubber mixes R-1, R-2, R-3, and R-4.

3.2.5 Dynamic adhesion fatigue test- De Mattia test.

The adhesion between textile cord and rubber can be tested by De Mattia fatigue test. Three H-test specimens were used for each case, the dimensions of which are 6.3mm x 3.2mm x 25mm. The test specimen is connected between two clamps which have slits of width 1.4mm. The upper clamp is connected to a calibrated spring. The required force can be adjusted by changing the length of the spring. The lower clamp is connected to eccentric drive with which the load can be adjusted. The load can be changed by changing the eccentricity. Two heaters are applied for testing the temperature, which can be adjusted at 90°C-100°C by moving the heaters forward or backward. (The arrangement is similar to that given on figure 10.b).

The adhesion between cord and rubber is fatigued when the sensor, which is connected to the spring, shifted from its place and the counter is automatically stopped. The rate is 300 cycles/min. and the number of cycles is registered automatically.

3.2.6 Dynamic adhesion fatigue- Bartha Dynamic Test.

Dynamic adhesion fatigue tests were carried out also on Bartha dynamic tester. The method used is described below.

3.2.6.1 Preparation and curing of specimen used for test.

The specimen used for the Bartha adhesion fatigue test is a solid rubber rod (of diameter 19.5 mm) with 20 cords embedded equidistantly along the length of specimen. To prepare such a specimen, the surface of two halves of a mould are coated with 10% gasoline solution of rubber matrix. The cords are wound by using a tentering frame. While winding the cords to be tested on the comb pair placed in the tentering frame, a constant weight is applied, providing pretension. The tension of the cord is adjusted after it is wound on the combs. Tensioning is needed because of shrinkage during curing. After adjusting the tentering frame to the correct distance, it is placed together with the combs in the curing mould. Then a coat of 10% gasoline solution of rubber matrix is applied again over the cords in the mould's halves. After the solution dried, the previously extruded and weighed rubber compound is placed into the bottom half of the mould. Then the holder straps are inserted in the mould and the mould is closed.

Prior to curing, the mould is preheated for 10 minutes. The compound is cured. In our experimental work, the two NR mixes, R-1 and R-2 were cured at 155°C/20 min. while the CR compounds, R-3 and R-4 were cured at 155°C/50 min. The cured specimens were relaxed for 24 hours before use.

3.2.6.2 Preparation of specimen for fatigue test.

After removing the combs from the cured specimens, 155 mm length is cut with the help of a template. A groove is cut at both ends of specimen along a template to prevent the specimen from slipping in the clamps of the fatigueing machine.

Every alternative cord is cut 15 mm left and right from its lengthwise midpoint, so the even cords are cut on the right and the odd cords are cut on the left side as can be seen from figure 11.

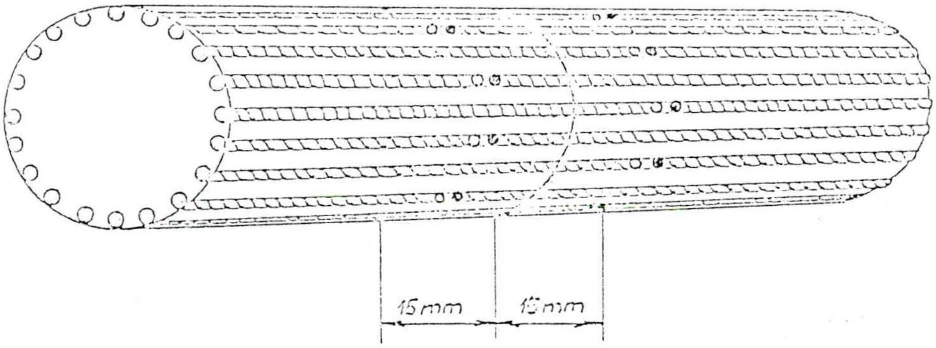


Fig.11 Bartha Test Specimen

3.2.6.3 Fatigue test

The specimen is placed into the fatigue tester and the radius of outer curvature is adjusted to 8 cm, the revolution counter is reset, and the motor is started. The force developed in the specimen is measured and then the dynamometer is adjusted to 70% of the earlier measured force value and fixed, the switching and signalling devices are set into automatic position and the rotation is started. The rate of rotation is 1360 cycles/min.

If part of the cords separate, the force developed in the specimen falls below the value set on the dynamometer. As a result the dynamometer makes the swinging arm deviate from its original perpendicular position. The switching device is activated and the motor and counter stop. Thus the number of cycles can be read from the counter.

3.3 Evaluation of the Test Results.

The effects of various factors on the test results were evaluated with statistical method: by the well known Analysis of Variance (ANOVA). Using ANOVA one can determine whether one or more factors have a real, statistically significant effect on a defined quantity, in our case on the test results (118).

In the course of our work the effects of two or three factors were studied; the two-way and the three-way ANOVA were applied accordingly. The measurements were carried out at different set-points, each one representing a combination of the levels of the relevant factors. At each set-points 5, 10, or 12 parallel tests were made, and their mean values and standard deviations were calculated. From the mean values the ANOVA tables were produced by a PC-computer programme while from the standard deviations the standard error of the relevant test methods were estimated.

Decisions regarding to the effect of the factor in question were made by comparison between the calculated F-statistics and the critical F-value at 95 per cent confidence level. (The latter is given in statistical tables). In those cases when the calculated value exceeded the critical value, we concluded that the relevant factor does have a significant effect on the results, otherwise we drew the opposite conclusion.

In case of positive decision the trends were analyzed comparing the mean values calculated at different levels of the factors.

In our experimental work, the independent variables (factors) were: the quality of cord, the presence of dipping solution (or the type of rubber compound), and the heat treatment conditions (temperature and time). The dependent variables (test results) were: the tensile properties, the dip pick-up quantity, and the cord-to-rubber adhesion.

A total of about 5000 test specimens were prepared and tested and the results were statistically evaluated.

4. RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

In this section, the results obtained from the experimental work are classified, discussed and the final conclusion will be summarized.

4.1 Experimental Systems

4.1.1 Cords, Dipping Solutions and Rubber Compounds

In this research two types of textile cords were used. These are nylon 6,6 and polyester cords. Three kinds for each one of them, namely C_1, C_2 and C_3 for nylon 6,6 and P_1,P_2 and P_3 for polyester cord were tested. Nylon 6,6 and polyester cords were chosen for this topic because they are highly demanded in the rubber industry as textile reinforcing materials. Their usage is very important in tires which consume around 60% of the textile reinforcing materials, due to their strength, temperature stability, acceptable fatigue resistance, reasonable cost and adhesion to elastomers (119).

Also two kinds of dipping solutions RFL-1 and RFL-2 were used for this research. RFL-1 dip is the conventional resorcinol formaldehyde latex used to adhere nylon cord to rubber, while RFL-2 is the one-step dip in which an activating material, based on a co-resin of resorcinol and p-chlorophenol with formaldehyde, is present. This dip is used mainly to adhere polyester cord to rubber. The results with the above two dipping solutions are compared in this study. Beside that four rubber compounds, R-1, R-2, R-3, and R-4 based on natural rubber (NR) and chloroprene rubber (CR) respectively, were tested. NR and CR were used in this research because both materials show high tear strength and tensile strength, even in the absence of reinforcing fillers (116).

A considerable number of systems (40 systems) were investigated, see table 9, in order to compare the behaviour of different systems and to have the opportunity to choose those systems with which we can achieve high levels of adhesion between textile cord and rubber compound.

Table 9: Textile cord-rubber systems investigated.

Cord	RFL-1				RFL-2			
	R-1	R-2	R-3	R-4	R-1	R-2	R-3	R-4
C_1	+	+	+	+	+	+	+	+
C_2	+	+	+	+	-	-	-	-
C_3	+	+	+	+	-	-	-	-
P_1	+	+	+	+	+	+	+	+
P_2	+	+	+	+	+	+	+	+
P_3	+	+	+	+	+	+	+	+

4.1.2 Heat treatment conditions

Different types of dipped and undipped nylon 6,6 and polyester cords were heat-treated at 160°C, 180°C and 220°C for different durations. These temperatures were chosen since nylon 6,6 and polyester cords have high melting points (about 260°C). At lower temperatures longer heat treatment times were chosen while for higher temperature shorter times were used, see table 10.

Table 10: Heat treatment conditions

Cord	RFL-1										
	160°C					180°C			220°C		
	3min	5min	7min	10min	15min	1min	3min	5min	1min	3min	5min
C_1	+	+	+	+	+	+	+	+	+	+	+
C_2	–	+	–	+	+	–	+	+	+	+	+
C_3	–	+	–	+	+	–	+	+	+	+	+
P_1	+	+	+	+	+	+	+	+	+	+	+
P_2	+	+	+	+	+	+	+	+	+	+	+
P_3	+	+	+	+	+	+	+	+	+	+	+

Cord	RFL-2										
	160°C					180°C			220°C		
	3min	5min	7min	10min	15min	1min	3min	5min	1min	3min	5min
C_1	–	+	–	+	+	–	+	+	+	+	+
C_2	–	–	–	–	–	–	–	–	–	–	–
C_3	–	–	–	–	–	–	–	–	–	–	–
P_1	–	+	–	–	+	–	+	+	+	+	+
P_2	–	+	–	–	+	–	+	+	+	+	+
P_3	–	+	–	–	+	–	+	+	+	+	+

Table 10 shows that the available cords were dipped with the two adhesive systems RFl-1 and RFL-2 and then heat-treated at the different temperatures for different times as illustrated, in order to clarify the important effect of the heat treatment conditions on the bonding between textile cord and rubber compounds.

The undipped cords were also heat-treated at the same temperatures and for the same durations to be able to compare between the tensile properties of the cords before and after dipping. The undipped cords were bonded to both natural rubber and chloroprene rubber compounds to investigate their adhesion levels.

4.2 Tensile Properties.

The tensile of the undipped and dipped nylon 6,6 and polyester cords were measured and statistically analyzed to investigate the effect of the dipping process and the heat treatment conditions (temperature and time) on their tensile strength.

All the measured data of the tensile properties for nylon 6,6 and polyester cords treated with both RFL-1 and RFL-2 adhesive systems are summarized in ten tables (Table I to Table X) and found in the appendix.

For the three types of nylon 6,6 cord, C_1, C_2 and C_3, treated with RFL-1 dip, the statistical analysis is summarized in table 11.

The variance analysis of the results, of course, has an

Table 11: The statistical analysis of tensile strength measurements of nylon 6,6 cords treated with RFL-1 dip.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	24348.6	1988.8	3.03
Factor B	1	540.0	44.1	3.87
Factor C	7	3.7	0.3	2.04
pure error	360	12.2		

Factor A = type of nylon 6,6 cord
Factor B = undipped and dipped cord
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Tensile strength Average (N)	Total average
A	1. C_1 cord	214.0	187.3
	2. C_2 cord	205.3	
	3. C_3 cord	142.5	
B	1. undipped	190.6	
	2. dipped	183.9	
C	1. 160°C/5 min.	187.7	
	2. 160°C/10 min.	187.7	
	3. 160°C/15 min.	187.7	
	4. 180°C/3 min.	186.2	
	5. 180°C/5 min.	186.9	
	6. 220°C/1 min.	188.6	
	7. 220°C/3 min.	186.8	
	8. 220°C/5 min.	186.7	

evident effect, it shows that the tensile properties of the three kinds of nylon 6,6 are different, the weakest one being the (C_3) cord as can be seen from table 7. It is noticeable that the tensile strength decreases after dipping but the heat treatment conditions have no significant effect on it.

On investigating the three types of polyester cords P_1, $P_2$and P_3 treated with RFL-1, it was found that their tensile properties were different, the strongest one was P_3 cord as can be seen from table 8 and from the variance analysis given in table 12. The qualitative picture is similar to that of nylon 6,6 cord except that at 220°C/5 min. there is a decrease in polyester cord strength since prolonged exposure to high temperatures can lead to permanent degradation of fibres (120).

Similar results were obtained for the three polyester cords P_1, P_2 and P_3 if they were treated with the second adhesive system RFL-2. As it can be seen from the statistical analysis of their tensile measurements,see table 13, that cord P_3 has the highest tensile strength while the other two, namely, P_1 and P_2 have similar tensile strength due to their similar structures. On the other hand the dipping process had a decreasing effect on the tensile strength. The effect of the heat treatment factor seems to be significant too. The tensile strength decreases at 220°C/3 min. and at 220°C/5min.

To compare the three nylon 6,6 cords C_1, C_2 and C_3 and the three polyester cords P_1, P_2 and P_3 treated with RFL-1 dip, their total averages were calculated at different levels of the factors discussed above in the statistical tables derived

Table 12: The statistical analysis of tensile strength measurements of polyester cords treated with RFL-1 dip.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	36023.2	1708.9	3.01
Factor B	1	2336.6	110.8	3.86
Factor C	10	35.1	1.7	1.85
pure error	660	21.1		

Factor A = type of polyester cord
Factor B = undipped and dipped cord
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Tensile strength Average (N)	Total average
A	1. P_1 cord	154.5	180.2
	2. P_2 cord	159.3	
	3. P_3 cord	226.8	
B	1. undipped	186.2	
	2. dipped	174.3	
C	1. 160°C/3 min.	180.2	
	2. 160°C/5 min.	182.0	
	3. 160°C/7 min.	179.7	
	4. 160°C/10 min.	180.9	
	5. 160°C/15 min.	180.0	
	6. 180°C/1 min.	180.3	
	7. 180°C/3 min.	181.1	
	8. 180°C/5 min.	181.2	
	9. 220°C/1 min.	182.9	
	10. 220°C/3 min.	180.4	
	11. 220°C/5 min.	173.5	

Table 13: The statistical analysis of tensile strength measurements of polyester cords treated with RFL-2 dip.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	21701.9	1382.1	3.01
Factor B	1	2313.3	147.3	3.86
Factor C	6	44.3	2.8	2.12
pure error	420	15.7		

Factor A = type of polyester cord
Factor B = undipped and dipped cord
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Tensile strength Average (N)	Total average
A	1. P_1 cord	154.4	178.4
	2. P_2 cord	157.1	
	3. P_3 cord	223.9	
B	1. undipped	185.8	
	2. dipped	171.0	
C	1. 160°C/5 min.	180.2	
	2. 160°C/15 min.	178.0	
	3. 180°C/3 min.	179.6	
	4. 180°C/5 min.	180.6	
	5. 220°C/1 min.	180.4	
	6. 220°C/3 min.	177.2	
	7. 220°C/5 min.	173.0	

for both nylon 6,6 and polyester cords, see tables 11 and 12. From these tables one can see that their total averages are nearly the same. The quality of cord has of course great effect on the tensile properties of both cords. Their tensile strengths decrease after dipping. This strength loss occurs because of solvation due to the moisture trapped inside the RFL adhesive shell on the outside of the cord bundle (116). The heat treatment conditions have negligible effect on the tensile strength of nylon 6,6 cords, and there is small decrease in tensile strength of polyester at high temperature (220°C/5 min.).

On the other hand, we compare polyester cord P_1 (ENKA 110/2 tex, 435/435 z/s twist) and nylon 6,6 cord C_1 (ICI 140/2 tex, 390/395 z/s twist), treated with RFL-2 adhesive system. From the analysis of variances, see table 14, similar results were also obtained and that in this case the heat treatment conditions had no effect on their tensile strengths.

Referring to tables I, II and III in the appendix which related to the tensile properties for nylon 6,6 (C_1, C_2 and C_3) cords respectively, treated with RFL-1 dip, it can be seen that in case of undipped nylon cords there is no change in tensile strength of the heat-treated and that of without heat treatment . The elastic modulus of the heat-treated ones and the Load At Specific Elongation (LASE) decreased, but the elongation at break increased, i.e, the cords become softer. The tensile strengths of the undipped cords were found to be more than that of the dipped ones, and as it is mentioned before, this is due to the presence of the adhesive solution

Table 14: The statistical analysis of tensile strength measurements of polyester and nylon 6,6 cords treated with RFL-2 dip.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	1	23005.9	1102.7	3.87
Factor B	1	1015.2	48.7	3.87
Factor C	6	17.4	0.8	2.13
pure error	280	20.9		

Factor A = type of cord
Factor B = undipped and dipped cord
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Tensile strength Average (N)	Total average
A	1. P_1 cord	154.4	183.1
	2. C_1 cord	211.7	
B	1. undipped	189.0	
	2. dipped	177.0	
C	1. 160°C/5 min.	185.1	
	2. 160°C/15 min.	183.7	
	3. 180°C/3 min.	183.2	
	4. 180°C/5 min.	185.0	
	5. 220°C/1 min.	183.7	
	6. 220°C/3 min.	181.3	
	7. 220°C/5 min.	179.2	

and higher humidity. As a result the modulus becomes smaller.

It can be also seen from tables I, II and III that the Load At Specific Elongation (LASE) is higher in case of dipped cords than undipped and heat-treated ones because the latter soften during the heat treatment.

Similar results were obtained for the tensile properties of nylon 6,6 (C_1) cord treated with RFL-2 adhesive system, as can be seen from table IV in the appendix.

In case of polyester cord (P_1, P_2 and P_3) treated with RFL-1 dip, their tensile properties were shown in tables V, VI and VII in the appendix. It can be seen from these tables that there is no change in the tensile strength of the undipped cords without heat treatment and that of heat-treated ones. The elongation at break of the heat-treated ones increased but their elastic modulus and the Load At Specific Elongation (LASE) decreased. The changes were found to be clear in case of polyester than nylon 6,6. The breaking extension or in other words the elongation at break of the undipped cords is bigger than that of the dipped ones because, similarly to nylon cords, the undipped ones soften during the heat treatment. At 5% elongation the load and consequently the modulus is higher in case of dipped cord than that of undipped one.

Similar results can be also found in case of polyester cords treated with RFL-2, see tables VIII, IX, and X.

4.3 Dip Pick-up Measurements

The nylon 6,6 and polyester cords were treated with RFL-1 and RFL-2 adhesive systems and heat-treated at different temperatures and durations. Their dip pick-ups were calculated using the method described in the experimental part. The dip pick-up mass per cord mass, per cord length, per cord outer surface (the surface area is based on diameter calculation) and per cord volume were calculated and summarized for various cords in Table XI in the appendix. The results were analyzed with the help of statistical methods described elsewhere.

On investigating the dip pick-up of the different types of polyester cord P_1, P_2 and P_3 treated with RFL-1 and from the analysis of variances, see table 15, one can see that the cords used in this study had similar dip pick-ups, about 10%. Obviously, more varied cord structure would give statistically significant differences in the dip pick-up. As expected the dip pick-up is not influenced by the heat treatment, which follows dipping.

Similar results were also obtained when polyester cords were treated with RFL-2 adhesive system, as can be seen from the statistical analysis shown in table 16.

On the other hand, in case of nylon 6,6 treated with RFL-1 and after calculating the pick-ups of the different types of it, a correlation was found between the pick-up quantity and the type of the cord. Two of the three cords, namely, C_1 and C_2 are similar in their pick-ups. They have higher pick-ups

Table 15: The statistical analysis of pick-up measurements of polyester cord treated with RFL-1.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	1.0	0.7	3.06
Factor C	10	0.3	0.2	1.89
pure error	165	1.4		

Factor A = type of polyester cord
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Average (%)	Total average
A	1. P_1 cord	9.7	10.0
	2. P_2 cord	10.0	
	3. P_3 cord	10.3	
C	1. 160°C/3 min.	10.4	
	2. 160°C/5 min.	9.6	
	3. 160°C/7 min.	9.8	
	4. 160°C/10 min.	10.3	
	5. 160°C/15 min.	9.8	
	6. 180°C/1 min.	10.5	
	7. 180°C/3 min.	10.0	
	8. 180°C/5 min.	10.0	
	9. 220°C/1 min.	9.9	
	10. 220°C/3 min.	9.9	
	11. 220°C/5 min.	9.7	

Table 16: The statistical analysis of pick-up measurements of polyester cord treated with RFL-2 dip.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	1.0	1.8	3.09
Factor C	6	0.1	0.2	2.19
pure error	105	0.6		

Factor A = type of polyester cord
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Average (%)	Total average
A	1. P_1 cord	9.6	9.7
	2. P_2 cord	10.2	
	3. P_3 cord	9.5	
C	1. 160°C/5 min.	9.9	
	2. 160°C/15 min.	9.7	
	3. 180°C/3 min.	9.9	
	4. 180°C/5 min.	9.4	
	5. 220°C/1 min.	9.9	
	6. 220°C/3 min.	9.8	
	7. 220°C/5 min.	9.7	

than that of the third one C3. The heat treatment had no significant effect on the pick-up quantity as can be seen from table 17.

Pick-up level is affected by the kind of textile material. On comparing the pick-ups of nylon 6,6 and polyester cords treated with RFL-1 and RFL-2 dipping solutions, (table 15, 16, 17, 18 and XI in the appendix), one can see that the pick-up of polyester is higher than that of nylon 6,6 in any reasonable comparison: based on weight of pick-up per cord weight, per meter of cord, per outer surface of the cord or per cord volume. This result is in contrast to our expectation since nylon is more polar than polyester, having a high concentration of active hydrogen in the amide groups.

Table 17: The statistical analysis of pick-up measurements of nylon 6,6 cords treated with RFL-1 dip.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	6.9	9.1	3.07
Factor C	7	0.8	1.1	2.08
pure error	120	0.8		

Factor A = type of nylon 6,6 cord
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Average (%)	Total average
A	1. C_1 cord	7.5	7.2
	2. C_2 cord	7.9	
	3. C_3 cord	6.1	
C	1. 160°C/5 min.	6.7	
	2. 160°C/10 min.	7.0	
	3. 160°C/15 min.	7.4	
	4. 180°C/3 min.	7.6	
	5. 180°C/5 min.	7.0	
	6. 220°C/1 min.	8.1	
	7. 220°C/3 min.	6.5	
	8. 220°C/5 min.	7.1	

Table 18: The statistical analysis of pick-up measurements of polyester and nylon 6,6 cords treated with RFL-2 dip.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	1	4.6	6.3	3.98
Factor C	6	0.2	0.3	2.23
pure error	70	0.7		

Factor A = type of cord
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Average (%)	Total average
A	1. P_1 cord	9.6	9.0
	2. C_1 cord	8.4	
C	1. 160°C/5 min.	9.3	
	2. 160°C/15 min.	8.5	
	3. 180°C/3 min.	9.4	
	4. 180°C/5 min.	8.8	
	5. 220°C/1 min.	9.2	
	6. 220°C/3 min.	8.9	
	7. 220°C/5 min.	8.9	

4.4 Adhesion Between Textile Cords And Rubber Compounds.

4.4.1 Static adhesion tests

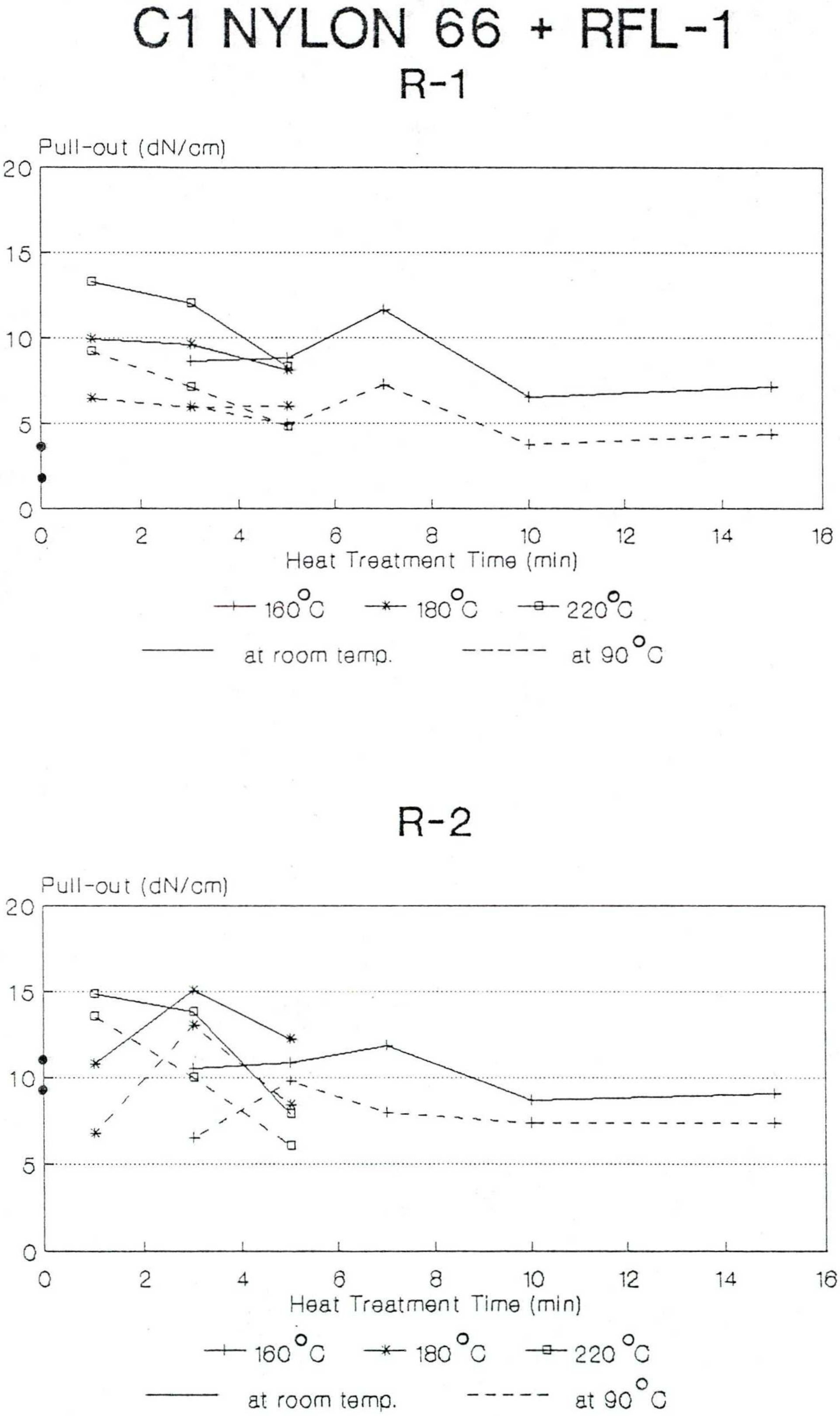
As mentioned before in the experimental part, four rubber compounds were used. These are: R-1 and R-2 compounds for natural rubber and R-3 and R-4 compounds for chloroprene rubber. A promoting material,based on resorcinol/hexa methylene tetramine, is added in R-2 and R-4 compounds to promote the adhesion of cord-to-rubber.

Three types of nylon 6,6 cord, namely, ICI 140/2 tex (C_1), ENKA 140/2 tex (C_2) and ENKA 94/2 tex (C_3) were used for the experimental work. Also three kinds of polyester cord, namely, ENKA 110/2 tex (P_1), Allied 110/2 tex (P_2) and Allied 110/3 tex (P_3) were used. The cords were dipped in both the Resorcinol-Formaldehyde-Latex (RFL-1) and RFL-2 adhesive systems. The latter is one-step dipping solution in which both the activating material, based on a co-resin of resorcinol and p-chlorophenol with formaldehyde, and RFL are included in a single-step dip. The specifications of these dipping solutions were given in the experimental part in tables 5 and 6 respectively.

After dipping, the cords were heat-treated at 160°C, 180°C, and 220°C for different durations. Both the undipped (without heat treatment) and dipped cords were bonded to the rubber compounds. The H-test specimens were made using the method mentioned before, in order to evaluate the adhesion between the rubber compounds and the textile cords. The pull-out force was determined at room temperature and at 90°C for all the rubber compounds. All the measured values for the adhesion of various cords are summarized in the appendix, (from Table XII to Table XXXI). All the test results were statistically analyzed.

For the first systems tested, which are nylon 6,6 cords (C_1), C_2 and C_3) treated with RFL-1 dip and bonded to natural rubber compounds R-1 and R-2, the static adhesion was evaluated (121). In each case we measured 12 H-adhesion test specimens and from the analysis of the results we can draw a conclusion that the tendency of the results at room temperature and at 90°C are similar but at 90°C with lower level of adhesion. The cord quality had a significant effect on the adhesion level. For cords C_1 and C_2 the results are similar but for cord C_3 the adhesion level is lower by about 20%. This is in line with the fact that cord C_3 has nearly 20% lower surface area than C_1 and C_2. (The total average for the adhesion levels calculated on the basis of surface area were found to be 4.2 N/mm^2, 3.9 N/mm^2, and 3.9 N/mm^2 for C_1, C_2, and C_3 respectively).

In accordance to our expectation, the dipping process increases the adhesion level, that is, higher adhesion level was achieved in case of dipped cords as can be seen from the statistical analysis of adhesion results shown in tables 19 and 20 for adhesion measured at room temperature and at 90°C respectively. The adhesion values for this system can be also seen from tables XII, XIII and XIV for C_1, C_2 and C_3 respectively, present in the appendix.



C1 NYLON 66 + RFL-1

R-1

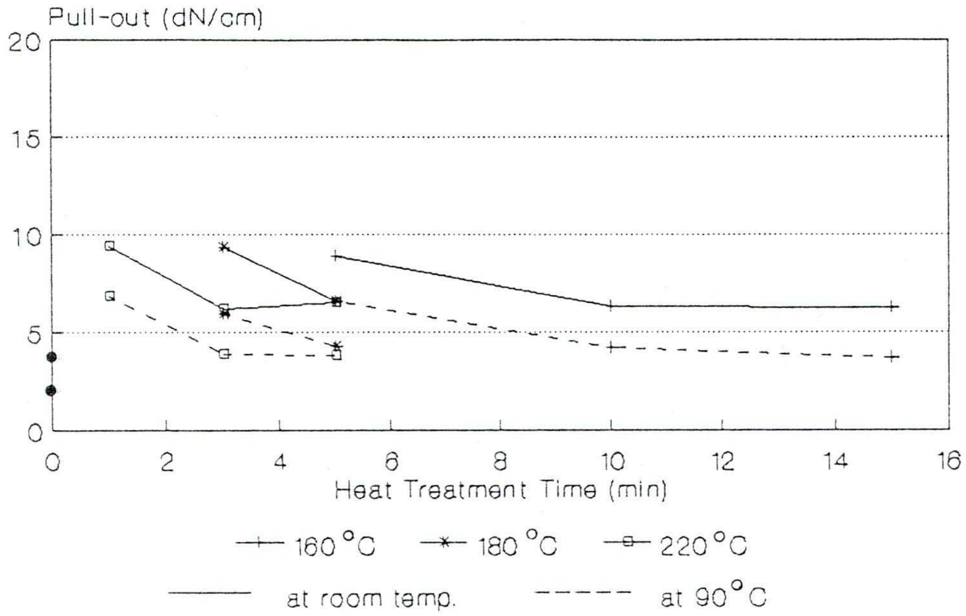
R-2

Figure 12: Effect of heat tretment time on adhesion between ICI 140/2 tex nylon 6,6 cord (C_1), dipped in RFL-1 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.84 dN/cm

C2 NYLON 66 + RFL-1

R-1



R-2

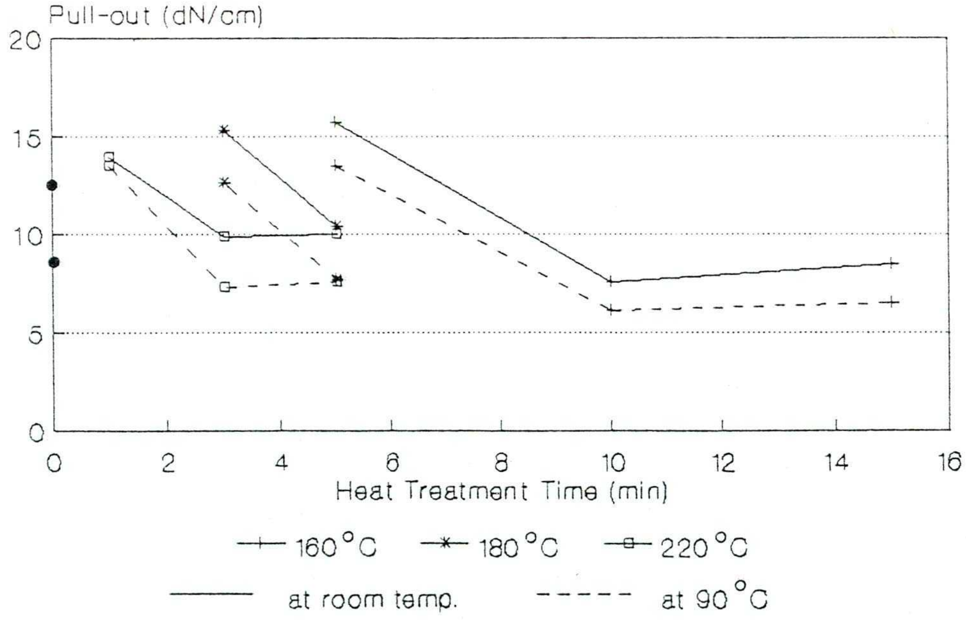
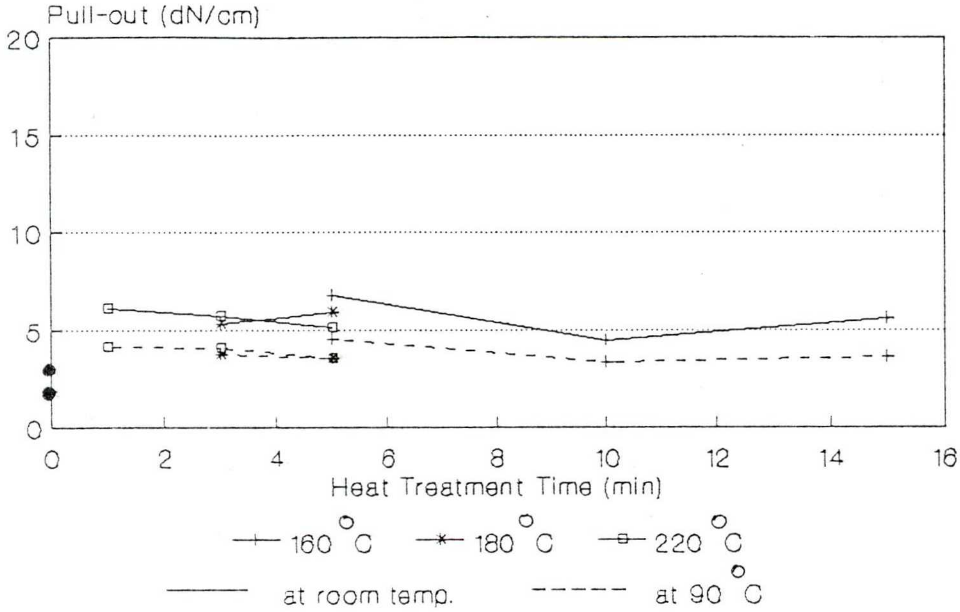


Figure 13: Effect of heat tretment time on adhesion between ENKA 140/2 tex nylon 6,6 cord (C_2), dipped in RFL-1 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.79 dN/cm

C3 NYLON 66 + RFL-1

R-1



R-2

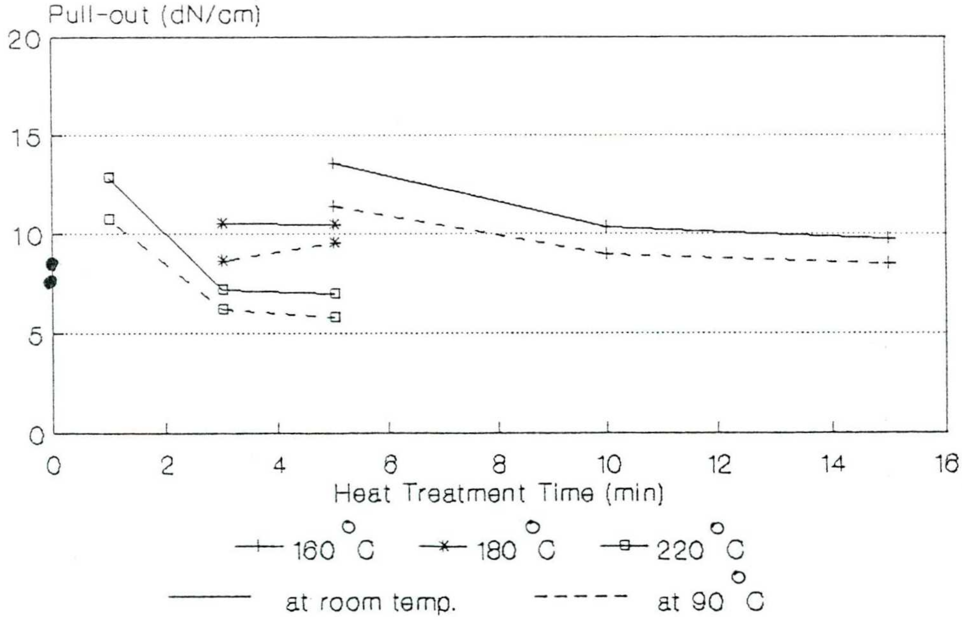


Figure 14: Effect of heat tretment time on adhesion between ENKA 94/2 tex nylon 6,6 cord (C3), dipped in RFL-1 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.63 dN/cm

Table 19: The statistical analysis of the adhesion measured at room temp. for nylon 6,6 treated with RFL-1 dip and bonded to NR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	27.0	33.1	3.01
Factor B	1	219.5	268.5	3.86
Factor C	8	18.6	22.7	1.96
pure error	648	0.8		

Factor A = type of nylon 6,6 cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. C_1 cord	10.1	9.0
	2. C_2 cord	9.3	
	3. C_3 cord	7.7	
B	1. R-1	7.0	
	2. R-2	11.0	
C	1. undipped	7.1	
	2. 160°C/5 min.	10.8	
	3. 160°C/10 min.	7.3	
	4. 160°C/15 min.	7.7	
	5. 180°C/3 min.	10.9	
	6. 180°C/5 min.	9.0	
	7. 220°C/1 min.	11.8	
	8. 220°C/3 min.	9.2	
	9. 220°C/5 min.	7.5	

Table 20: The statistical analysis of the adhesion measured at 90°C for nylon 6,6 treated with RFL-1 and bonded to NR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	7.8	14.4	3.01
Factor B	1	284.9	525.2	3.86
Factor C	8	15.7	29.0	1.96
pure error	648	0.5		

Factor A = type of nylon 6,6 cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. C_1 cord	7.4	6.8
	2. C_2 cord	6.9	
	3. C_3 cord	6.1	
B	1. R-1	4.5	
	2. R-2	9.1	
C	1. undipped	5.2	
	2. 160°C/5 min.	8.5	
	3. 160°C/10 min.	5.6	
	4. 160°C/15 min.	5.7	
	5. 180°C/3 min.	8.3	
	6. 180°C/5 min.	6.6	
	7. 220°C/1 min.	9.7	
	8. 220°C/3 min.	6.4	
	9. 220°C/5 min.	5.3	

By carrying out variance analysis, shown in tables 19 and 20 one can see that heat treatment conditions had strong effect on the adhesion values. The tests made at different temperatures, illustrated in figures 12, 13 and 14, showed that higher adhesion levels are achieved at the first heat treatment time in every case and on increasing the time, lower adhesion values were obtained. The results seem to contradict to those of Takeyama and Matsui (27), see figure 8, since we didn't obtain well defined maximum curves for the dependence of the pull-out force on the heat treatment time. Probably the adhesive system they used needed more severe heat treatment than ours, to obtain good adhesion.

The test results indicate that one can achieve higher adhesion level by using promoting material in the rubber compound R-2 if it is compared with R-1, as illustrated in the figures 12, 13 and 14 for C_1, C_2 and C_3 respectively. As one can see from these figures, the promoting material increases the adhesion of both the dipped cords and undipped ones. It is important to choose correct heat treatment conditions (temperature and time), otherwise it may destroy the effect of the dipping process on the adhesion.

On testing the effect of the heat treatment temperature on the adhesion level, it was found that at different applied temperatures long dwell time or too high oven temperature is detrimental. From our results, see figure 15, one can see that the adhesion level obtained at temperature higher than 160°C and after short time (3 minutes) was found to be better than that obtained after (5 minutes). This obtained result is

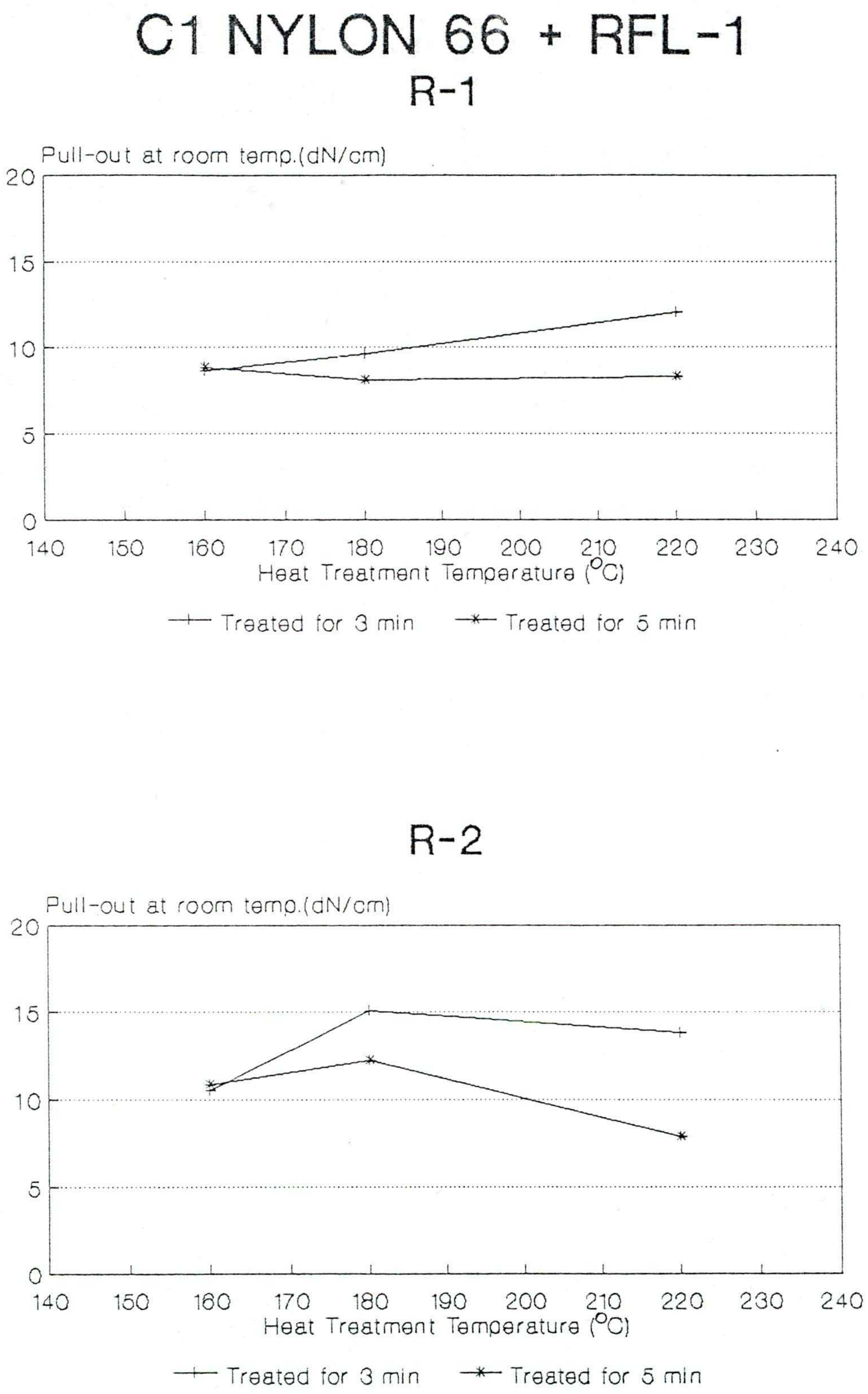
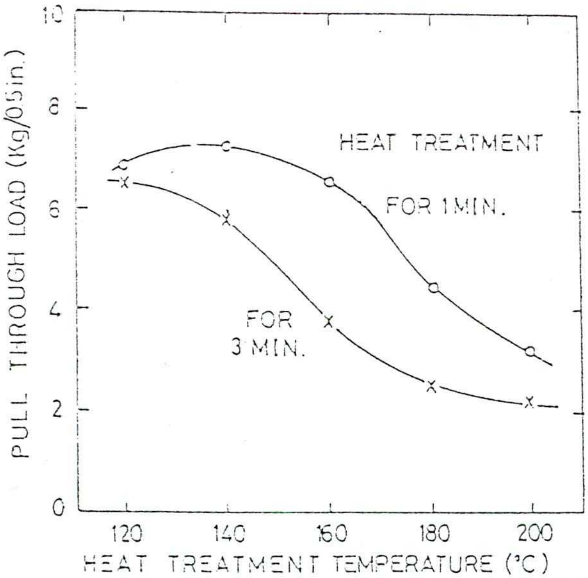


Figure 15: Effect of heat tretment temperature on adhesion between ICI 140/2 tex nylon 6,6 cord (C_1),dipped in RFL-1 dip,and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature.

Average standard deviation= 1.09 dN/cm

due to the fact that severe heat treatment causes too much crosslinking of the rubber component in the adhesive. Hence, miscibility of adhesive with the unvulcanized rubber to be bonded decreases, and adhesion decreases.

The tendency of our results is similar to those found in the literature (27), shown in figure 16, although the numerical results are different the Japanese scientist obtained the optimum adhesion level at lower temperature (140°C/1 min.). One has to conclude that optimum conditions should be determined empirically for each system.



(27)

FIG. 16—Effect of heat treatment conditions on adhesion.

Similar results to nylon 6,6 were obtained with polyester cords P_1, P_2 and P_3 treated with RFL-1 dip and bonded to the natural rubber compounds R-1 and R-2. From the test results shown in tables XV, XVI and XVII in the appendix for P_1, P_2 and P_3 respectively, and by the help of statistical analysis, see tables 21 and 22 for the adhesion measurements at room temperature and at 90°C respectively, one can see that P_1 and P_2 cords have similar adhesion values, where as P_3 cord has higher value than P_1 and P_2 by about 15%. This is because the radius of P_3 is bigger than that of P_1 and P_2, and that the cord pull-out force is increasing with increasing surface area. Theoretical considerations show that in the case of long embedded cords it is directly proportional to the square root of the cord radius or cord perimeter (122). (The total average of adhesion values on the basis of surface area were calculated to be 4.4 N/mm^2, 4.2 N/mm^2, 4.0 N/mm^2 for P_1, P_2, and P_3 respectively).

From the analysis of variances in tables 21 and 22, one can see that there is an improvement in the adhesion levels of polyester cord with the rubber mix R-2 compared to R-1. As can be seen from figures 17, 18 and 19 for polyester cord P_1, P_2 and P_3 respectively, that the promoting material present in R-2 compound also promote the adhesion of the undipped cord. The improvement in adhesion between polyester cord and NR using the ordinary RFL-1 adhesive system may be due to penetration of the dip into the structure of the cord which leads to better wettability which in turn may be the factor

Table 21: The statistical analysis of the adhesion measured at room temp. for polyester cords treated with RFL-1 and bonded to NR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	10.7	27.1	3.00
Factor B	1	16.7	42.4	3.85
Factor C	11	8.6	21.7	1.80
pure error	864	0.4		

Factor A = type of polyester cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	7.6	8.0
	2. P_2 cord	7.7	
	3. P_3 cord	8.8	
B	1. R-1	7.5	
	2. R-2	8.5	
C	1. undipped	5.9	
	2. 160°C/3 min.	7.5	
	3. 160°C/5 min.	7.7	
	4. 160°C/7 min.	9.1	
	5. 160°C/10 min.	9.1	
	6. 160°C/15 min.	6.9	
	7. 180°C/1 min.	9.5	
	8. 180°C/3 min.	7.3	
	9. 180°C/5 min.	7.4	
	10. 220°C/1 min.	9.8	
	11. 220°C/3 min.	8.8	
	12. 220°C/5 min.	7.2	

Table 22: The statistical analysis of the adhesion measured at 90°C for polyester cords treated with RFL-1 dip and bonded to NR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	3.5	18.8	3.00
Factor B	1	45.6	241.5	3.85
Factor C	11	3.6	19.0	1.80
pure error	864	0.2		

Factor A = type of polyester cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	5.3	5.6
	2. P_2 cord	5.4	
	3. P_3 cord	6.0	
B	1. R-1	4.8	
	2. R-2	6.4	
C	1. undipped	4.6	
	2. 160°C/3 min.	5.1	
	3. 160°C/5 min.	5.7	
	4. 160°C/7 min.	5.5	
	5. 160°C/10 min.	5.6	
	6. 160°C/15 min.	5.0	
	7. 180°C/1 min.	5.7	
	8. 180°C/3 min.	5.2	
	9. 180°C/5 min.	5.3	
	10. 220°C/1 min.	7.2	
	11. 220°C/3 min.	6.9	
	12. 220°C/5 min.	5.1	

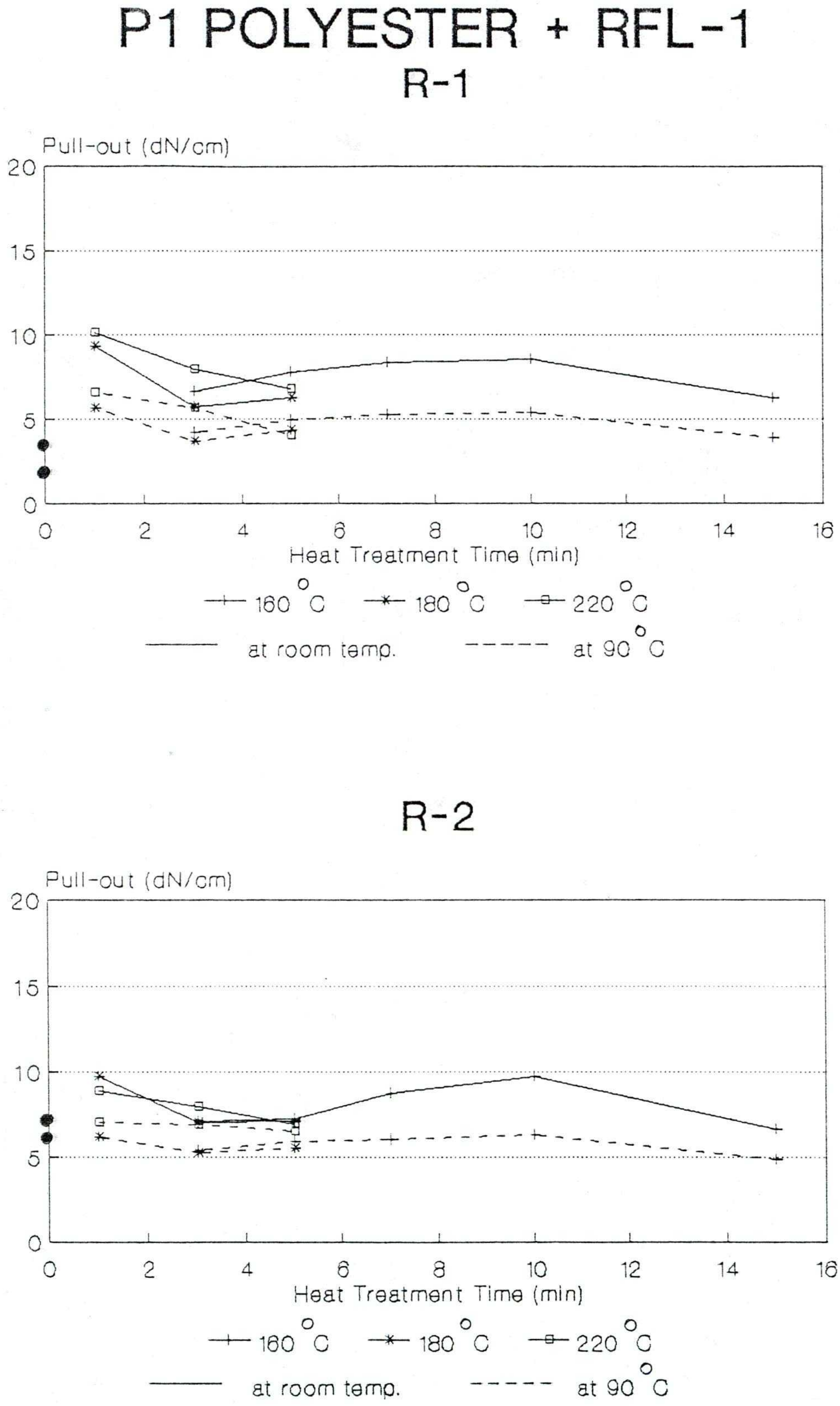
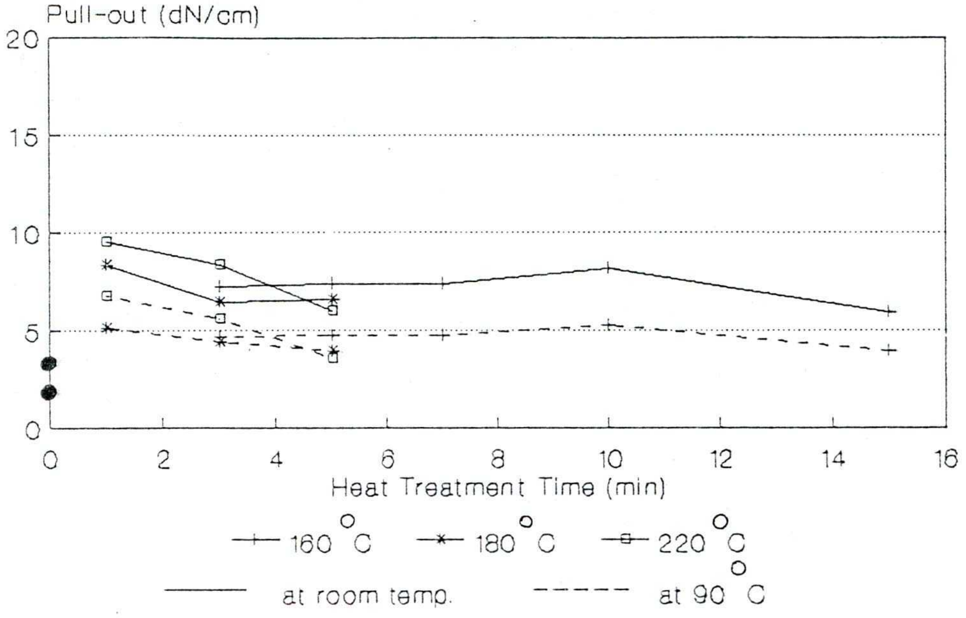


Figure 17: Effect of heat treatment time on adhesion between ENKA 110/2 tex polyester cord (P_1), dipped in RFL-1 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.49 dN/cm

P2 POLYESTER + RFL-1

R-1



R-2

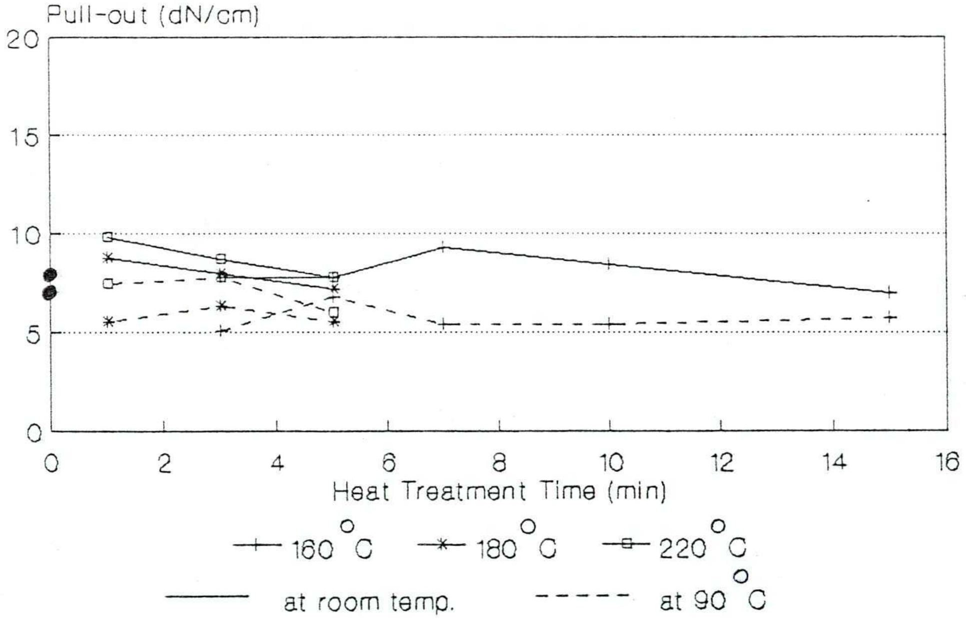
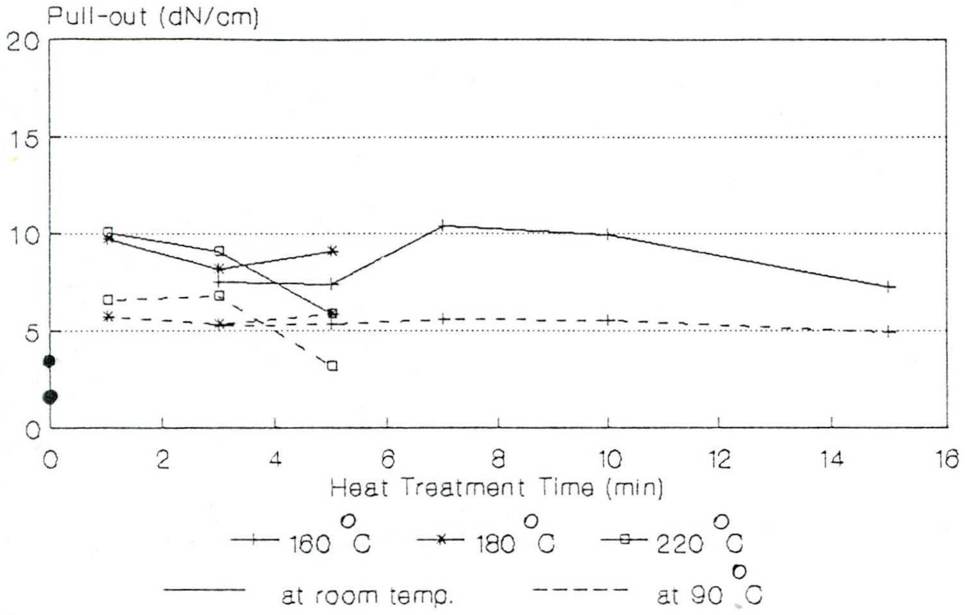


Figure 18: Effect of heat treatment time on adhesion between Allied 110/2 tex polyester cord (P2), dipped in RFL-1 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.53 dN/cm

P3 POLYESTER + RFL-1

R-1



R-2

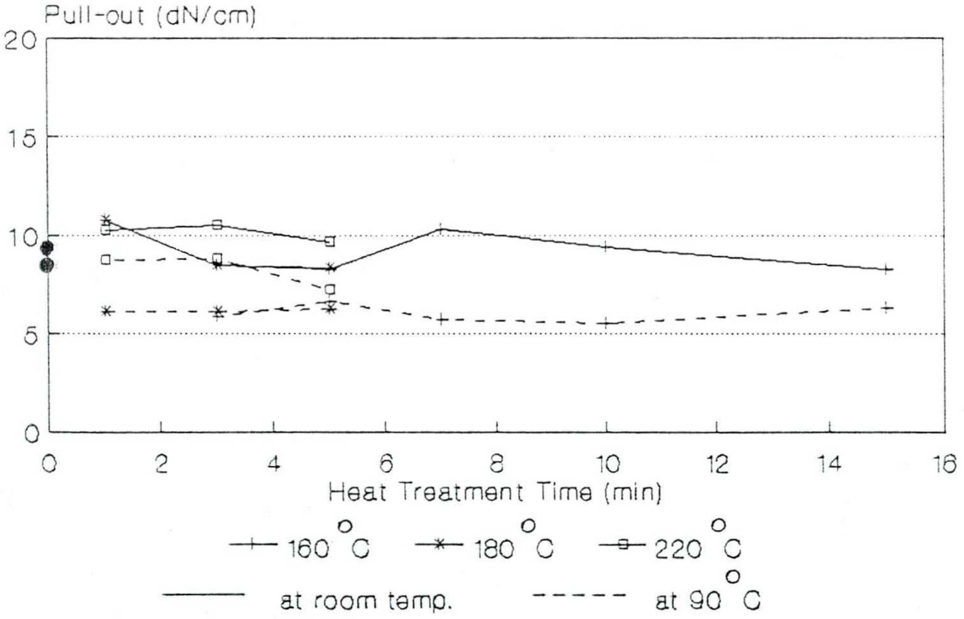


Figure 19: Effect of heat treatment time on adhesion between Allied 110/3 tex polyester cord (P3), dipped in RFL-1 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature and at 90°C.
Average standard deviation= 0.53 dN/cm

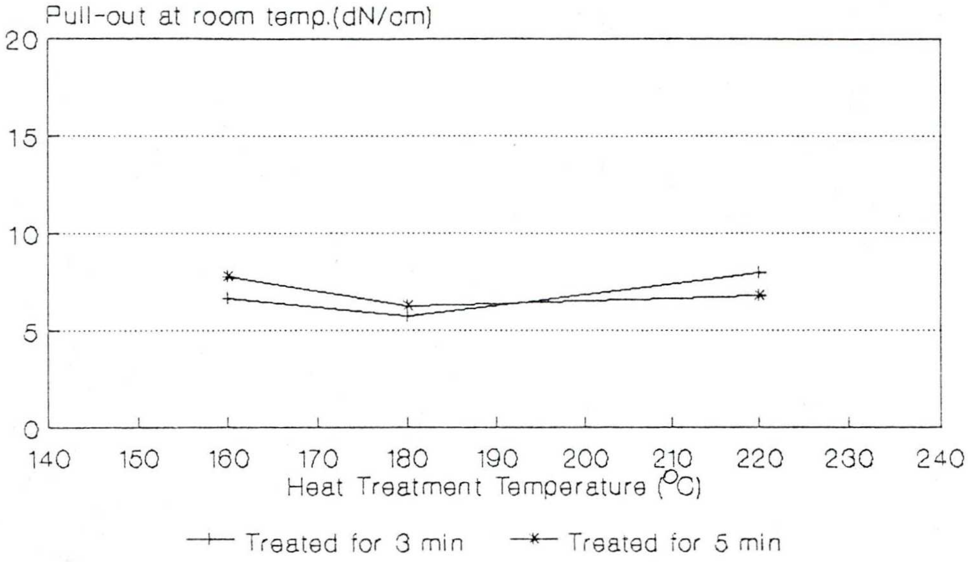
of promoting the adhesion level of polyester cord. This is also proved by the high dip pick-up obtained in case of the polyester treated with RFL-1 system. It can be also shown from tables 21 and 22 and figures 17, 18 and 19 that heat treatment conditions have a significant effect on the adhesion and that good bonding levels were obtained at higher temperature since polyester needs higher heat treatment temperature in order to obtain good adhesion levels (45).

Figures 20, 21 and 22 for polyester cords P_1, P_2 and P_3 respectively, show the effect of the heat treatment temperature on the adhesion. One can see that usually slightly higher adhesion levels can be obtained at 220°C and for shorter time (3 min.) than for longer time (5 min.).

Similar results to that of nylon 6,6 and polyester cords treated with RFL-1 dip and bonded to NR compounds, were obtained, with polyester cords P_1, P_2 and P_3 treated with RFL-2 adhesive system and bonded to NR compounds R-1 and R-2. The adhesion was evaluated (123). The adhesion values for this system are shown in tables XVIII, XIX and XX for P_1, P_2 and P_3 respectively in the appendix. From the statistical analysis of the test results, see tables 23 and 24 for the adhesion measured at room temperature and at 90°C respectively, it can be seen that the adhesion values for cords P_1 and P_2 are similar but in case of cord P_3 the adhesion is higher by about 21%. This may be due to the fact that the pull-out force is related to the cylindrical surface equivalent to the cord and that the surface area of P_3 is higher than that of P_1 and P_2 by about 24%. (The total

P1 POLYESTER + RFL-1

R-1



R-2

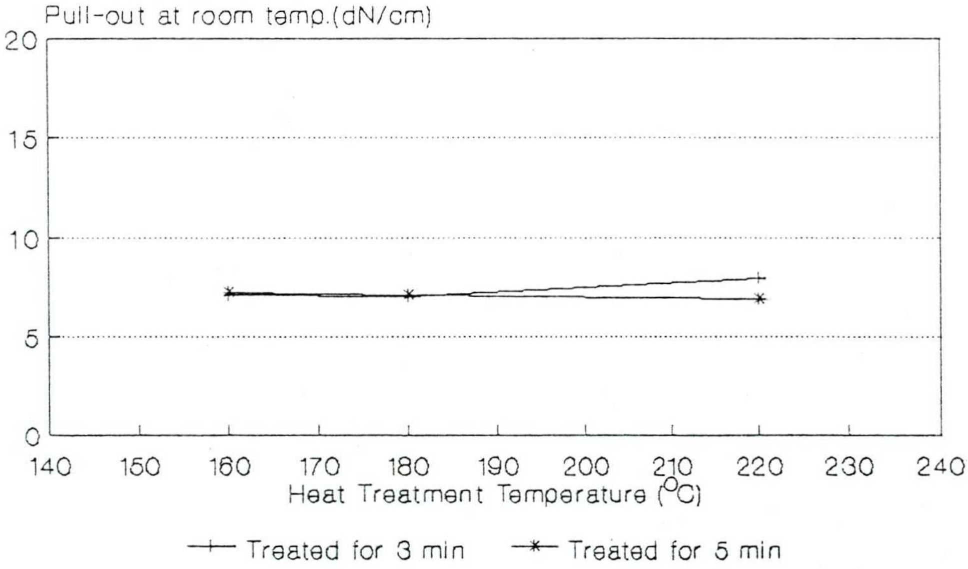


Figure 20: Effect of heat treatment temperature on adhesion between ENKA 110/2 tex polyester cord (P1), dipped in RFL-1 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature.

Average standard deviation= 0.55 dN/cm

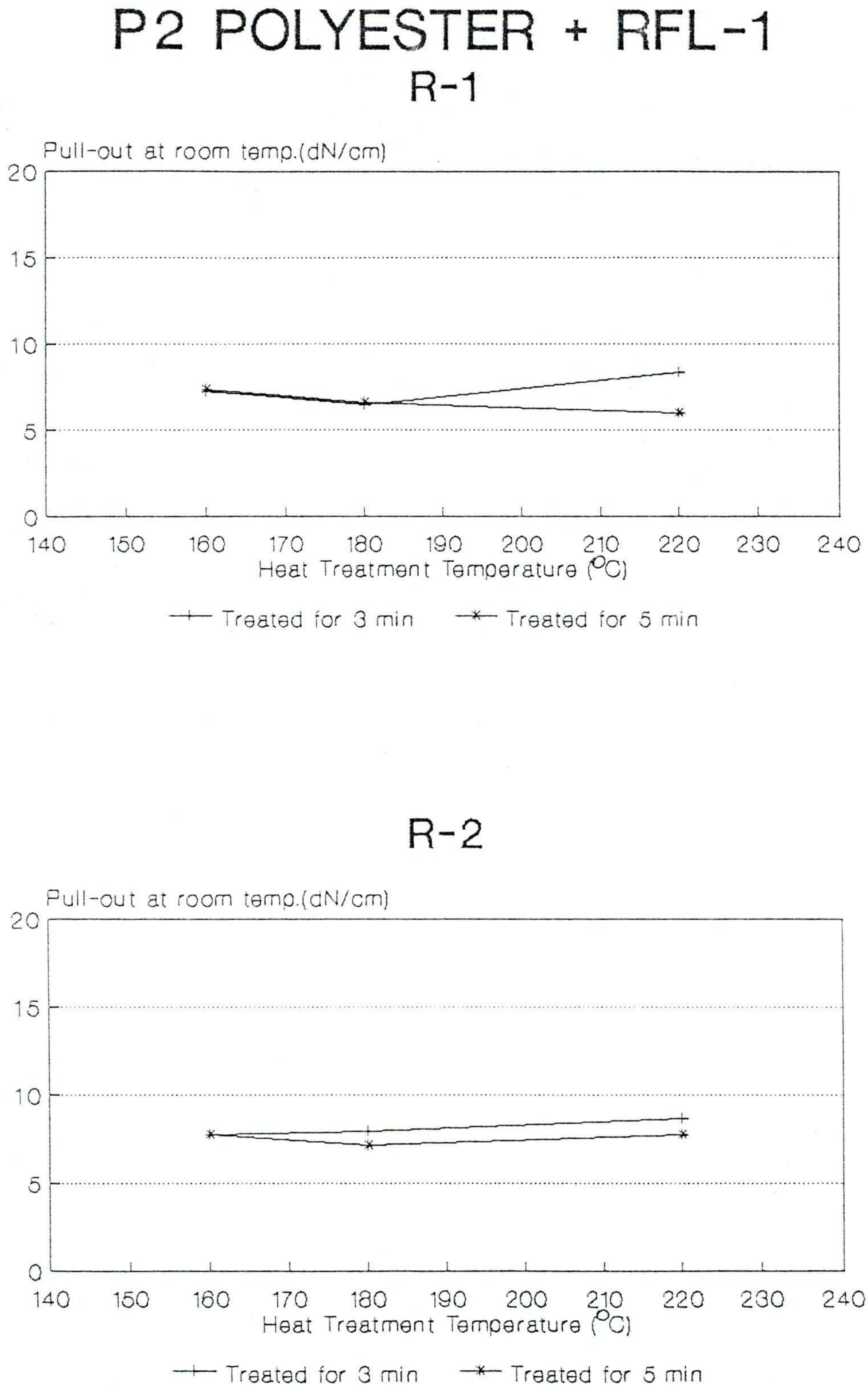
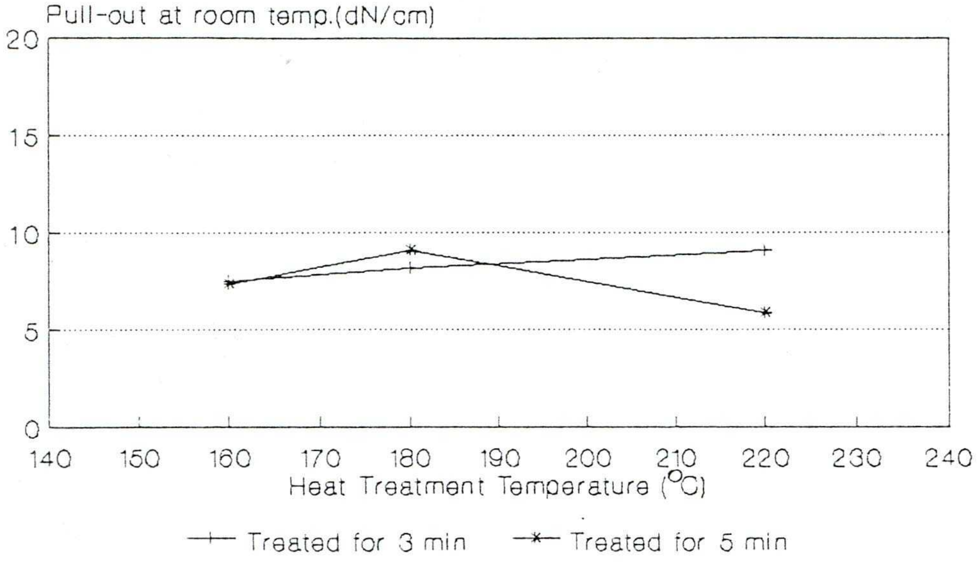


Figure 21: Effect of heat treatment temperature on adhesion between Allied 110/2 tex polyester cord (P2), dipped in RFL-1 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature.
Average standard deviation= 0.62 dN/cm

P3 POLYESTER + RFL-1

R-1



R-2

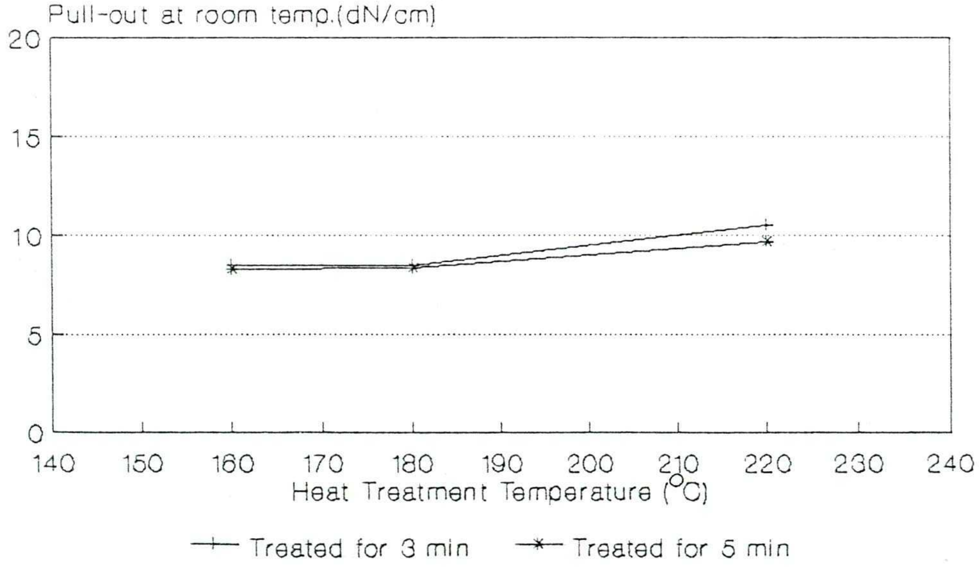


Figure 22: Effect of heat treatment temperature on adhesion between Allied 110/3 tex polyester cord (P3), dipped in RFL-1 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature.

Average standard deviation= 0.79 dN/cm

Table 23: The statistical analysis of the adhesion measured at room temp. for polyester cord treated with RFL-2 dip and bonded to NR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	28.6	28.9	3.01
Factor B	1	68.4	69.0	3.86
Factor C	7	37.7	38.1	2.03
pure error	576	1.0		

Factor A = type of polyester cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	10.5	10.7
	2. P_2 cord	9.6	
	3. P_3 cord	12.2	
B	1. R-1	9.6	
	2. R-2	12.0	
C	1. undipped	5.9	
	2. 160°C/5 min.	9.3	
	3. 160°C/15 min.	9.7	
	4. 180°C/3 min.	11.2	
	5. 180°C/5 min.	11.3	
	6. 220°C/1 min.	11.7	
	7. 220°C/3 min.	13.6	
	8. 220°C/5 min.	13.6	

Table 24: The statistical analysis of the adhesion measured at 90°C for polyester cord treated with RFL-2 dip and bonded to NR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	10.5	18.6	3.01
Factor B	1	108.1	191.7	3.86
Factor C	7	12.6	22.3	2.03
pure error	576	0.6		

Factor A = type of polyester cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	7.0	7.3
	2. P_2 cord	6.7	
	3. P_3 cord	8.3	
B	1. R-1	5.9	
	2. R-2	8.9	
C	1. undipped	4.6	
	2. 160°C/5 min.	6.5	
	3. 160°C/15 min.	6.9	
	4. 180°C/3 min.	7.6	
	5. 180°C/5 min.	7.4	
	6. 220°C/1 min.	7.9	
	7. 220°C/3 min.	9.6	
	8. 220°C/5 min.	8.2	

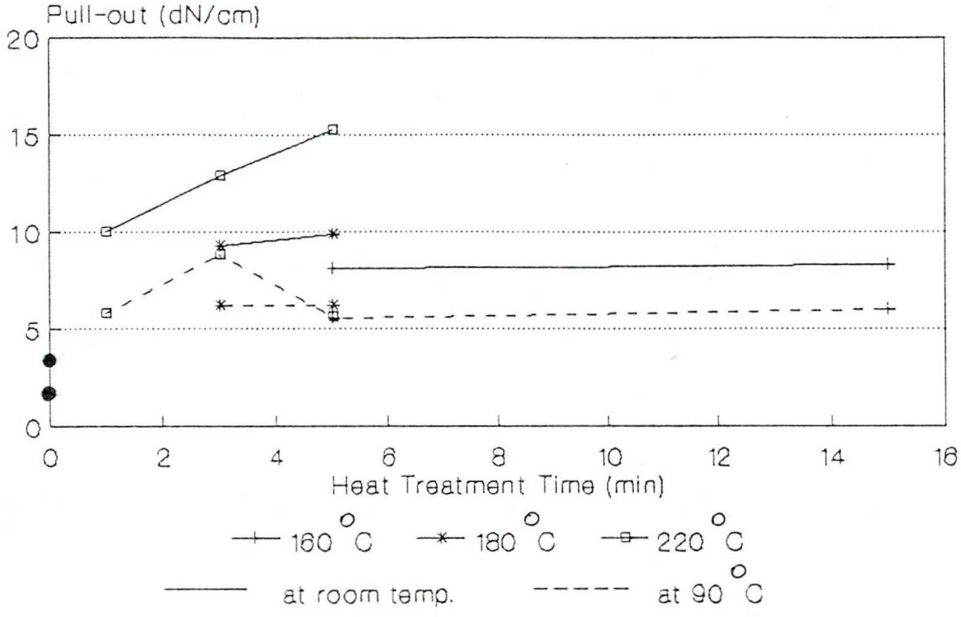
average of the adhesion value based on the surface area were calculated to be 6.0 N/mm^2, 5.2 N/mm^2, and 5.5 N/mm^2 for P_1, P_2, and P_3 respectively).

Figures 23, 24 and 25 for P_1, P_2 and P_3 cords respectively, illustrate that one can achieve higher adhesion levels by using promoting material as in case of NR compound R-2. The figures also show that in every case higher adhesion levels were obtained at higher heat treatment temperature and that in most cases 220°C/3 min. is the best heat treatment conditions.

comparing our results to that obtained by Rayner (66) for polyester cord treated with one-step dip, it was found that in the literature the optimum value of adhesion is obtained at shifted time or after very short time (about 50 secs) which is very difficult to be controlled, beside that this time is depending on the efficiency of the machine. On the other hand, the author did not show any measured data for the adhesion on the curve, as can be seen from figure 26.

P1 POLYESTER + RFL-2

R-1



R-2

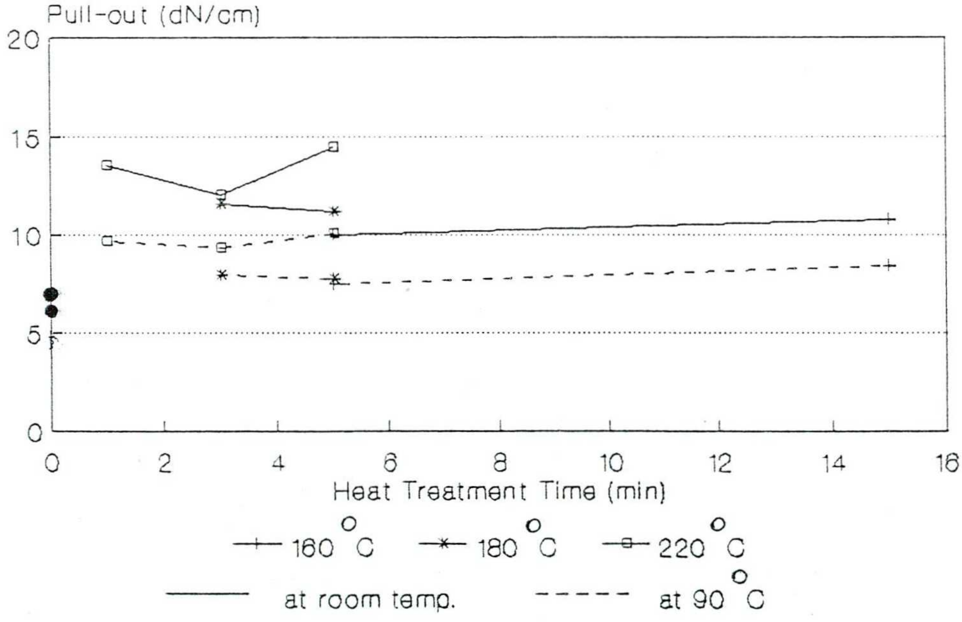


Figure 23: Effect of heat treatment time on adhesion between ENKA 110/2 tex polyester cord (P1), dipped in RFL-2 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.83 dN/cm

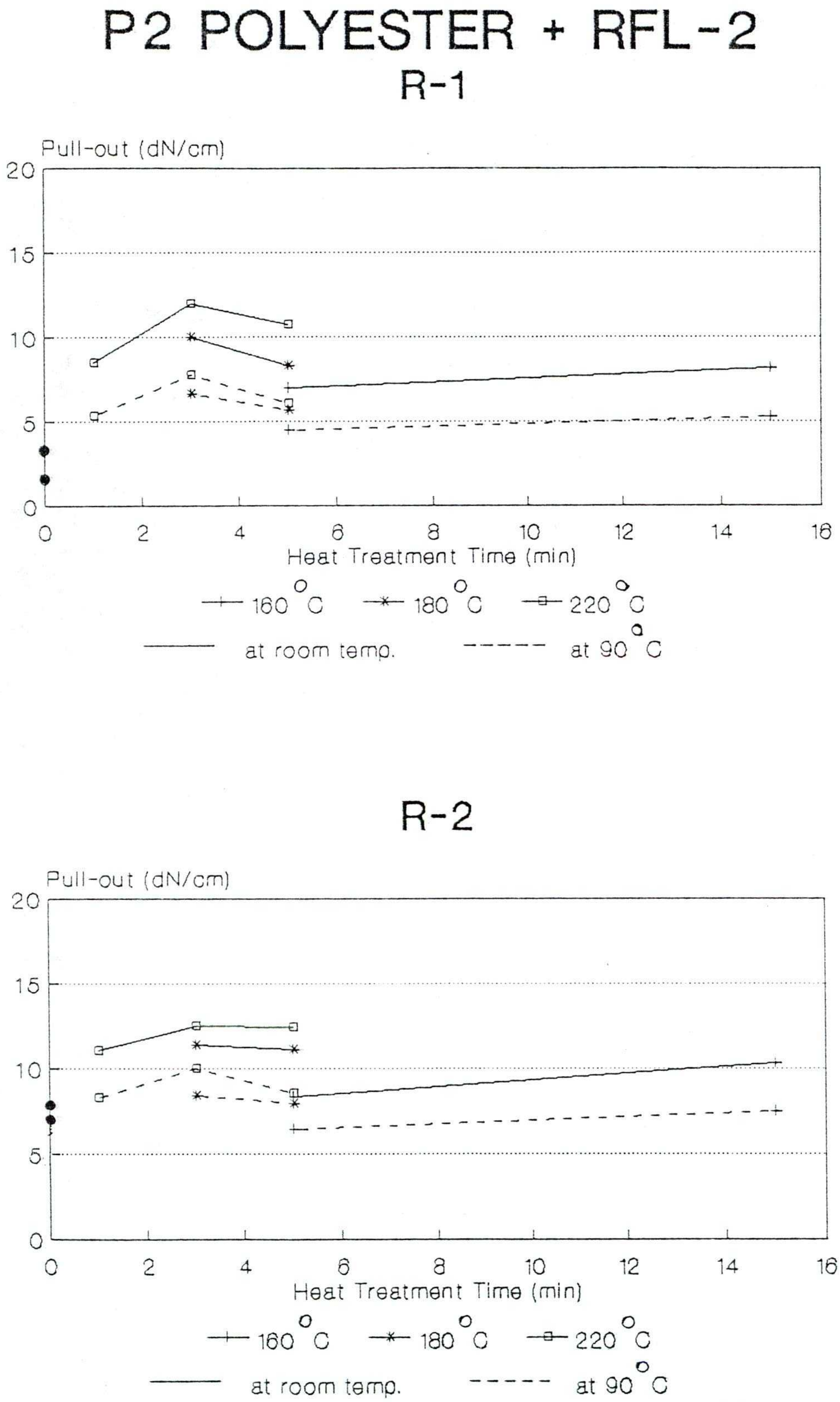
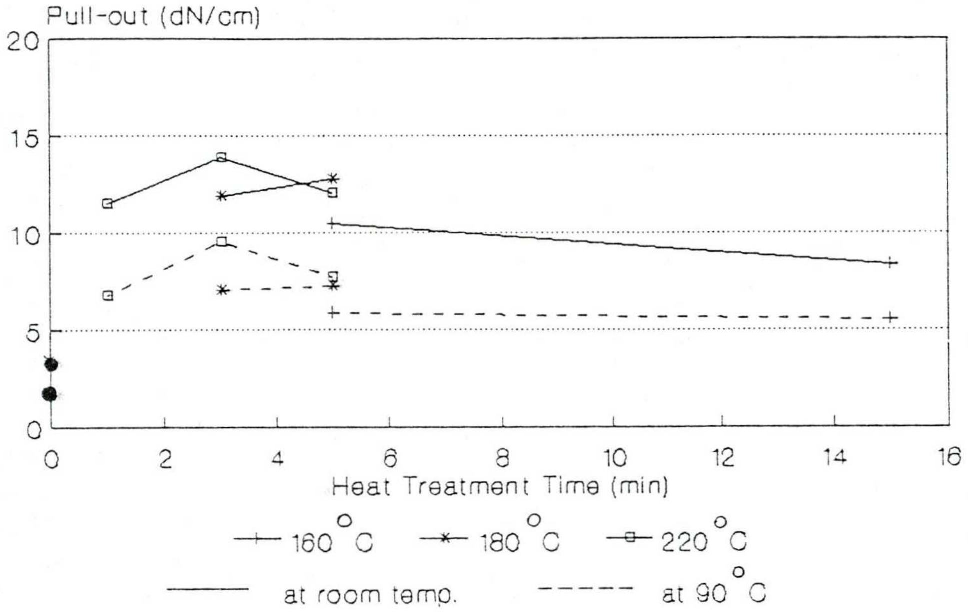


Figure 24: Effect of heat treatment time on adhesion between Allied 110/2 tex polyester cord (P2), dipped in RFL-2 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.80 dN/cm

P3 POLYESTER + RFL-2

R-1



R-2

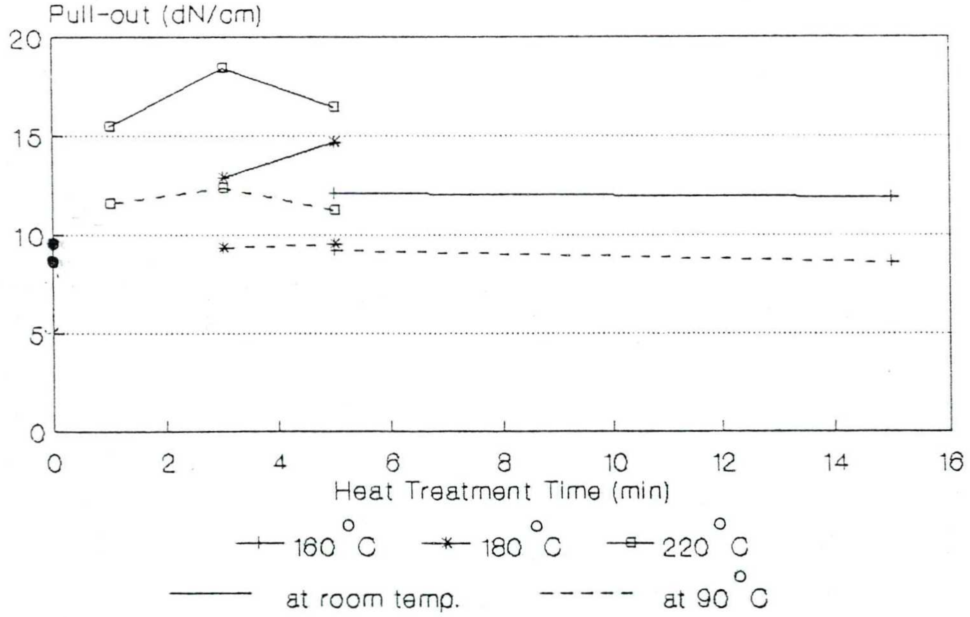
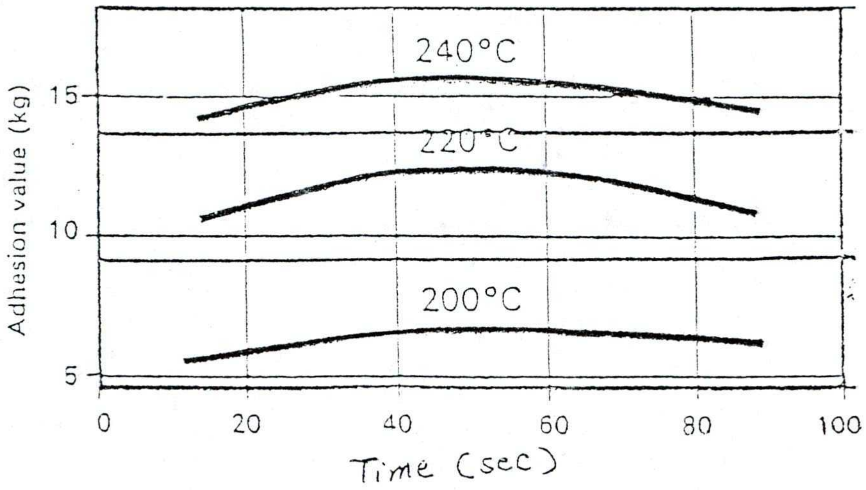


Figure 25: Effect of heat treatment time on adhesion between Allied 110/3 tex polyester cord (P3), dipped in RFL-2 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.87 dN/cm

Fig.26. Effect of dip-cure temperature and time on resulting adhesion of 1100 dtex × 3 (3/1,000 den) Terylene cord; 6·4 mm (¼-inch) pull-out T-test at 20°C.(66)



Another system tested is the polyester cords P_1, P_2 and P_3 treated with RFL-2 dip and bonded to chloroprene rubber compounds R-3 and R-4. The results were found to be similar to that obtained with polyester cords bonded to NR and treated with the same adhesive system. The adhesion values for this system can be seen in tables XXI, XXII and XXIII for P_1, P_2 and P_3 respectively in the appendix. It can be shown from tables 25 and 26 that P_3 cord has higher adhesion level than that of P_1 and P_2 by about 23%. (The total averages of the adhesion values on the basis of surface area were found to be 5.5 N/mm^2, 5.1 N/mm^2, and 5.2 N/mm^2 for P_1, P_2, and P_3 respectively). It can also be seen from the two tables and figures 27, 28 and 29 that the dipping process increases the adhesion levels by about factor of two. From the figures one

Table 25: The statistical analysis of the adhesion measured at room temp. for polyester cord treated with RFL-2 dip and bonded to CR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	26.0	28.9	3.01
Factor B	1	17.2	19.2	3.86
Factor C	7	32.4	36.1	2.03
pure error	576	0.9		

Factor A = type of polyester cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	9.5	10.1
	2. P_2 cord	9.3	
	3. P_3 cord	11.6	
B	1. R-3	10.7	
	2. R-4	9.5	
C	1. undipped	4.7	
	2. 160°C/5 min.	10.1	
	3. 160°C/15 min.	10.2	
	4. 180°C/3 min.	11.0	
	5. 180°C/5 min.	10.2	
	6. 220°C/1 min.	11.0	
	7. 220°C/3 min.	11.9	
	8. 220°C/5 min.	11.9	

Table 26: The statistical analysis of the adhesion measured at 90°C for polyester cord treated with RFL-2 dip and bonded to CR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	9.3	22.1	3.01
Factor B	1	3.4	8.1	3.86
Factor C	7	14.4	34.1	2.03
pure error	576	0.4		

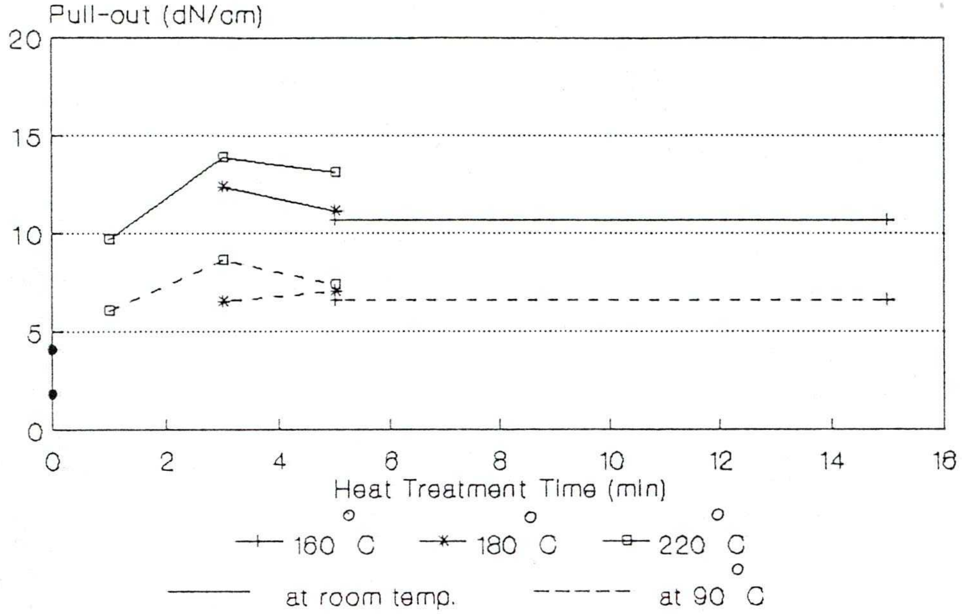
Factor A = type of polyester cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	5.8	6.2
	2. P_2 cord	5.7	
	3. P_3 cord	7.1	
B	1. R-3	6.4	
	2. R-4	5.9	
C	1. undipped	2.6	
	2. 160°C/5 min.	6.0	
	3. 160°C/15 min.	6.2	
	4. 180°C/3 min.	6.5	
	5. 180°C/5 min.	6.4	
	6. 220°C/1 min.	6.9	
	7. 220°C/3 min.	7.5	
	8. 220°C/5 min.	7.4	

P1 POLYESTER + RFL-2

R-3



R-4

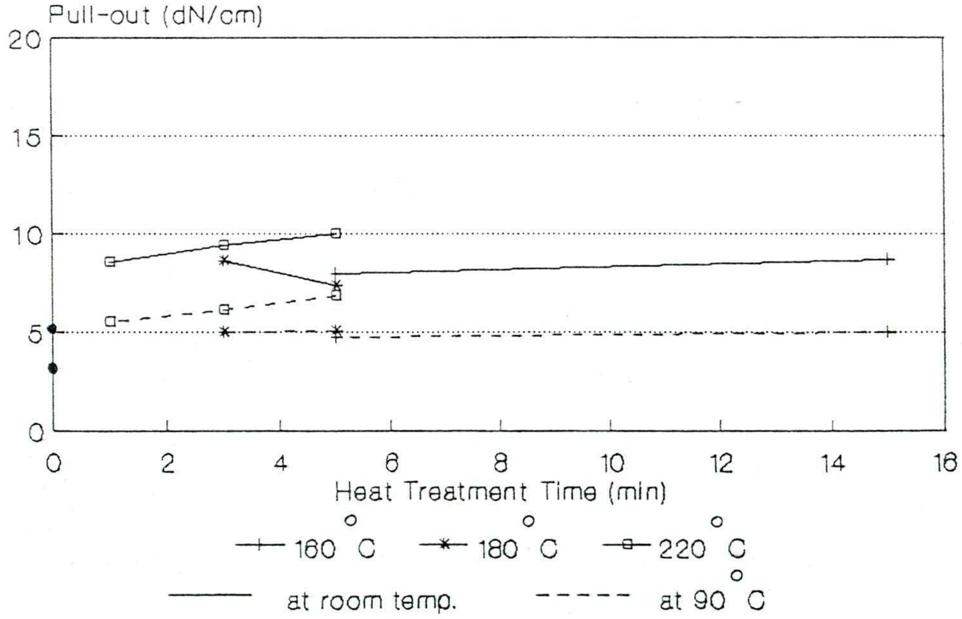
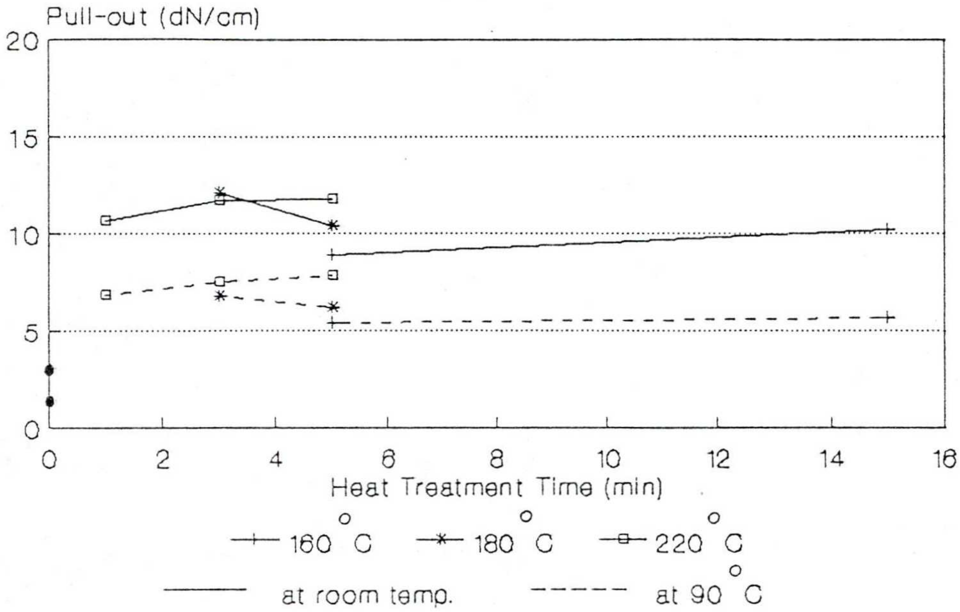


Figure 27: Effect of heat treatment time on adhesion between ENKA 110/2 tex polyester cord (P1), dipped in RFL-2 dip, and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature and at 90°C.
Average standard deviation= 0.75 dN/cm

P2 POLYESTER + RFL-2

R-3



R-4

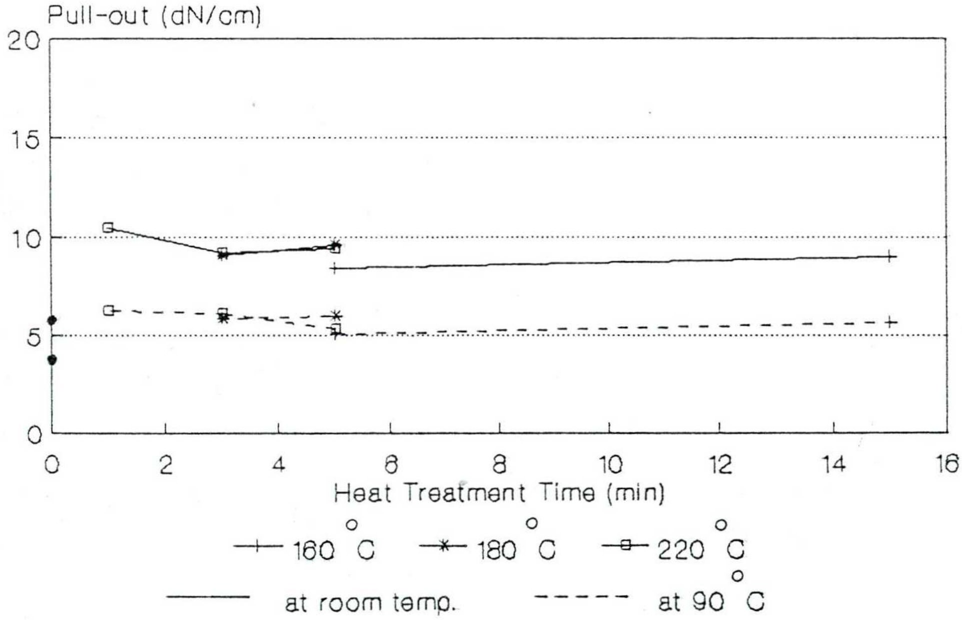


Figure 28: Effect of heat treatment time on adhesion between Allied 110/2 tex polyester cord (P2), dipped in RFL-2 dip, and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.77 dN/cm

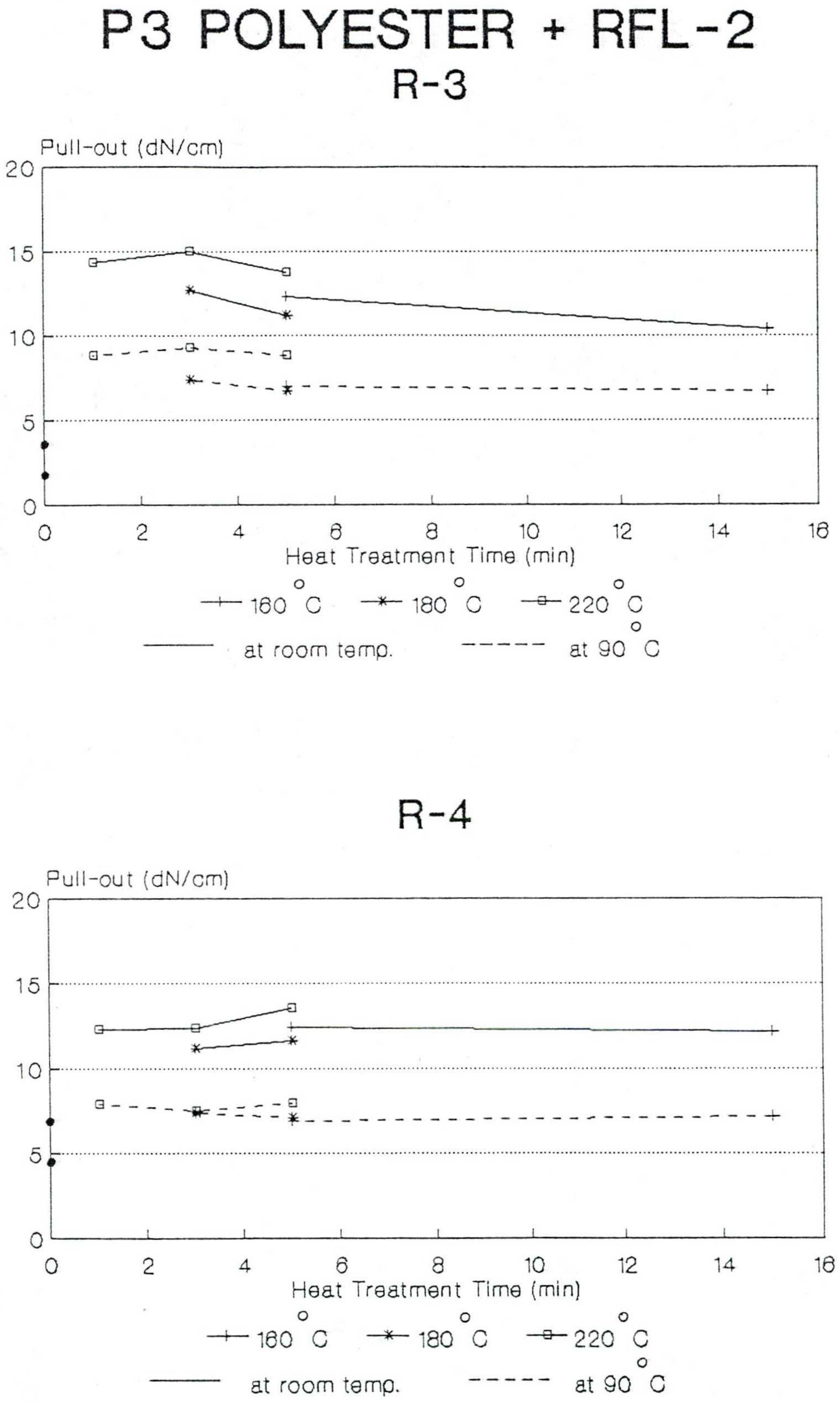


Figure 29: Effect of heat treatment time on adhesion between Allied 110/3 tex polyester cord (P3), dipped in RFL-2 dip, and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.88 dN/cm

can see that in all cases higher adhesion levels can be achieved at 220°C, and that the heat treatment conditions had a significant effect on the adhesion levels. On the other hand the figures also show that the addition of promoting material to the chloroprene rubber compound, as in case of compound R-4, has no effect in increasing the adhesion level. In this special case, or in other words, when chloroprene rubber is bonded to polyester cords treated with RFL-2 dip, higher adhesion levels can be obtained without addition of promoting material. This result differs than that obtained in case of polyester treated with RFL-2 dip but bonded to NR compound where higher adhesion levels were obtained in case of R-2 compound where promoting material is added, see figures 23, 24 and 25.

Another system consisting of nylon 6,6 cords C_1, C_2 and C_3 treated with RFL-1 dip and bonded to chloroprene rubber was investigated (124). The adhesion values for this system are shown in tables XXIV, XXV and XXVI in the appendix for the three cords. It was found from our results that this system a little bit differs from the others discussed above. From tables 27 and 28, one can see that in contrast to our expectation, it was found that cord C_2 has lower adhesion levels than that of C_1 although they have similar structure. On the other hand about 45% higher adhesion values were found in the case of C_1 cord than with C_3. This is because the surface area of C_1 is higher than that of C_3 by about 23%. (The total averages of the adhesion values on the basis of surface area are 4.9 N/mm^2, 3.5 N/mm^2, and 4.2 N/mm^2 for C_1,

Table 27: The statistical analysis of the adhesion measured at room temp. for nylon 6,6 treated with RFL-1 dip and bonded to CR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	80.4	63.0	3.01
Factor B	1	309.0	242.1	3.86
Factor C	8	24.3	19.0	1.96
pure error	648	1.3		

Factor A = type of nylon 6,6 cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. C_1 cord	12.0	9.5
	2. C_2 cord	8.3	
	3. C_3 cord	8.3	
B	1. R-3	7.1	
	2. R-4	11.9	
C	1. undipped	5.1	
	2. 160°C/5 min.	11.3	
	3. 160°C/10 min.	7.9	
	4. 160°C/15 min.	8.9	
	5. 180°C/3 min.	11.3	
	6. 180°C/5 min.	10.1	
	7. 220°C/1 min.	10.2	
	8. 220°C/3 min.	11.0	
	9. 220°C/5 min.	9.9	

Table 28: The statistical analysis of the adhesion measured at 90°C for nylon 6,6 treated with RFL-1 and bonded to CR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	25.4	51.5	3.01
Factor B	1	171.6	348.1	3.86
Factor C	8	8.0	16.2	1.96
pure error	648	0.5		

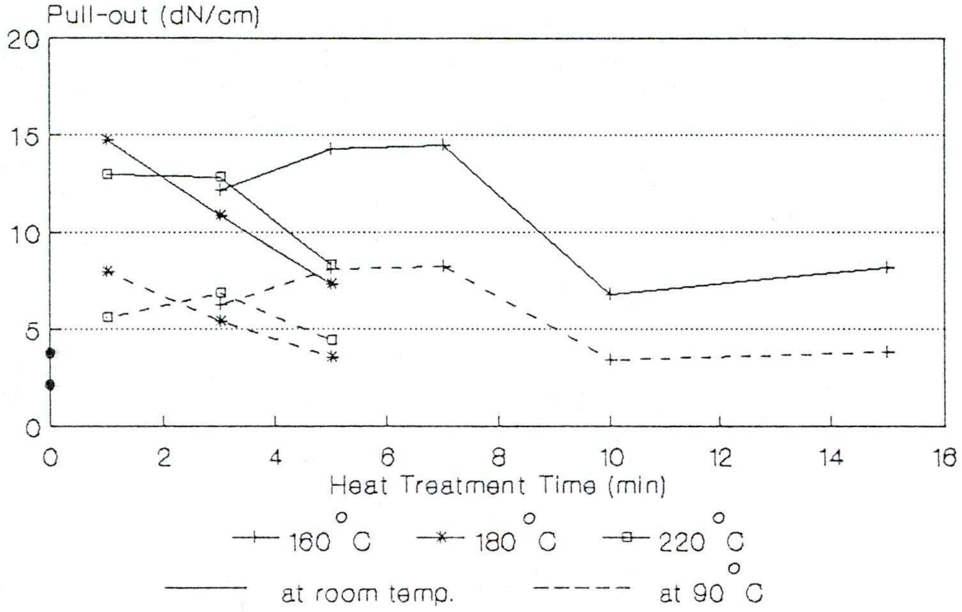
Factor A = type of nylon 6,6 cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. C_1 cord	6.6	5.2
	2. C_2 cord	4.4	
	3. C_3 cord	4.5	
B	1. R-3	3.4	
	2. R-4	7.0	
C	1. undipped	2.6	
	2. 160°C/5 min.	6.4	
	3. 160°C/10 min.	4.4	
	4. 160°C/15 min.	4.8	
	5. 180°C/3 min.	6.1	
	6. 180°C/5 min.	5.4	
	7. 220°C/1 min.	5.5	
	8. 220°C/3 min.	6.0	
	9. 220°C/5 min.	5.5	

C1 NYLON 66 + RFL-1

R-3



R-4

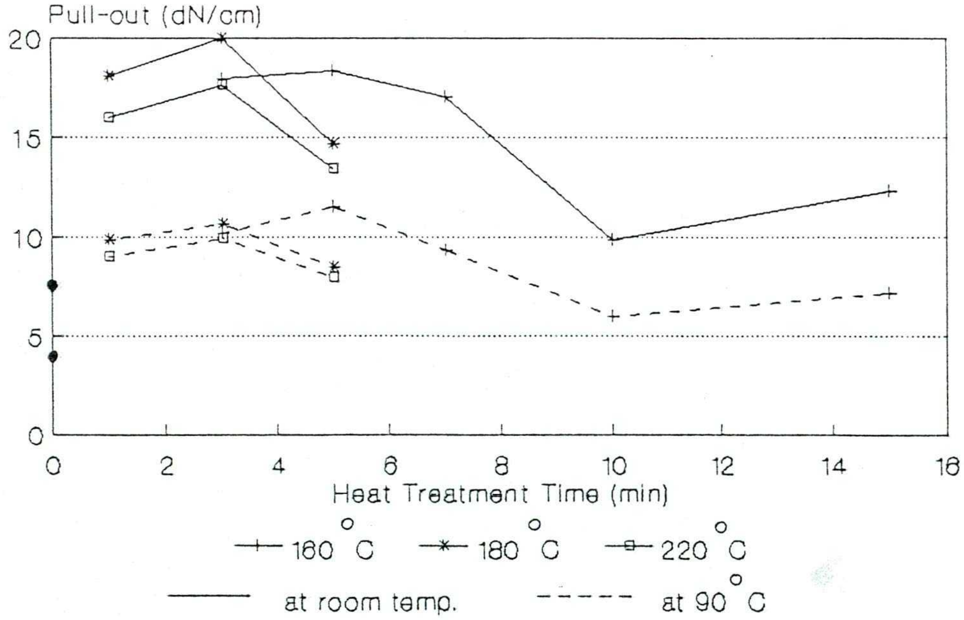
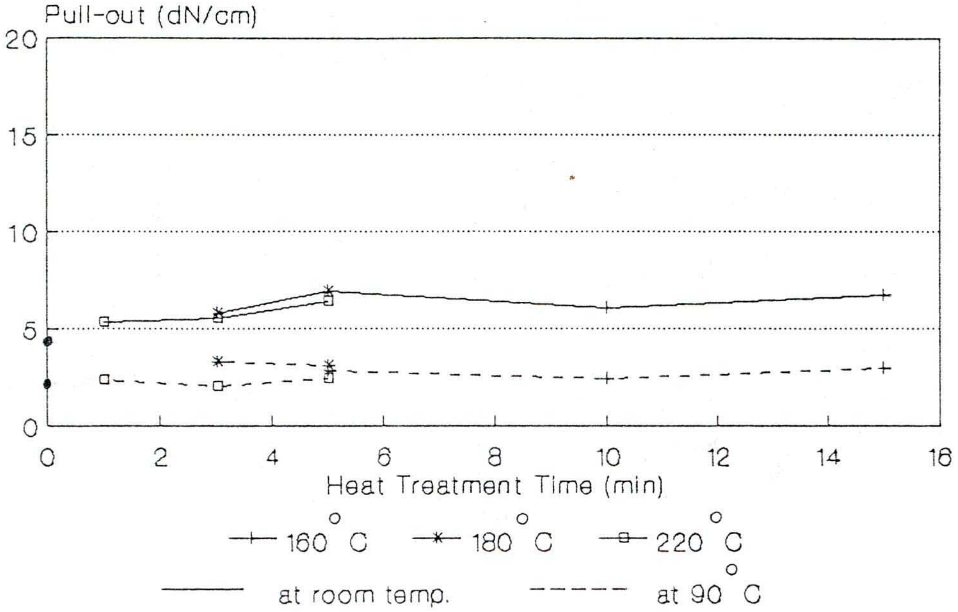


Figure 30: Effect of heat treatment time on adhesion between ICI 140/2 tex nylon 6,6 cord (C1), dipped in RFL-1 dip, and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature and at 90°C.
Average standard deviation= 1.05 dN/cm

C2 NYLON 66 + RFL-1

R-3



R-4

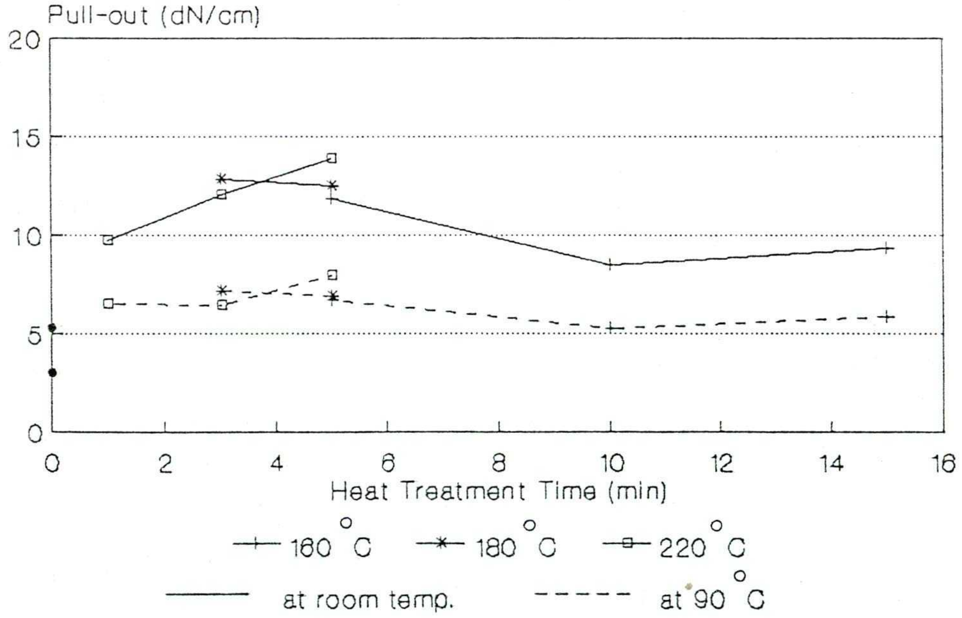
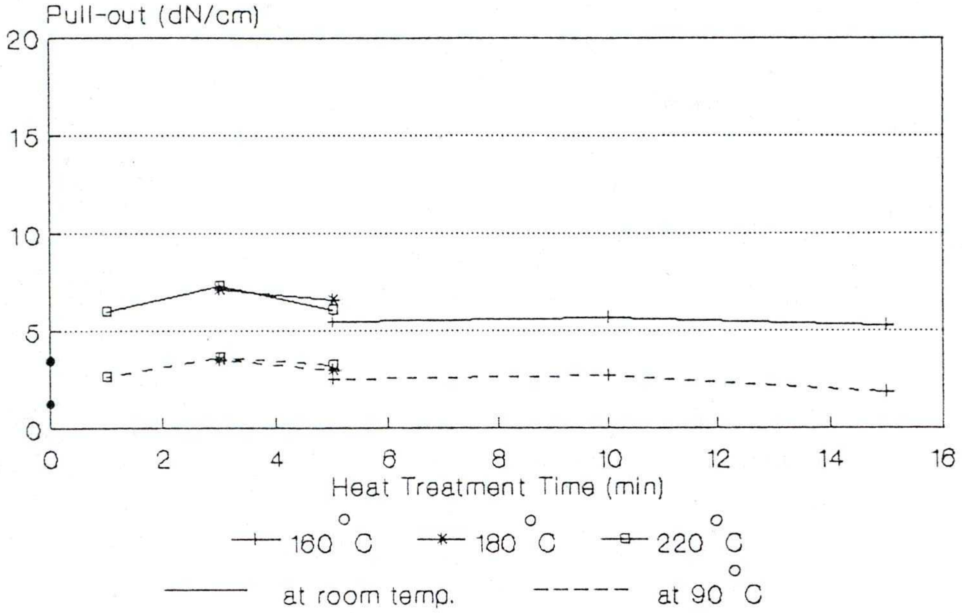


Figure 31: Effect of heat treatment time on adhesion between ENKA 140/2 tex nylon 6,6 cord (C2), dipped in RFL-1 dip, and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.79 dN/cm

C3 NYLON 66 + RFL-1

R-3



R-4

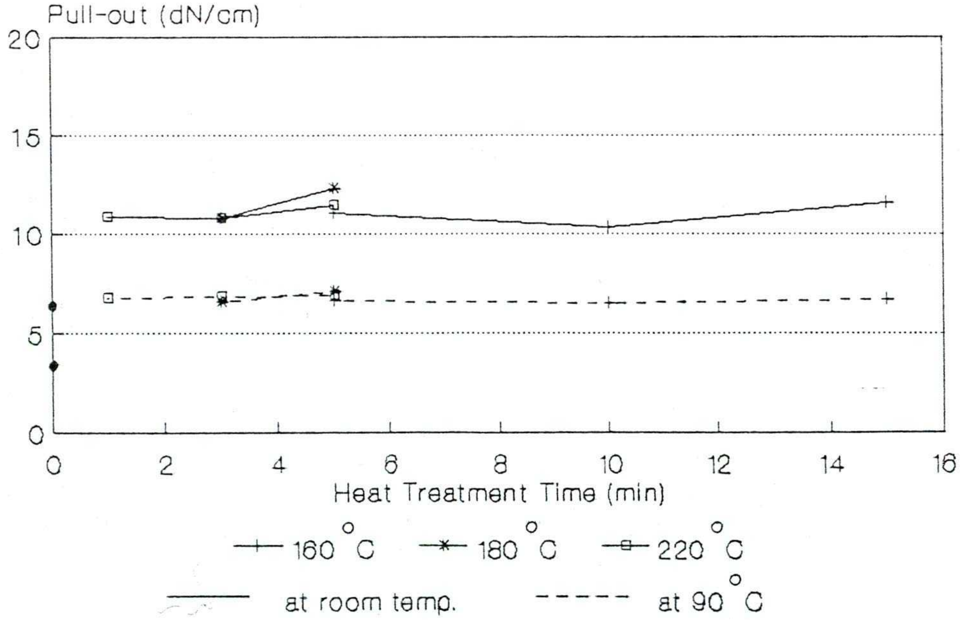
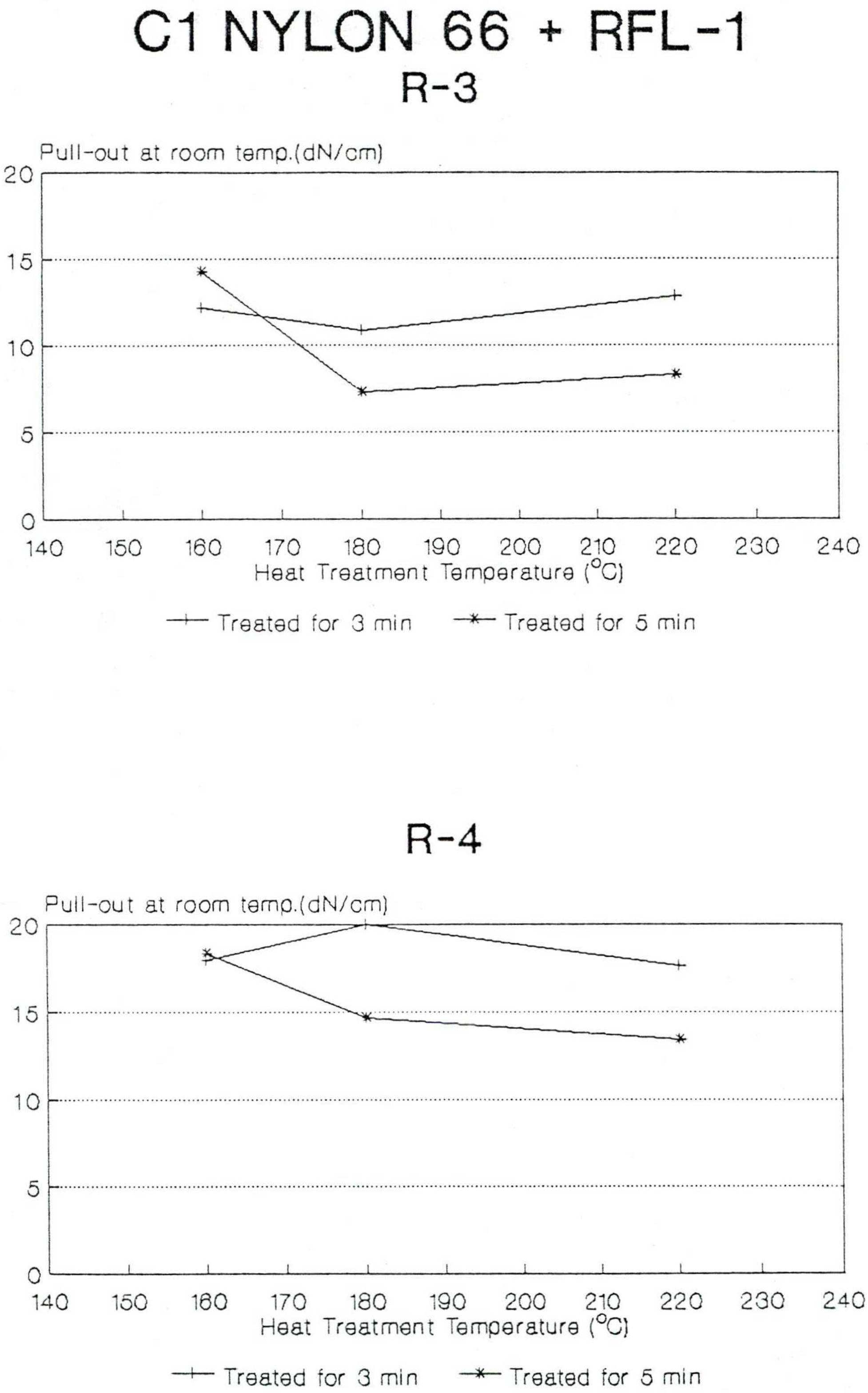


Figure 32: Effect of heat treatment time on adhesion between ENKA 94/2 tex nylon 6,6 cord (C3), dipped in RFL-1 dip, and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.75 dN/cm



C1 NYLON 66 + RFL-1

R-3

R-4

Figure 33: Effect of heat treatment temperature on adhesion between ICI 140/2 tex nylon 6,6 cord (C1), dipped in RFL-1 dip and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature.

Average standard deviation= 1.29 dN/cm

C_2, and C_3 respectively). Figures 30, 31 and 32 show that, using promoting material in the rubber compound, as in case of rubber compound R-4, one can achieve adhesion levels higher than that obtained with rubber compound R-3. These figures also show that usually higher adhesion levels were achieved at the short heat treatment times and on increasing the time, lower adhesion values were obtained.

Figure 33 also illustrates the effect of the heat treatment temperature after dipping nylon 6,6 cord in the RFL-1 adhesive system. This figure shows that adhesion level always decreases if the cord is heat-treated for longer times and at very high temperature .

Another system consisting of polyester cords P_1, P_2 and P_3 treated with RFL-1 and bonded to chloroprene rubber compounds, was tested. From the analysis of the results which can be seen from tables XXVII, XXVIII and XXIX in the appendix for the three cords, and from tables 29 and 30, it can be concluded that in contrast to our expectation cord P_3 did not give higher adhesion level than that of P_1 and P_2 although its surface area is higher by about 24%. On the contrary its adhesion level was found to be similar to that of P_1 and higher than that of P_2 by about 13% only. (The total averages of the adhesion values on the basis of surface area were found to be 4.9 N/mm^2, 4.2 N/mm^2, and 3.9 N/mm^2 for P_1, P_2, and P_3 respectively). With this system it was also found that the promoting material present in CR compound R-4, which bonded to polyester cords treated with RFL-1 dip, increases the adhesion as can be seen from figures 34, 35 and

Table 29: The statistical analysis of the adhesion measured at room temp. for polyester cords treated with RFL-1 and bonded to CR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	7.5	9.5	3.00
Factor B	1	63.4	80.4	3.85
Factor C	11	16.3	20.7	1.80
pure error	864	0.8		

Factor A = type of polyester cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	8.6	8.3
	2. P_2 cord	7.7	
	3. P_3 cord	8.7	
B	1. R-3	7.4	
	2. R-4	9.3	
C	1. undipped	4.7	
	2. 160°C/3 min.	8.4	
	3. 160°C/5 min.	8.5	
	4. 160°C/7 min.	10.3	
	5. 160°C/10 min.	10.1	
	6. 160°C/15 min.	7.2	
	7. 180°C/1 min.	10.8	
	8. 180°C/3 min.	7.0	
	9. 180°C/5 min.	8.2	
	10. 220°C/1 min.	7.8	
	11. 220°C/3 min.	8.5	
	12. 220°C/5 min.	8.3	

Table 30: The statistical analysis of the adhesion measured at 90°C for polyester cords treated with RFL-1 dip and bonded to CR.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	2	2.3	8.3	3.00
Factor B	1	53.4	189.8	3.85
Factor C	11	6.9	24.3	1.80
pure error	864	0.3		

Factor A = type of polyester cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	5.1	4.8
	2. P_2 cord	4.5	
	3. P_3 cord	4.9	
B	1. R-3	3.9	
	2. R-4	5.7	
C	1. undipped	2.6	
	2. 160°C/3 min.	4.9	
	3. 160°C/5 min.	4.7	
	4. 160°C/7 min.	5.9	
	5. 160°C/10 min.	5.9	
	6. 160°C/15 min.	4.0	
	7. 180°C/1 min.	6.7	
	8. 180°C/3 min.	3.8	
	9. 180°C/5 min.	4.8	
	10. 220°C/1 min.	4.6	
	11. 220°C/3 min.	4.9	
	12. 220°C/5 min.	4.8	

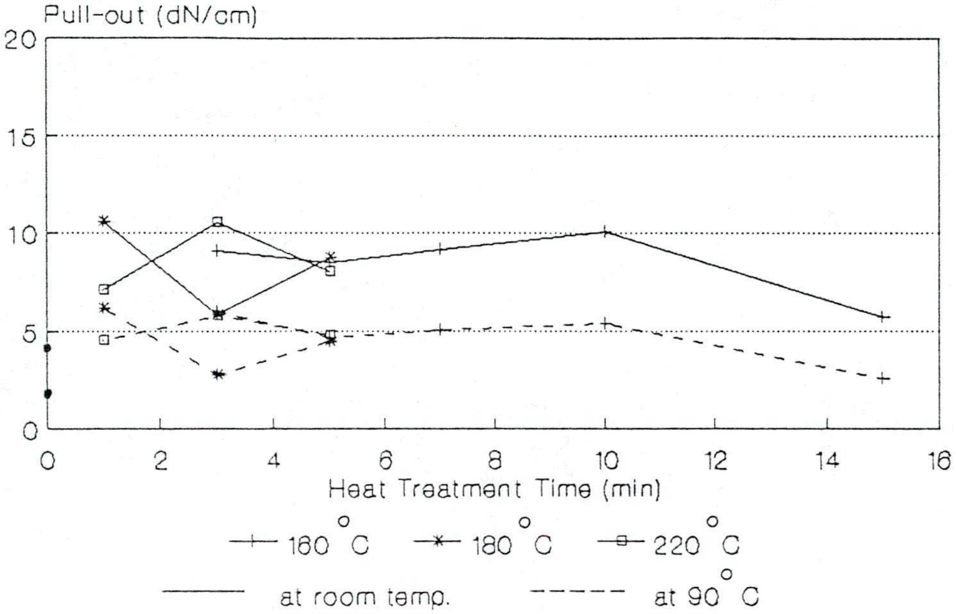
36 for the three cods P_1, P_2 and P_3 respectively.

On comparing the bonding of nylon 6,6 and polyester cords to natural rubber using RFL-1 adhesive system, and by calculating the total averages of the adhesion levels for both nylon 6,6 and polyester cords, see tables 19, 20, 21 and 22, one can conclude that higher adhesion values were obtained for nylon 6,6 than that obtained for polyester. However, we can say that an improvement in the adhesion of polyester cord can be achieved since the total average of the adhesion levels in case of nylon 6,6 exceeds that of polyester cords by about 13% only. Their diameters are larger than that of polyester and that the total average of adhesion values on the basis of surface area are (4.0 N/mm^2 and 4.2 N/mm^2 for nylon and polyester respectively). Thus polyester has better adhesion per mm^2.

Similar discussion can be drawn on the adhesion levels measured at 90°C. From these tables also, one can see that for the two textile cords the presence of promoting material in rubber compound (as in case of R-2 compound) has significant effect on the adhesion values. It was found that it increases the adhesion levels on the basis of surface area by 35% on the average. Also one can conclude that for both cords the heat treatment conditions had a significant effect on the adhesion levels. As we can see that higher adhesion levels were achieved at the shorter heat treatment times for nylon 6,6 while polyester cord needed more severe heat treatment conditions to obtain high levels of adhesion. The adhesion of nylon 6,6 and that of polyester cords treated

P1 POLYESTER + RFL-1

R-3



R-4

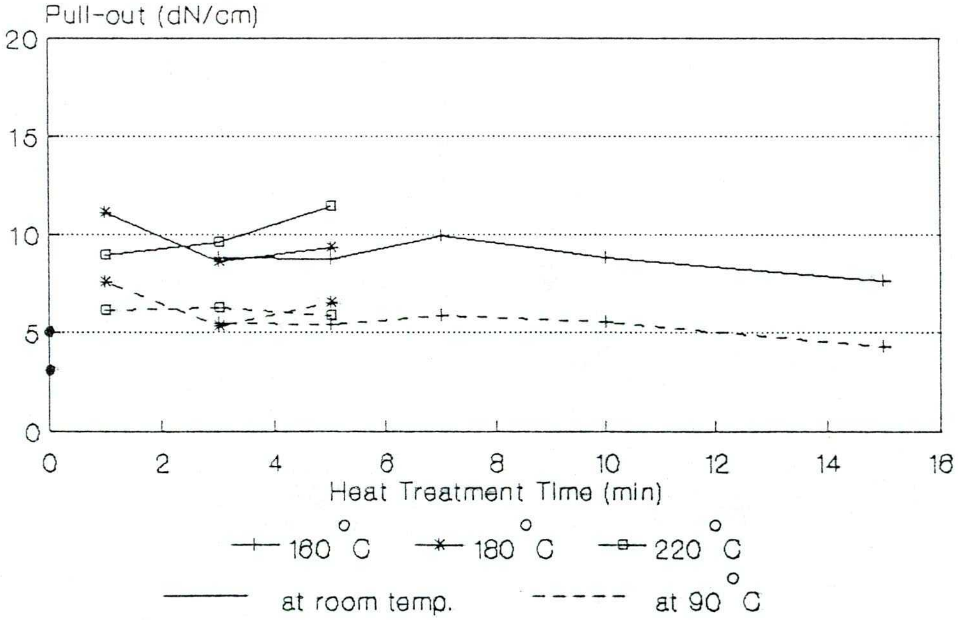
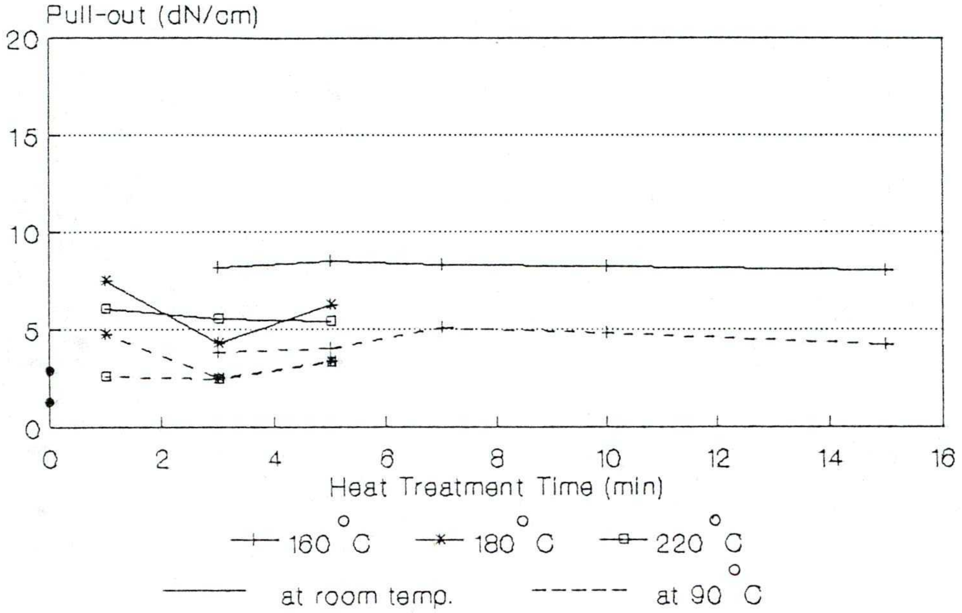


Figure 34: Effect of heat treatment time on adhesion between ENKA 110/2 tex polyester cord (P1), dipped in RFL-1 dip, and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.76 dN/cm

P2 POLYESTER + RFL-1

R-3



R-4

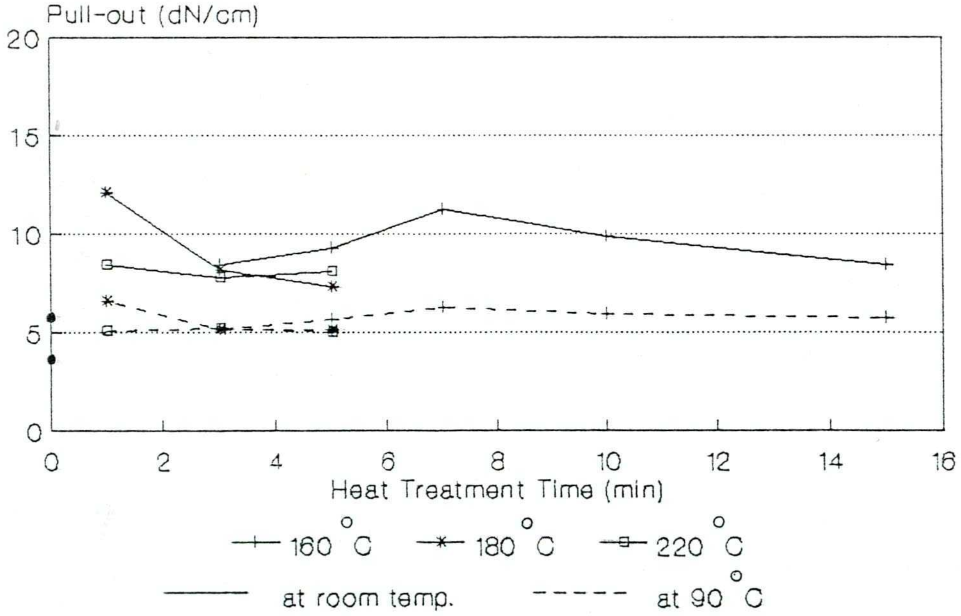
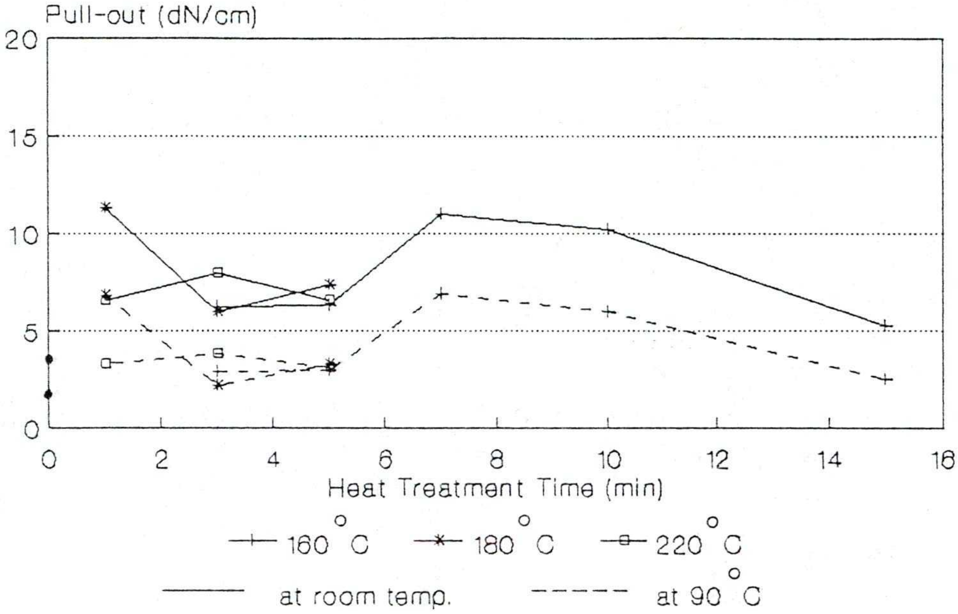


Figure 35: Effect of heat treatment time on adhesion between Allied 110/2 tex polyester cord (P2), dipped in RFL-1 dip, and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.65 dN/cm

P3 POLYESTER + RFL-1

R-3



R-4

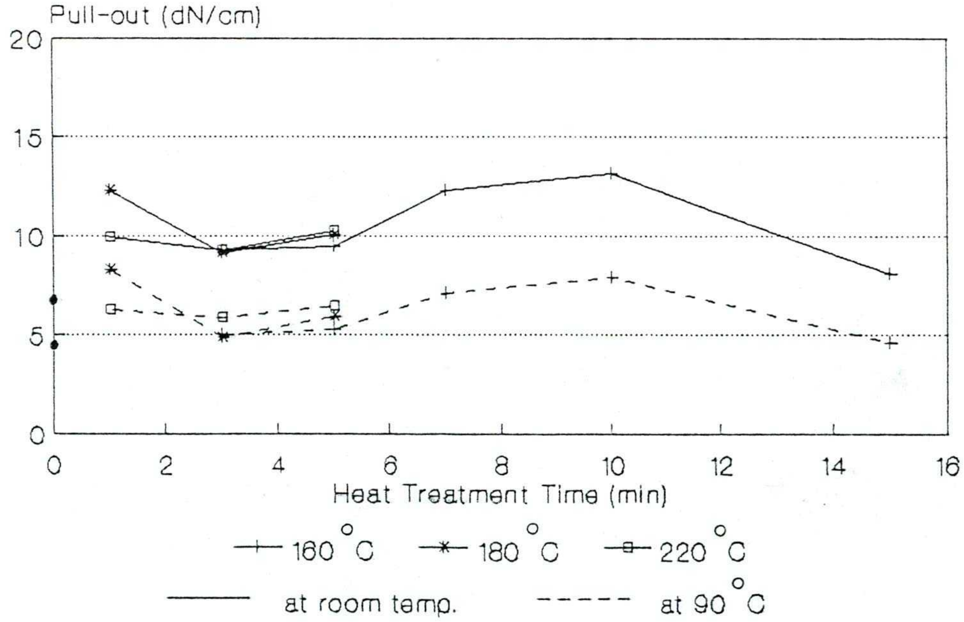


Figure 36: Effect of heat treatment time on adhesion between Allied 110/3 tex polyester cord (P3), dipped in RFL-1 dip, and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature and at 90°C.
Average standard deviation= 0.71 dN/cm

with RFL-1 and bonded to chloroprene rubber compounds are another two systems which can be compared. On comparing the total averages of their adhesion values, see tables 27, 28, 29 and 30, one can conclude that the adhesion values of nylon 6,6 are higher than that of polyester by about 15%. The average difference in cord diameter between nylon and polyester is 16%, thus polyester has better adhesion per mm^2. (The total average were 4.2 N/mm^2 and 4.3 N/mm^2 for nylon and polyester respectively). The promoting material increases their adhesion levels on the basis of surface area by about 49% on the average. These tables also show that the heat treatment conditions affect the adhesion levels of both nylon 6,6 and polyester cords.

On the other hand, on comparing nylon 6,6 cords treated with RFL-1 dip and bonded to NR to that bonded to CR and treated with the same dip, see tables 19, 20, 27, 28, one can conclude that the adhesion levels on the basis of surface area , in case of nylon 6,6 bonded to CR, are higher than that bonded to NR by about 5%. The promoting material has similar effect in both cases, as in case of NR compound R-2 and CR compound R-4, since it increases the adhesion levels per mm^2 by about 65% on the average. The tables also illustrate that there is a difference between the two systems concerning the effect of the cord quality on the adhesion levels. In the former in which the cords were bonded to NR, C_1 and C_2 had similar adhesion values whereas in the latter where the cords were bonded to CR, C_1 had higher adhesion value than that of C_2 by about 45% although they have similar structures.

When we compare polyester cords treated with RFL-1 dip and bonded to NR to that bonded to CR and also treated with RFL-1 dip, see tables 21, 22, 29 and 30, it can be concluded that the total averages of the adhesion levels are similar. The heat treatment conditions have significant effect on the adhesion values in both cases. The promoting material, present in either NR compound R-2 or in CR compound R-4, increases the adhesion levels per mm^2 by about 20% on the average. The only difference between the two systems is that, in case of polyester bonded to NR it was found that the adhesion value of P_3 cord is higher than that of P_1 and P_2 whereas in case of that bonded to CR it was found that the adhesion value of P_3 is similar to that of P_1 and higher than that of P_2 by about 13%.

On comparing another two systems of polyester cords treated with RFL-2, the first system is bonded to NR compounds R-1 and R-2 and the second system is bonded to CR compounds R-3 and R-4. From tables 23, 24, 25 and 26, one can see that the total averages of the adhesion levels in case of that bonded to NR exceeds the other one by about 6% only, and that the averages of adhesion per mm^2 of the first system exceeds that of the second by 6% too. The only difference between them is that the presence of the promoting material in the CR compound R-4 does not show any improvement in the adhesion levels over R-3 while its presence in NR compound R-2 shows an improvement in the adhesion levels over R-1 by about 25%.

Both polyester and nylon 6,6 cords were used with NR compounds using the same adhesive system RFL-2. The adhesion values for nylon 6,6 (C_1) treated with RFL-2 and bonded to NR is given in table XXX in the appendix. On evaluating their adhesion to NR and by the help of the statistical analysis shown in tables 31 and 32 for the adhesion measured at room temperature and at 90°C respectively, one can see that polyester cord had higher adhesion values per mm^2 than that of nylon 6,6 cord by about 20% (5.0 N/mm^2 for C_1 and 6.0 N/mm^2 for P_1). These tables show that there is an evident effect of the rubber compound on the adhesion values. This can be also seen from figures 23 and 37 on comparing polyester and nylon 6,6 cords that higher adhesion levels can be achieved in case of compound R-2, in which bonding material is present, than R-1 by about 20%. It can be also concluded from tables 31 and 32 and the figures that the heat treatment conditions had significant effect on the adhesion levels of the two cords.

On comparing nylon 6,6 cord treated with RFL-2 and bonded to CR compounds and polyester cord also treated with RFL-2 and bonded to CR. The adhesion values for nylon 6,6 (C_1) cord treated with RFL-2 and bonded to CR is shown in table XXXI in the appendix. One can see from tables 33 and 34 that the average adhesion value on the basis of surface area is higher in case of nylon 6,6 (C_1) than that of polyester (P_1) by about 6% (5.8 N/mm^2 for C_1 and 5.5 N/mm^2 for P_1). Also from these tables and figures 27 and 38, one can conclude that the heat treatment conditions have an effect on the adhesion

Table 31: The statistical analysis of adhesion of polyester and nylon 6,6 cords treated with RFL-2 and bonded to NR, measured at room temp.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	1	22.2	17.4	3.87
Factor B	1	34.6	27.0	3.87
Factor C	7	28.4	22.2	2.13
pure error	384	1.3		

Factor A = type of cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	10.5	11.4
	2. C_1 cord	12.2	
B	1. R-1	10.3	
	2. R-2	12.4	
C	1. undipped	6.5	
	2. 160°C/5 min.	10.0	
	3. 160°C/15 min.	9.3	
	4. 180°C/3 min.	11.4	
	5. 180°C/5 min.	12.1	
	6. 220°C/1 min.	14.1	
	7. 220°C/3 min.	14.2	
	8. 220°C/5 min.	13.4	

Table 32: The statistical analysis of adhesion of polyester and nylon 6,6 cords treated with RFL-2 and bonded to NR, measured at 90°C.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	1	15.6	28.8	3.87
Factor B	1	51.9	66.2	3.87
Factor C	7	11.1	20.4	2.13
pure error	384	0.5		

Factor A = type of cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	7.0	7.7
	2. C_1 cord	8.4	
B	1. R-1	6.5	
	2. R-2	9.0	
C	1. undipped	4.8	
	2. 160°C/5 min.	7.0	
	3. 160°C/15 min.	6.8	
	4. 180°C/3 min.	7.4	
	5. 180°C/5 min.	8.2	
	6. 220°C/1 min.	9.4	
	7. 220°C/3 min.	10.2	
	8. 220°C/5 min.	8.2	

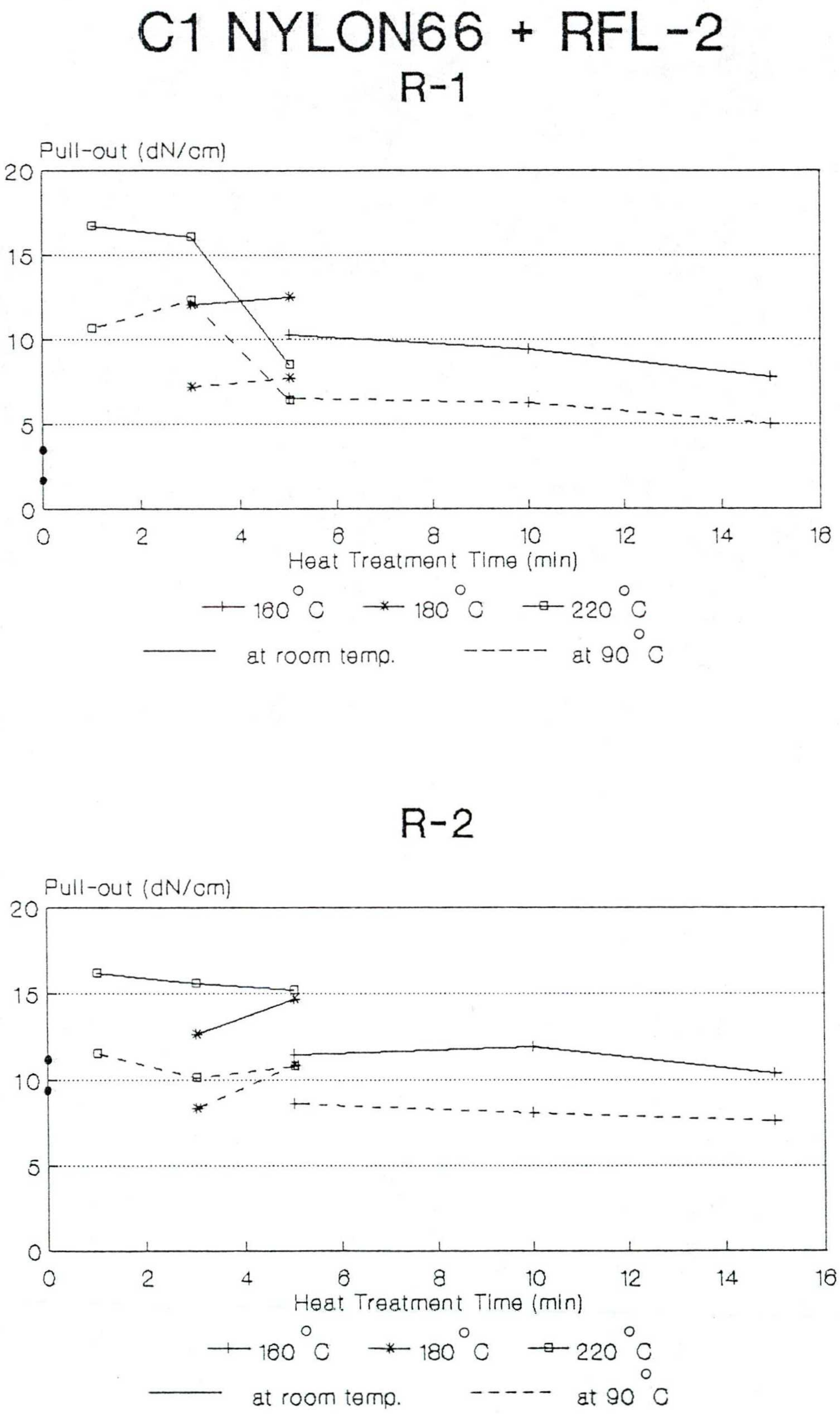


Figure 37: effect of heat treatment time on adhesion between ICI 140/2 tex nylon 6,6 cord (C_1), dipped in RFL-2 dip, and two natural rubber compounds R-1 and R-2 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 0.92 dN/cm

levels but in case of RFL-2 the presence of the promoting material in (R-4) compound does not show an improvement in the adhesion levels over that obtained with (R-3) compound.

Table 33: The statistical analysis of adhesion of polyester and nylon 6,6 cords treated with RFL-2 and bonded to CR, measured at room temp.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	1	172.9	149.3	3.87
Factor B	1	6.3	5.4	3.87
Factor C	7	41.3	35.7	2.13
pure error	384	1.2		

Factor A = type of cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	9.5	11.8
	2. C_1 cord	14.1	
B	1. R-3	12.2	
	2. R-4	11.3	
C	1. undipped	5.0	
	2. 160°C/5 min.	10.9	
	3. 160°C/15 min.	10.7	
	4. 180°C/3 min.	12.3	
	5. 180°C/5 min.	11.5	
	6. 220°C/1 min.	14.2	
	7. 220°C/3 min.	15.3	
	8. 220°C/5 min.	14.3	

Table 34: The statistical analysis of adhesion of polyester and nylon 6,6 cords treated with RFL-2 and bonded to CR, measured at 90°C.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor A	1	16.3	27.8	3.87
Factor B	1	0.01	0.02	3.87
Factor C	7	12.0	20.4	2.13
pure error	384	0.6		

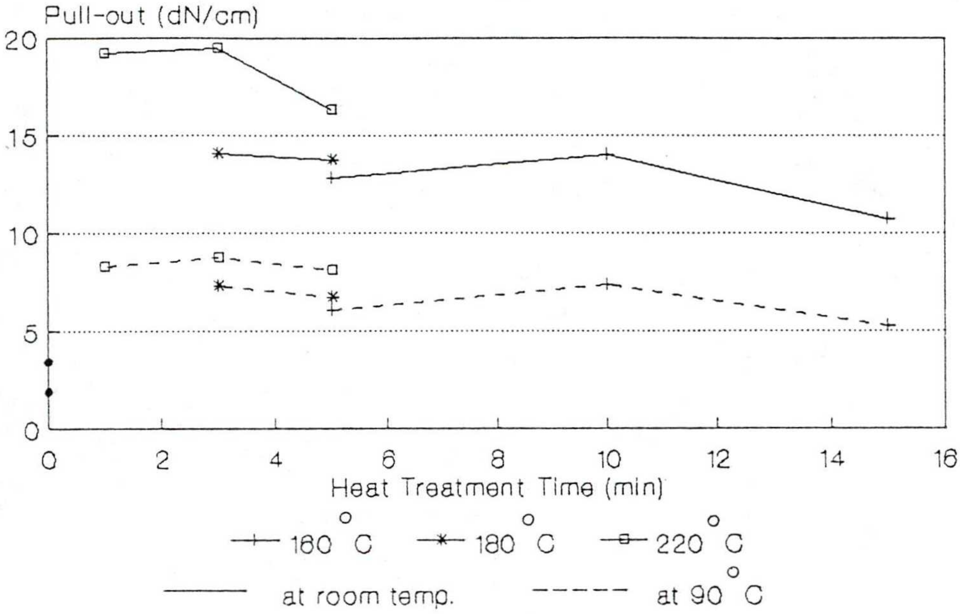
Factor A = type of cord
Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Pull-out force Average (dN/cm)	Total average
A	1. P_1 cord	5.8	6.5
	2. C_1 cord	7.2	
B	1. R-3	6.4	
	2. R-4	6.5	
C	1. undipped	2.6	
	2. 160°C/5 min.	6.2	
	3. 160°C/15 min.	5.9	
	4. 180°C/3 min.	7.0	
	5. 180°C/5 min.	6.6	
	6. 220°C/1 min.	7.4	
	7. 220°C/3 min.	8.0	
	8. 220°C/5 min.	8.0	

C1 NYLON66 + RFL-2

R-3



R-4

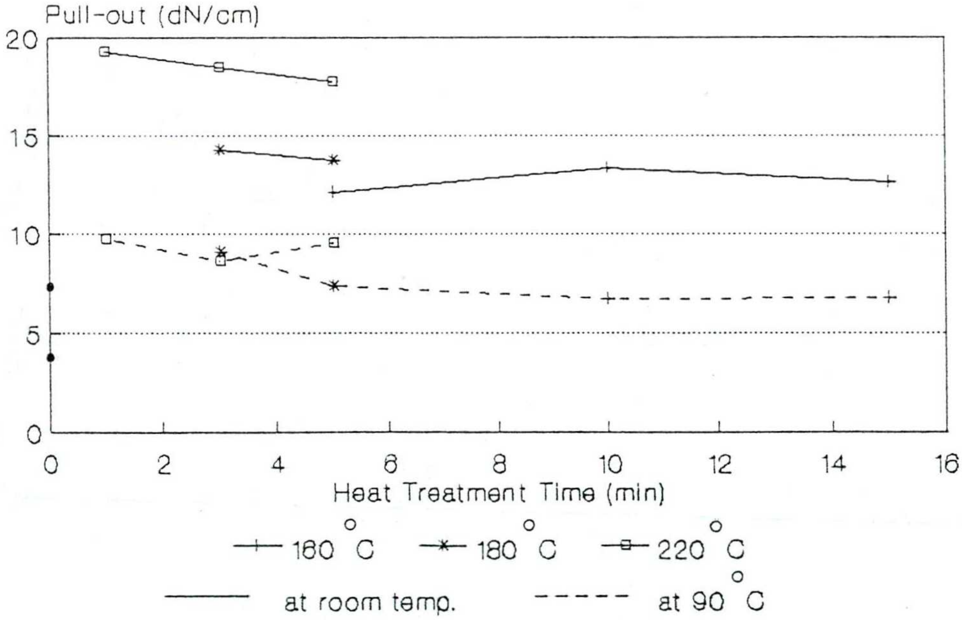


Figure 38: effect of heat treatment time on adhesion between ICI 140/2 tex nylon 6,6 cord (C_1), dipped in RFL-2 dip, and two chloroprene rubber compounds R-3 and R-4 measured in H-pull-out test at room temperature and at 90°C.

Average standard deviation= 1.00 dN/cm

4.4.2 Dynamic adhesion fatigue tests

Fatigue is the dynamic property of the rubber-textile composites which causes deterioration and failure after a repetition of stress. Testing of fatigue is done by the laboratory apparatus but this of course does not simulate exactly the conditions which occur in tires on the roads or belts and hoses. Our scope was to clarify the effect of the heat treatment conditions on the fatigue life of the rubber-cord composite, and to compare the results of static adhesion tests to dynamic fatigue tests.

4.4.2.1 De Mattia fatigue test

First we discuss the results of the De Mattia fatigue test. In order to evaluate the potential of this test a series of preliminary experiments was carried out using various levels of prestress and an amplitude of ± 0.2 dN. The prestress was chosen for 20, 40, 60, 80, 100% of the static pull-out force. Three test specimens were tested at each level. As expected at 20 and 40% prestress, no failure occurred even after more than 4 million cycles, above this level failures did occur, but the results were badly scattered, for example at 60% between 700 and 1000000 cycles, at 80 and 100% some test specimens failed immediately, but there was one sample which didn't fail at the 80% level even after 4 million cycles. The preliminary results indicated clearly, that it would be very difficult- if not possible- to obtain reproducible results with the De Mattia test. This conclusion is in agreement with that of Brodsky (93) and others (125,126).

Instead of trying to optimize the De Mattia fatigue test for rubber-cord adhesion we turned to another method, developed by Bartha (109).

4.4.2.2 Bartha dynamic adhesion fatigue test

Our attempts were made to try another available apparatus which was Bartha dynamic fatigue tester. The description of this method was presented in the experimental part.

Two types of textile cord, namely nylon 6,6 and polyester cords were dipped in the two adhesive systems RFL-1 and RFL-2 and heat-treated at different temperatures and for different durations. These dipped cords were used to build up Bartha test specimens by using two compounds of NR, namely, R-1 and R-2 and two other compounds of chloroprene rubber R-3 and R-4.

A/ By using NR compounds

Figures 39, 40, 41 and 42 for dipped nylon 6,6 (C_1) and polyester (P_1) cords in the two adhesive systems, respectively, indicates the results obtained in Bartha dynamic adhesion fatigue test. It can be seen from these figures and from statistical analysis shown in tables 35, 36, 37, and 38 that the heat treatment conditions had an effect

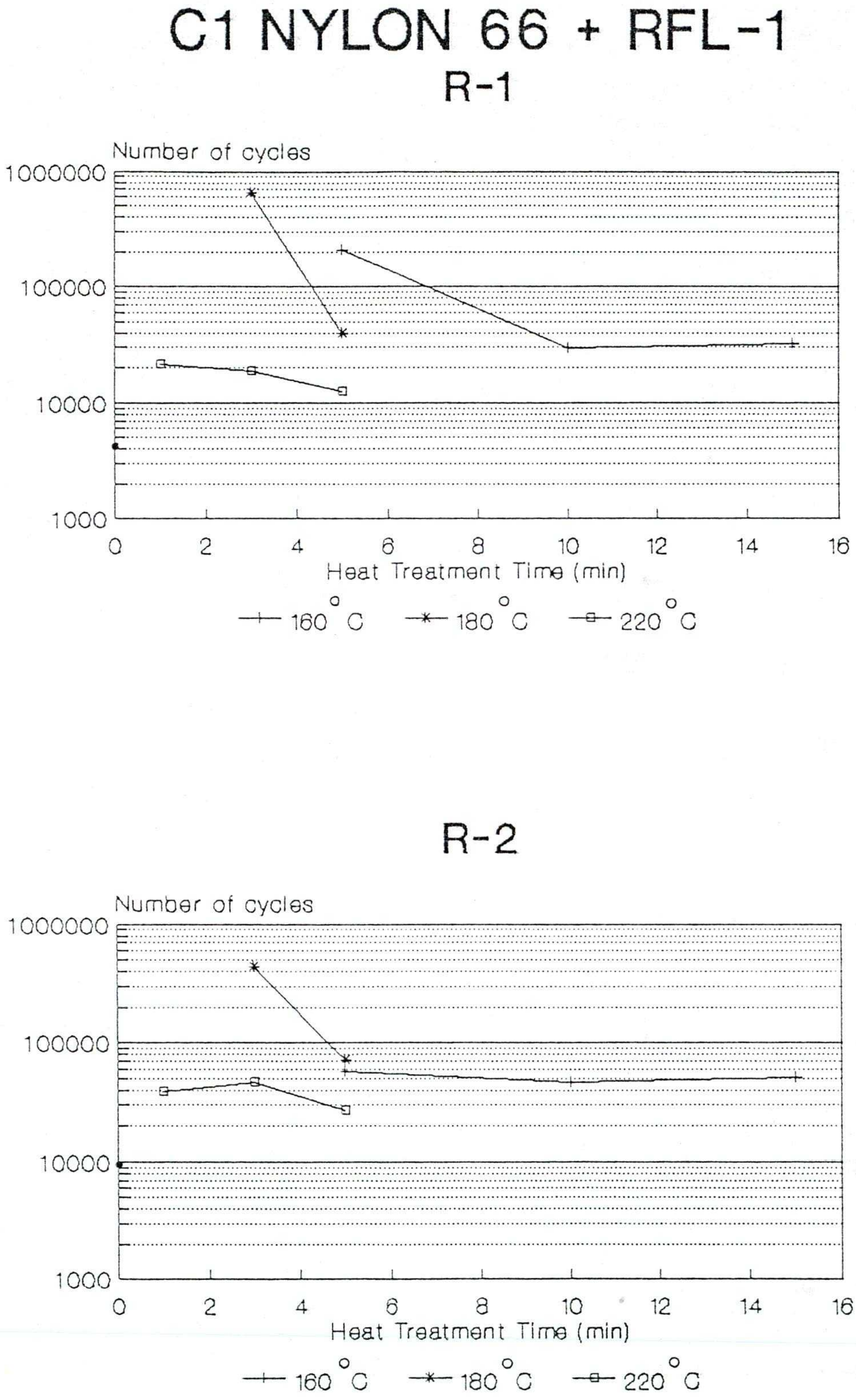
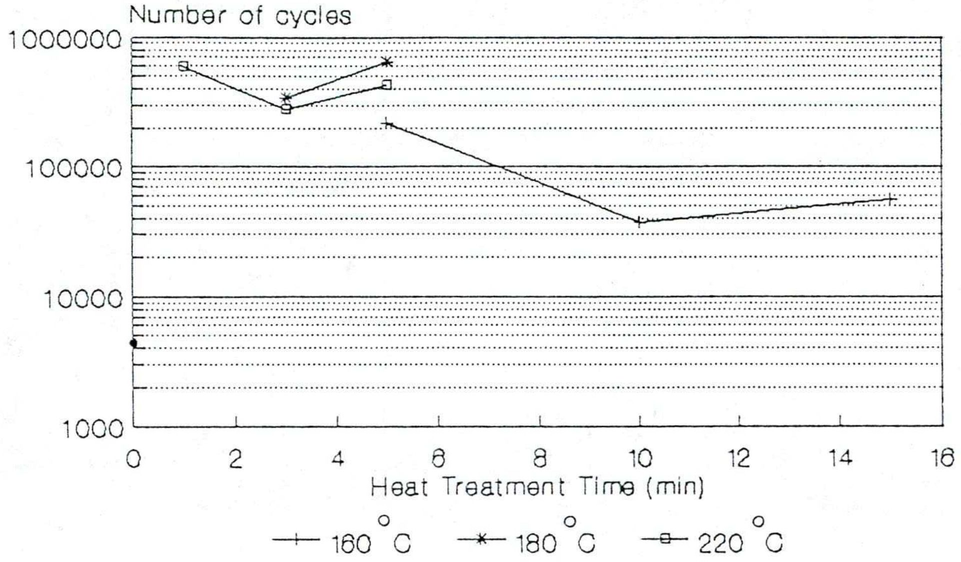


Figure 39: Effect of heat treatment conditions on the adhesion fatigue life between ICI 140/2 tex nylon 6,6 cord (C1), dipped in RFL-1 dip, and two natural rubber compounds R-1 and R-2.

Logarithmic average standard deviation= 0.15

C1 NYLON 66 + RFL-2

R-1



R-2

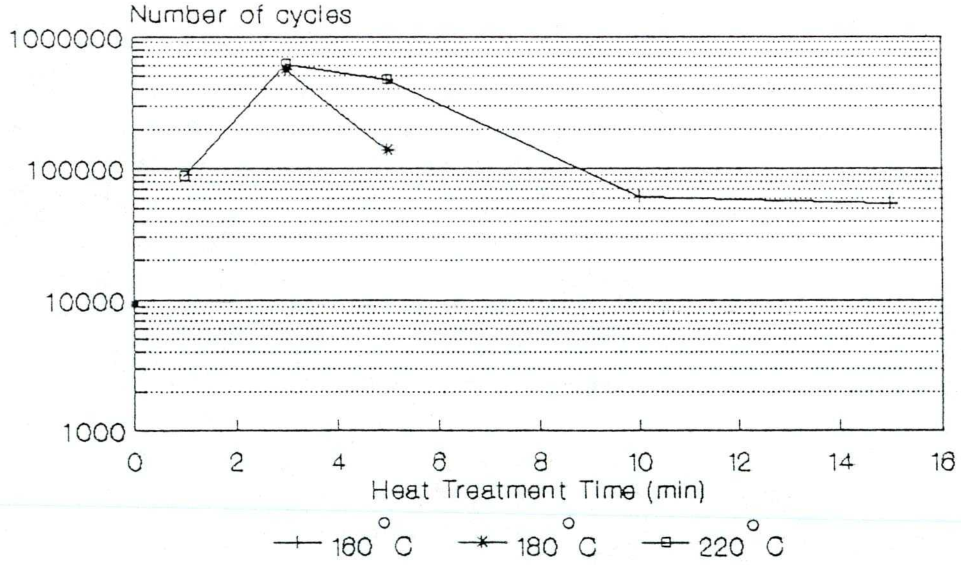


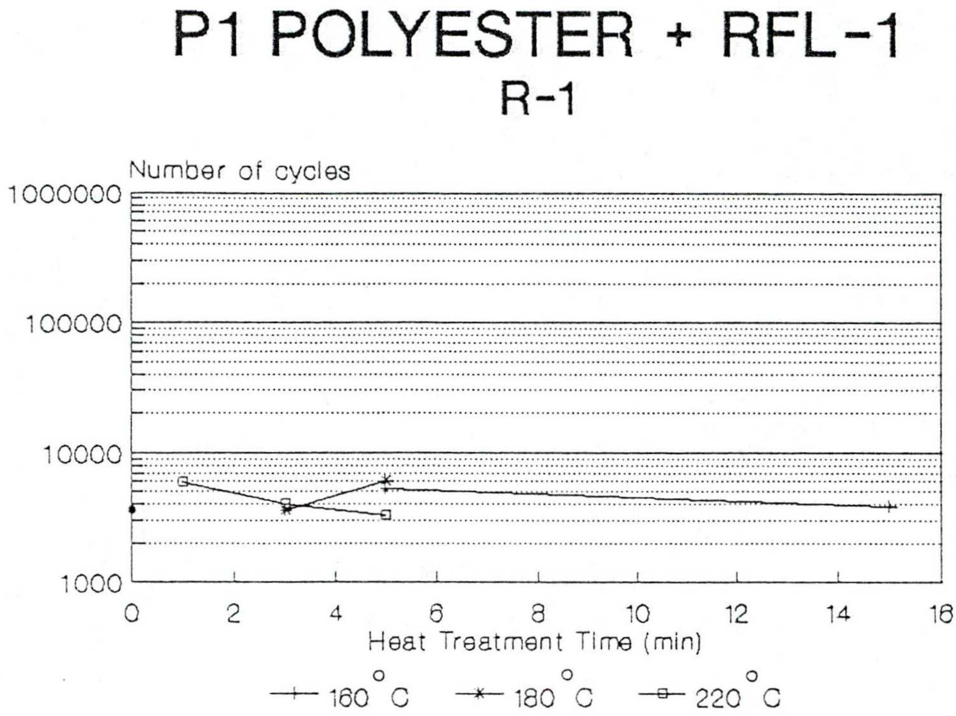
Figure 40: Effect of heat treatment conditions on the adhesion fatigue life between ICI 140/2 tex nylon 6,6 cord (C1), dipped in RFL-2 dip, and two natural rubber compounds R-1 and R-2.

logarithmic average standard deviation= 0.17

on the fatigue life. The fatigue life of the undipped (without heat treatment) nylon 6,6 and polyester cords in the compound R-1 is similar, 3700 and 3500 cycles respectively. Using an adhesion promoting additive (as in case of R-2) gives marked improvement to about 9000 and 16000 cycles. As expected dipping increases the fatigue life further. In case of nylon 6,6 short heat treatment times (1-5 min.) give better results, and RFL-2 is better than RFL-1. On the other hand the effect of the adhesion promoting material in R-2 has little effect.

In the case of polyester dipped with RFL-1 the fatigue life of the adhesion is poor, only about 4500 cycles with the compound R-1 (see figure 41). We have to note, however that the RFL-1 dipping solution was not designed for polyester. If the compound contains the adhesion promoter (R-2) then the fatigue life increases by two orders of magnitude, the average being about 300000 cycles, see figure 41 and table 37. This value is similar to the best results obtained with the nylon 6,6 cord (see figures 39 and 40), and shows, that a properly designed compound can give excellent adhesion to polyester even with a traditional RFL dipping solution. If nylon 6,6 and polyester cords were treated with RFL-2 adhesive system, good fatigue lives can be noticed for both cords as one can see from figures 40 and 42.

The correlation between static adhesion test results and dynamic one, is shown in figures (43) and (44) for nylon 6,6 and polyester cord respectively. From these figures and from the calculation of the correlation coefficient (it ranges



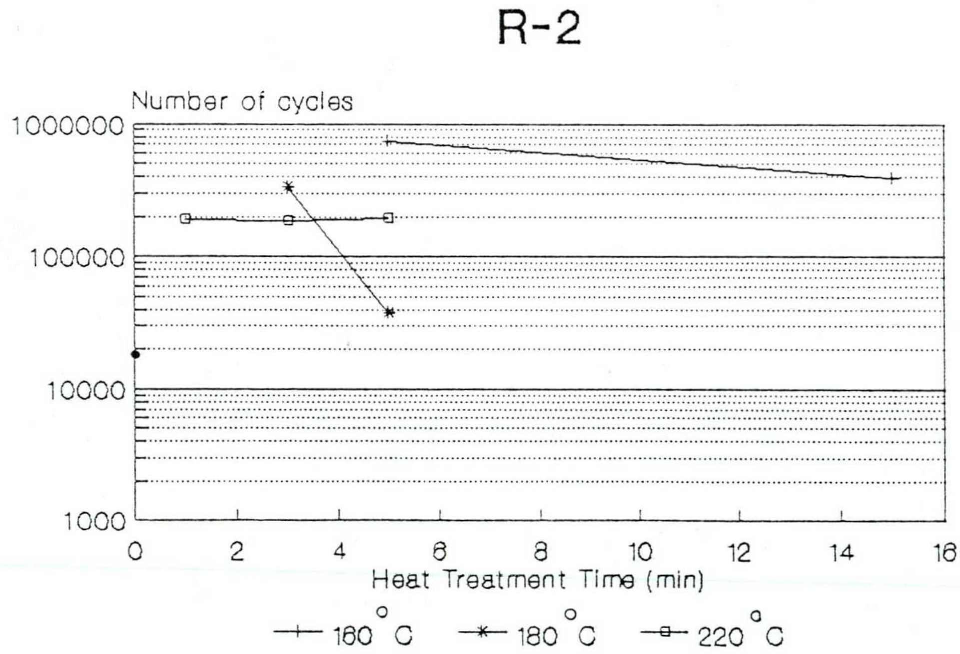
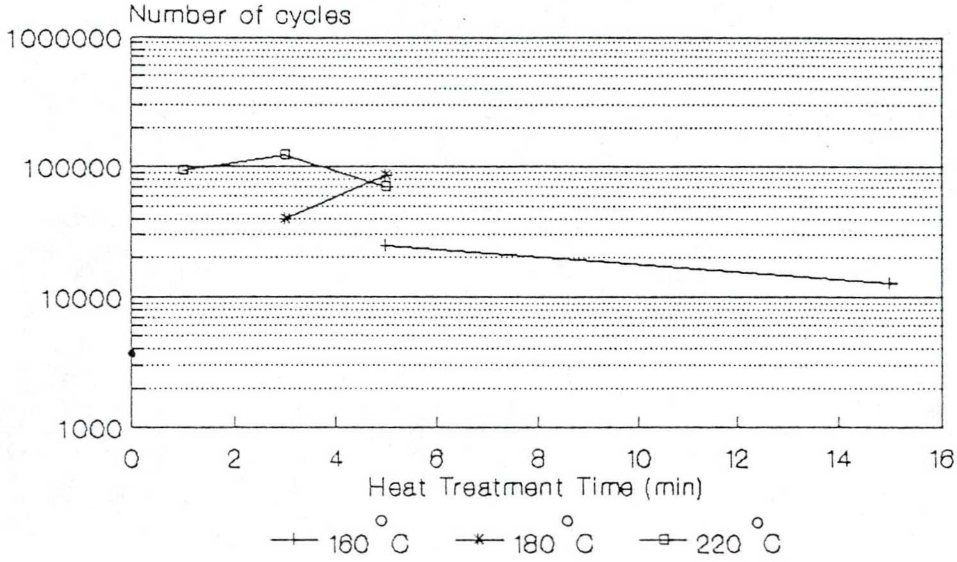


Figure 41: Effect of heat treatment conditions on the adhesion fatigue life between ENKA 110/2 tex polyester cord (P1), dipped in RFL-1 dip,and two natural rubber compounds R-1 and R-2.

Logarithmic average standard deviation= 0.13

P1 POLYESTER + RFL-2


R-1

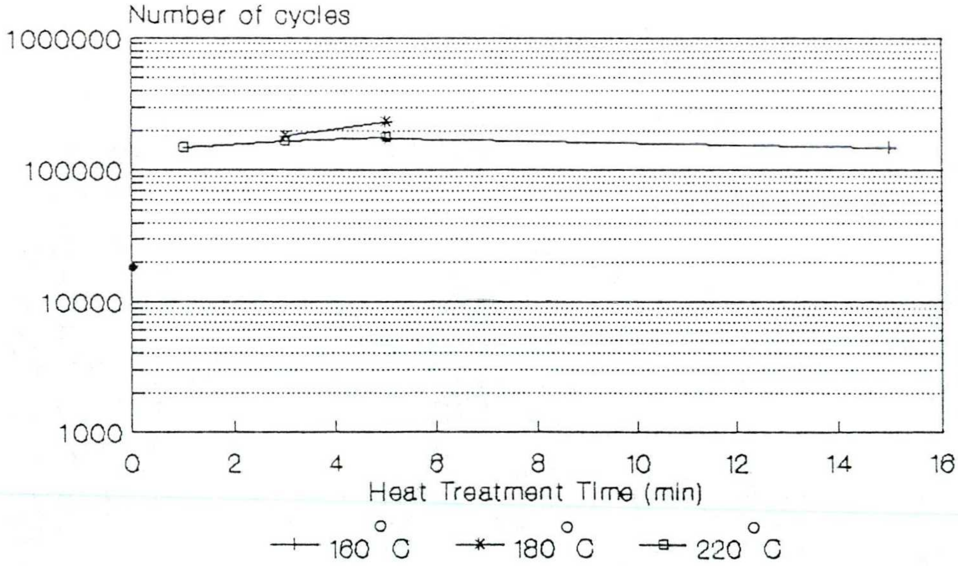

R-2

Figure 42: Effect of heat treatment conditions on the adhesion fatigue life between ENKA 110/2 tex polyester cord (P_1), dipped in RFL-2 dip, and two natural rubber compounds R-1 and R-2.

Logarithmic average standard deviation= 0.10

Table 35: The statistical analysis of Bartha dynamic adhesion fatigue test of C_1 nylon 6,6 cord treated with RFL-1 and bonded to NR compunds.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor B	1	0.1	4.9	4.02
Factor C	8	0.6	30.6	2.11
pure error	54	0.0		

Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Average Log(No.of cycles)	Total average
B	1. R-1	4.6	4.7
	2. R-2	4.7	
C	1. undipped	3.8	
	2. 160°C/5 min.	5.0	
	3. 160°C/10 min.	4.6	
	4. 160°C/15 min.	4.6	
	5. 180°C/3 min.	5.7	
	6. 180°C/5 min.	4.7	
	7. 220°C/1 min.	4.5	
	8. 220°C/3 min.	4.5	
	9. 220°C/5 min.	4.3	

Table 36: The statistical analysis of Bartha dynamic adhesion fatigue test of C_1 nylon 6,6 cord treated with RFL-2 and bonded to NR compunds.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor B	1	0.0	0.0	4.02
Factor C	8	0.8	29.7	2.11
pure error	54	0.0		

Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Average Log(No.of cycles)	Total average
B	1. R-1	5.2	5.2
	2. R-2	5.2	
C	1. undipped	3.8	
	2. 160°C/5 min.	5.5	
	3. 160°C/10 min.	4.7	
	4. 160°C/15 min.	4.8	
	5. 180°C/3 min.	5.6	
	6. 180°C/5 min.	5.5	
	7. 220°C/1 min.	5.4	
	8. 220°C/3 min.	5.6	
	9. 220°C/5 min.	5.7	

Table 37: The statistical analysis of Bartha dynamic adhesion fatigue test of P_1 polyester cord treated with RFL-1 and bonded to NR compunds.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor B	1	9.8	530.6	4.04
Factor C	7	0.2	8.5	2.21
pure error	48	0.0		

Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Average Log(No.of cycles)	Total average
B	1. R-1	3.6	4.4
	2. R-2	5.2	
C	1. undipped	3.9	
	2. 160°C/5 min.	4.8	
	3. 160°C/15 min.	4.6	
	4. 180°C/3 min.	4.5	
	5. 180°C/5 min.	4.2	
	6. 220°C/1 min.	4.5	
	7. 220°C/3 min.	4.4	
	8. 220°C/5 min.	4.4	

Table 38: The statistical analysis of Bartha dynamic adhesion fatigue test of P_1 polyester cord treated with RFL-2 and bonded to NR compunds.

Source	Degrees of freedom	Variance	F-statistic	Critical F-value
Factor B	1	1.2	137.5	4.04
Factor C	7	0.4	41.7	2.21
pure error	48	0.0		

Factor B = type of the rubber compound
Factor C = heat treatment conditions

Averages of factors at different levels

Source	Level	Average Log(No.of cycles)	Total average
B	1. R-1	4.6	4.9
	2. R-2	5.1	
C	1. undipped	3.9	
	2. 160°C/5 min.	4.8	
	3. 160°C/15 min.	4.6	
	4. 180°C/3 min.	4.9	
	5. 180°C/5 min.	5.2	
	6. 220°C/1 min.	5.1	
	7. 220°C/3 min.	5.2	
	8. 220°C/5 min.	5.0	

from 0.32 to 0.44 in both cases), one can conclude that a positive correlation exists, but it is unexpectedly poor. This result leads to an important conclusion that, from the quality control point of view one must consider the dynamic test side by side with the static one and that ignoring the dynamic adhesion tests can lead to serious problems in the rubber products especially in tires.

B/ By using CR compounds

The textile cords, nylon 6,6 (C_1) and polyester (P_1) cords were dipped in both RFL-1 and RFL-2 adhesive systems and heat-treated in an oven. Bartha test specimens were built using these dipped cords and two chloroprene rubber compounds R-3 and R-4.

Many trials were made in order to test these samples on Bartha tester but negative results were obtained in each case, i.e, debonding of the cords was observed within few seconds. This phenomenon may be explained by the fact that the elastic modulus and hardness of CR is about two times higher than that of NR, therefore the stress in the cord-rubber interface is higher when the test specimen is bent. This leads to quick fatigue.

One may speculate, that by increasing the bending radius of the test specimen in the Bartha test would decrease the stress in the cord-rubber interface, and give better results. An optimization of the Bartha test however is outside of the scope of the present work. One can conclude,

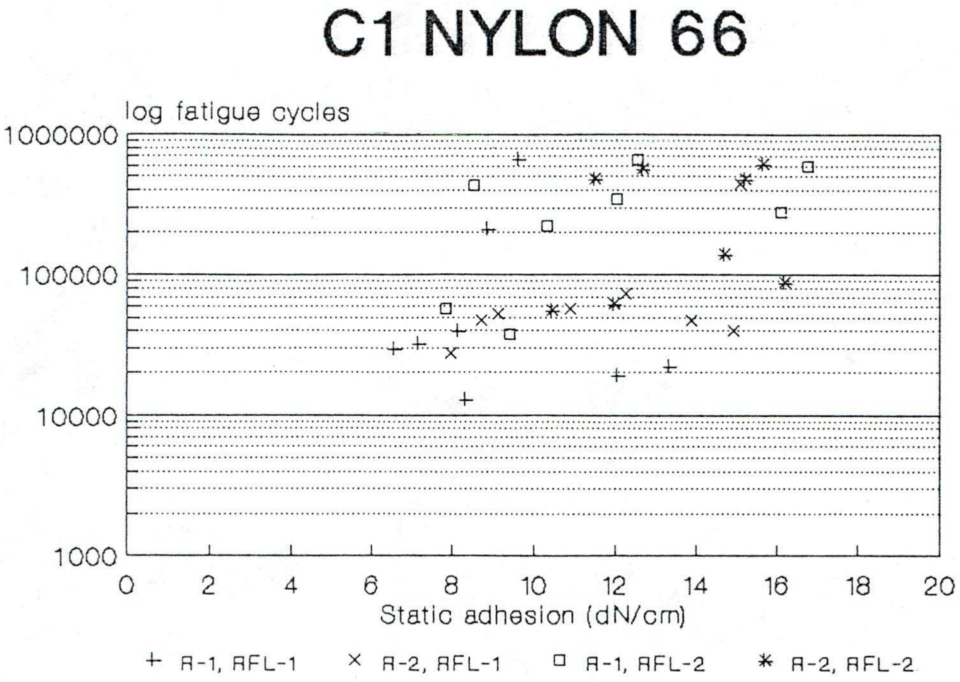


Fig.43 Correlation between static and dynamic adhesion

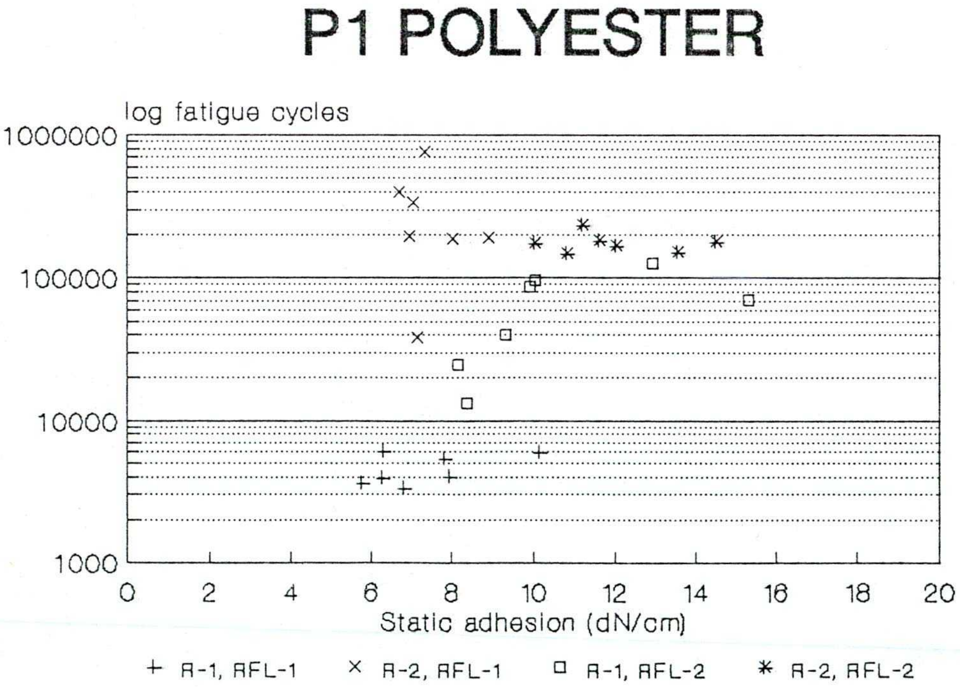


Fig.44 Correlation between static and dynamic adhesion

that the Bartha test can be successfully used to assess the dynamic fatigue properties of the cord-rubber bond, if the modulus of the compound is in a suitable range.

5. CONCLUSION

5. Conclusion

Results of my investigations are concluded in the following statements.

1. The investigation of the tensile properties of heat treated undipped and dipped cords revealed that:

1.1 The heat treatment (under our experimental conditions) didn't have a significant effect on the tensile strength of the undipped cords, but their elastic modulus decreased and elongation at break increased, i.e., the cords become softer. The changes were more pronounced in the case of polyester than nylon 6,6.

1.2 The dipping process decreases the tensile strength of all the cords. This can be attributed to the solvation due to the moisture trapped inside the adhesive layer on the outside of the cord bundle. At the same time the elongation at break shows insignificant changes in the case of nylon 6,6 cords and some increase in the case of polyester. There is a minor change in the elastic modulus in both cases.

2. The amount of dip pick-up of the various cords was compared on a pick-up mass per cord mass, per cord volume, per cord outer surface and per cord length basis.

In all these comparisons somewhat surprisingly the polyester cords had higher pick-up than nylon 6,6 cords.

3. Static adhesion tests were carried out on 6 different cords with 2 dipping solutions and 4 rubber compounds, on a total of 40 systems. The results showed that:

3.1 The heat treatment conditions of the dipped cords had a significant effect on the static adhesion. Short heat treatment times gave optimal results with nylon 6,6, but polyester needed more severe heat treatment conditions for optimum adhesion.

3.2 The presence of resorcinol, hexamethylene tetramine as adhesion promoting materials in the NR based R-2 and CR based R-4 compounds resulted in a significant improvement of the static adhesion, with the exception of RFL-2 dipped cords embedded into polychloroprene.

3.3 In the static adhesion tests the RFL-2 dipping solution which was developed specifically for polyester, showed only a slight improvement over the conventional RFL-1. (In this respect the dynamic adhesion tests gave drastically different results, see later).

4. Investigations concerning dynamic adhesion fatigue tests revealed that:

4.1 The De Mattia adhesion fatigue test is not well suited to measure the fatigue of the textile cord-rubber bond. At low pretension (20, 40% of the static pull-out force) the bond is not fatigued, at higher pretension the results are badly scattered, or the bond is fatigued after few cycles.

4.2 The Bartha fatigue test proved to be suitable to determine the adhesion fatigue in the NR compounds. The correlation between static adhesion test and dynamic one is unexpectedly poor (correlation coefficient ranges from 0.32-0.44). For example there was practically no difference in the static adhesion results of the RFL-1 dipped polyester cords embedded into the NR compounds R-1 and R-2, but their fatigue life changed by almost two orders of magnitude, indicating the positive effect of the adhesion promoting materials present in the compound R-2.

This result leads to an important conclusion that from the quality control point of view one must consider the dynamic test side by side with the static one, and that ignoring the dynamic test can lead to serious problems in the rubber products especially in tires.

In case of using chloroprene rubber compounds R-3 and R-4 under the standard conditions of the Bartha test , the textile cord-rubber bond showed quick fatigue. This can be attributed to the greater modulus and hardness of CR compared to that of NR. At the given curvature of the test specimen the stress on the bond was too high to show reasonable fatigue life. To optimize the Bartha test was beyond the scope of the present study.

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APPENDIX

Table I: Tensile properties of undipped and dipped C_1 nylon 6,6 cord using RFL-1 dipping solution.

undipped cord	without heat-treatment	heat-treated										
		160°C					180°C			220°C		
		3 min	5 min	7 min	10 min	15 min	1 min	3 min	5 min	1 min	3 min	5 min
Tensile strength (N)	219.0	220.8	220.0	221.4	218.2	217.8	221.6	215.0	216.8	220.4	220.8	217.0
Elongation at break (%)	26.9	29.5	32.2	35.8	33.1	33.9	28.3	33.7	36.2	28.8	30.1	29.4
Elongation at 45 N (%)	9.9	11.7	12.1	13.3	12.6	12.5	11.4	12.7	12.6	10.8	12.0	12.0
68 N (%)	12.5	14.8	15.7	17.2	16.3	16.4	14.3	16.5	16.5	13.7	15.3	15.4
90 N (%)	14.4	17.0	18.3	19.9	19.0	19.2	16.3	19.2	18.9	15.6	17.5	17.7
(LASE) at 5% * (N)	20.0	17.0	18.0	15.6	15.4	16.0	18.0	15.6	15.6	20.0	15.8	16.2

dipped cord	heat-treated										
	160°C					180°C			220°C		
	3 min	5 min	7 min	10 min	15 min	1 min	3 min	5 min	1 min	3 min	5 min
Tensile strength (N)	216.9	212.2	210.6	211.4	210.6	209.6	211.5	212.4	210.3	205.0	205.3
Elongation at break (%)	27.6	28.4	27.3	27.8	27.7	26.6	27.9	27.4	26.1	25.2	25.4
Elongation at 45 N (%)	10.7	10.9	10.9	10.3	10.8	10.8	10.5	10.1	9.6	9.6	9.5
68 N (%)	13.9	13.9	14.2	13.4	13.9	14.0	13.5	13.1	12.5	12.3	12.3
90 N (%)	16.1	16.3	16.5	15.6	16.2	16.2	15.8	15.2	14.6	14.5	14.6
(LASE) at 5% * (N)	19.4	20.0	19.4	20.0	20.0	19.0	19.4	20.0	20.2	22.1	22.0

* (LASE) = Load At Specific Elongation.

Table II: Tensile properties of undipped and dipped C_2 nylon 6,6 cord using RFL-1 dipping solution.

Undipped cord	Without heat-treatment	Heat-treated							
		160°C			180°C		220°C		
		5 min.	10 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	208.5	207.4	209.4	208.8	207.6	207.8	208.0	207.2	210.4
Elongation at break (%)	29.0	35.1	34.6	36.3	37.0	39.2	30.3	33.3	34.3
Elongation at 45 N (%)	9.9	13.0	13.0	13.2	11.1	14.0	10.9	12.8	12.7
68 N (%)	12.5	16.7	16.6	17.0	17.7	18.3	13.9	16.3	16.2
90 N (%)	14.4	19.5	19.2	19.8	20.7	21.8	15.9	18.7	18.8
(LASE) at 5% (N)	20.0	15.0	15.2	15.2	15.0	15.2	19.0	15.2	15.2

Dipped cord	Heat-treated							
	160°C			180°C		220°C		
	5 min.	10 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	202.0	203.0	201.3	202.0	202.0	204.1	202.1	201.0
Elongation at break (%)	28.9	28.9	29.6	28.4	28.3	28.3	28.3	29.3
Elongation at 45 N (%)	10.9	10.8	11.5	10.6	10.4	10.5	10.4	10.5
68 N (%)	13.8	13.7	14.5	13.6	13.4	13.4	13.2	13.4
90 N (%)	16.0	15.9	16.9	15.7	15.6	15.5	15.4	15.7
(LASE) at 5% (N)	18.0	19.5	17.9	18.8	20.0	19.7	20.0	20.0

Table III: Tensile properties of undipped and dipped C3 nylon 6,6 cord using RFL-1 dipping solution.

Undipped cord	Without heat-treartment	Heat-treated							
		160°C			180°C		220°C		
		5 min.	10 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	144.0	146.7	146.1	145.7	141.2	142.1	147.1	147.0	146.2
Elongation at break (%)	30.1	33.5	34.5	33.0	31.5	31.8	30.6	32.4	32.8
Elongation at 45 N (%)	13.9	16.1	16.6	15.8	16.0	15.9	14.1	15.4	15.8
68 N (%)	17.0	19.6	20.3	19.5	19.7	19.5	17.2	18.7	19.3
90 N (%)	19.5	22.3	23.1	22.1	22.5	22.1	19.7	21.3	21.9
(LASE) at 5% (N)	12.4	10.6	10.0	10.6	10.8	10.4	12.2	10.0	10.0

Dipped cord	Heat-treated							
	160°C			180°C		220°C		
	5 min.	10 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	138.1	137.8	141.9	139.6	140.5	141.5	138.4	140.0
Elongation at break (%)	27.7	27.8	28.9	27.2	27.7	28.4	28.5	28.9
Elongation at 45 N (%)	13.8	13.6	13.9	13.3	13.8	13.5	13.9	13.4
68 N (%)	17.1	16.9	17.3	16.5	17.1	16.9	17.4	16.9
90 N (%)	19.6	19.5	20.0	19.1	19.7	19.6	20.2	19.7
(LASE) at 5% (N)	12.8	13.4	13.6	13.9	14.0	14.0	14.0	14.0

Table IV: Tensile properties of undipped and dipped C_1 nylon 6,6 cord using RFL-2 adhesive system.

Undipped cord	Without heat-treatment	Heat-treated							
		160°C			180°C		220°C		
		5 min.	10 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	219.0	220.0	218.2	217.8	215.0	216.8	220.4	220.8	217.0
Elongation at break (%)	26.9	32.2	33.1	33.9	33.7	36.2	28.8	30.1	29.4
Elongation at 45 N (%)	9.9	12.1	12.6	12.5	12.7	12.6	10.8	12.0	12.0
68 N (%)	12.5	15.7	16.3	16.4	16.5	16.5	13.7	15.3	15.4
90 N (%)	14.4	18.3	19.0	19.2	19.2	18.9	15.6	17.5	17.7
(LASE) at 5% (N)	20.0	18.0	15.4	16.0	15.6	15.6	20.0	15.8	16.2

Dipped cord	Heat-treated							
	160°C			180°C		220°C		
	5 min.	10 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	204.5	207.0	206.2	207.3	212.4	204.1	200.4	200.8
Elongation at break (%)	28.9	28.7	25.2	26.1	27.6	27.4	26.2	27.0
Elongation at 45 N (%)	12.0	11.6	10.1	10.3	10.6	10.5	10.6	10.2
68 N (%)	15.4	15.0	13.1	13.1	13.6	13.6	13.7	13.1
90 N (%)	17.9	17.4	15.3	15.4	15.9	16.0	16.2	15.5
(LASE) at 5% (N)	18.0	18.0	20.3	20.0	19.9	19.7	19.8	19.9

Table V: Tensile properties of undipped and dipped P_1 polyester cord using RFL-1 dipping solution.

Undipped cord	Without heat-treatment	Heat-treated										
		160°C					180°C			220°C		
		3 min	5 min	7 min	10 min	15 min	1 min	3 min	5 min	1 min	3 min	5 min
Tensile strength (N)	157.4	156.0	162.4	158.9	157.2	160.0	161.0	158.8	159.2	160.3	161.8	156.2
Elongation at break (%)	15.4	23.4	22.3	29.9	28.4	30.7	23.2	19.9	26.9	17.3	24.5	27.9
Elongation at 45 N (%)	6.7	12.9	11.7	17.4	16.6	17.6	12.1	10.2	15.0	8.1	13.2	16.4
68 N (%)	8.7	15.6	14.6	21.2	20.1	21.6	14.9	12.8	18.4	10.4	16.3	19.9
90 N (%)	10.2	17.5	16.5	23.5	22.3	24.0	16.9	14.6	20.6	12.1	18.4	22.1
(LASE) at 5% (N)	32.2	20.0	22.7	20.0	20.0	19.4	22.0	24.1	20.0	27.9	22.4	20.0

Dipped cord	Heat-treated										
	160°C					180°C			220°C		
	3 min	5 min	7 min	10 min	15 min	1 min	3 min	5 min	1 min	3 min	5 min
Tensile strength (N)	148.1	151.6	149.0	147.1	152.0	148.8	150.5	151.3	154.5	150.4	143.3
Elongation at break (%)	18.2	17.2	19.3	19.4	19.1	19.7	17.5	18.6	18.7	17.1	18.1
Elongation at 45 N (%)	8.7	7.3	9.6	9.7	8.6	9.7	7.4	7.2	6.9	6.2	6.8
68 N (%)	11.8	10.4	12.9	13.0	12.0	13.1	10.8	11.6	10.5	9.5	10.5
90 N (%)	13.8	12.4	14.8	15.0	14.2	15.2	12.9	13.7	13.0	11.8	13.1
(LASE) at 5% (N)	31.0	34.3	30.0	30.0	32.0	30.0	34.8	33.3	35.0	37.3	35.6

Table VI: Tensile properties of undipped and dipped P_2 polyester cord using RFL-1 dipping solution.

Undipped cord	Without heat-treatment	Heat-treated										
		160°C					180°C			220°C		
		3 min	5 min	7 min	10 min	15 min	1 min	3 min	5 min	1 min	3 min	5 min
Tensile strength (N)	156.7	162.8	161.7	160.0	164.0	163.1	159.4	164.3	161.0	166.9	162.1	157.0
Elongation at break (%)	20.8	28.3	23.5	30.7	30.0	34.6	23.9	22.9	34.1	22.2	28.8	28.4
Elongation at 45 N (%)	7.6	13.5	10.0	15.4	14.4	17.1	10.6	8.7	17.2	8.0	13.6	14.4
68 N (%)	10.1	16.6	12.8	19.1	17.8	21.0	13.5	11.5	21.2	10.6	16.9	17.7
90 N (%)	12.0	18.8	14.8	21.4	20.0	23.6	15.5	13.4	23.8	12.5	19.1	19.9
(LASE) at 5% (N)	30.3	23.5	25.5	22.4	23.0	21.3	25.4	26.9	21.0	29.0	22.6	22.2

Dipped cord	Heat-treated										
	160°C					180°C			220°C		
	3 min	5 min	7 min	10 min	15 min	1 min	3 min	5 min	1 min	3 min	5 min
Tensile strength (N)	158.6	161.4	152.4	162.1	154.6	160.2	157.4	154.9	153.7	153.9	152.7
Elongation at break (%)	23.9	24.4	22.6	24.0	23.7	24.8	21.0	20.8	22.1	23.1	22.3
Elongation at 45 N (%)	10.0	9.7	9.9	9.4	9.9	10.1	7.1	7.1	7.3	7.6	7.3
68 N (%)	13.5	13.2	13.3	13.0	13.4	13.8	10.7	10.6	11.3	11.8	11.2
90 N (%)	15.6	15.5	15.5	15.2	15.7	16.1	13.0	12.9	14.1	14.7	14.0
(LASE) at 5% (N)	28.6	30.0	28.4	30.0	30.0	28.0	35.0	35.0	35.0	35.0	35.0

Table VII: Tensile properties of undipped and dipped P3 polyester cord using RFL-1 dipping solution.

Undipped cord	Without heat-treatment	Heat-treated										
		160°C					180°C			220°C		
		3 min	5 min	7 min	10 min	15 min	1 min	3 min	5 min	1 min	3 min	5 min
Tensile strength (N)	235.4	238.3	231.1	240.6	241.6	229.5	240.4	236.0	241.0	241.9	239.0	229.4
Elongation at break (%)	22.9	30.5	26.1	33.3	33.2	36.6	24.8	25.3	33.0	24.4	37.2	32.7
Elongation at 45 N (%)	5.9	10.6	8.3	11.6	11.3	14.5	6.8	7.6	11.6	6.6	13.6	14.0
68 N (%)	8.8	14.7	11.5	16.7	16.1	19.6	9.9	10.8	16.1	9.6	19.1	18.8
90 N (%)	10.7	16.9	13.5	19.3	18.6	22.5	11.9	12.9	18.7	11.5	22.0	21.4
(LASE) at 5% (N)	39.6	31.1	31.5	31.2	30.0	25.5	36.0	34.5	29.6	36.0	26.5	25.4

Dipped cord	Heat-treated										
	160°C					180°C			220°C		
	3 min	5 min	7 min	10 min	15 min	1 min	3 min	5 min	1 min	3 min	5 min
Tensile strength (N)	217.5	224.0	217.5	213.5	220.5	211.8	219.8	219.5	220.3	215.0	202.3
Elongation at break (%)	24.7	23.8	24.7	23.7	23.5	23.0	26.4	24.4	26.5	24.3	23.3
Elongation at 45 N (%)	6.7	5.5	6.5	6.3	5.4	5.7	6.6	5.6	5.9	5.3	5.3
68 N (%)	11.4	9.7	11.3	10.9	9.6	9.9	11.6	10.0	10.4	9.1	9.1
90 N (%)	13.9	12.5	13.9	13.5	12.4	12.6	14.7	12.9	13.7	10.9	12.2
(LASE) at 5% (N)	39.1	43.2	38.7	38.5	42.9	41.7	39.5	41.0	40.6	43.5	43.4

Table VIII: Tensile properties of undipped and dipped P_1 polyester cord using RFL-2 adhesive system.

Undipped cord	Without heat-treatment	Heat-treated						
		160°C		180°C		220°C		
		5 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	157.4	162.4	160.0	158.8	159.2	160.3	161.8	156.2
Elongation at break (%)	15.4	22.3	30.7	19.9	26.9	17.3	24.5	27.9
Elongation at 45 N (%)	6.7	11.7	17.6	10.2	15.0	8.1	13.2	16.4
68 N (%)	8.7	14.6	21.6	12.8	18.4	10.4	16.3	19.9
90 N (%)	10.2	16.5	24.0	14.6	20.6	12.1	18.4	22.1
(LASE) at 5% (N)	32.2	22.7	19.4	24.1	20.0	27.9	22.4	20.0

Dipped cord	Heat-treated						
	160°C		180°C		220°C		
	5 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	153.3	150.9	151.6	151.4	149.8	142.3	142.9
Elongation at break (%)	16.4	17.3	20.3	18.2	17.8	19.8	18.5
Elongation at 45 N (%)	6.4	7.0	9.8	8.0	7.2	8.5	8.0
68 N (%)	9.6	10.0	13.3	11.3	10.8	12.7	12.0
90 N (%)	11.6	12.1	15.5	13.5	13.2	15.3	14.5
(LASE) at 5% (N)	37.0	34.6	28.4	31.6	36.3	30.0	31.8

Table IX: Tensile properties of undipped and dipped P_2 polyester cord using RFL-2 adhesive system

Undipped cord	Without heat-treatment	Heat-treated						
		160°C		180°C		220°C		
		5 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	156.7	161.7	163.1	164.3	161.0	166.9	162.1	157.0
Elongation at break (%)	20.8	23.5	34.6	22.9	34.1	22.2	28.8	28.4
Elongation at 45 N (%)	7.6	10.0	17.1	8.7	17.2	8.0	13.6	14.4
68 N (%)	10.1	12.8	21.0	11.5	21.2	10.6	16.9	17.7
90 N (%)	12.0	14.8	23.6	13.4	23.8	12.5	19.1	19.9
(LASE) at 5% (N)	30.3	25.5	21.3	26.9	21.0	29.0	22.6	22.2

Dipped cord	Heat-treated						
	160°C		180°C		220°C		
	5 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	152.7	150.4	152.5	154.6	151.2	150.6	150.7
Elongation at break (%)	22.1	22.8	24.9	24.8	23.2	24.6	22.8
Elongation at 45 N (%)	9.1	9.9	10.6	10.3	8.3	9.2	8.0
68 N (%)	11.2	13.5	14.3	14.1	12.4	13.7	12.0
90 N (%)	14.7	15.7	16.8	16.5	15.2	16.7	14.8
(LASE) at 5% (N)	29.7	28.4	28.0	29.0	31.6	30.0	32.6

Table X: Tensile properties of undipped and dipped P3 polyester cord using RFL-2 adhesive system.

Undipped cord	Without heat-treatment	Heat-treated						
		160°C		180°C		220°C		
		5 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	235.4	231.1	229.5	236.0	241.0	241.9	239.0	229.4
Elongation at break (%)	22.9	26.1	36.6	25.3	33.0	24.4	37.2	32.4
Elongation at 45 N (%)	5.9	8.3	14.5	7.6	11.6	6.6	13.6	14.0
68 N (%)	8.8	11.5	19.6	10.8	16.1	9.6	19.1	18.8
90 N (%)	10.7	13.5	22.5	12.9	18.7	11.5	22.0	21.4
(LASE) at 5% (N)	39.6	31.5	25.5	34.5	29.6	36.0	26.5	25.4

Dipped cord	Heat-treated						
	160°C		180°C		220°C		
	5 min.	15 min.	3 min.	5 min.	1 min.	3 min.	5 min.
Tensile strength (N)	220.1	213.8	214.3	216.5	212.3	207.2	201.9
Elongation at break (%)	26.7	28.5	27.7	28.3	26.8	26.5	25.1
Elongation at 45 N (%)	7.5	8.9	8.1	8.1	6.5	6.5	6.2
68 N (%)	12.1	14.1	13.2	13.4	11.1	11.1	10.4
90 N (%)	14.7	16.9	16.1	16.3	14.5	14.5	13.6
(LASE) at 5% (N)	36.2	32.3	34.5	35.0	38.8	38.8	40.5

Table XI: Comparison of dip pick-up.

Adhesive system	Textile cord	Dip pick-up			
		weight%	mg/m cord length	mg/cm^2 cord outer surface	mg/cm^3 cord volume
RFL-1	Nylon 6,6 (C_1)	7.5	22.7	o.932	48.1
	Nylon 6,6 (C_2)	7.9	24.6	1.036	54.8
	Nylon 6,6 (C_3)	6.1	12.9	0.653	41.6
RFL-2	Nylon 6,6 (C_1)	8.4	25.5	1.048	54.2
RFL-1	Polyester (P_1)	9.7	24.1	1.383	99.6
	Polyester (P_2)	10.0	23.8	1.296	88.5
	Polyester (P_3)	10.3	37.7	1.700	96.4
RFL-2	Polyester (P_1)	9.6	23.9	1.374	98.8
	Polyester (P_2)	10.2	24.3	1.323	90.3
	Polyester (P_3)	9.5	34.8	1.570	89.0

Table XII: The adhesion values measured at room temp. and at 90°C for nylon 6,6 (C_1) cord treated with RFL-1 dip and bonded to NR compounds R-1 and R-2.

Heat treatment conditions (°C/min.)	R-1		R-2	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.75	1.77	11.22	9.44
160°C/3 min.	8.61	5.99	10.54	6.50
160°C/5 min.	8.83	4.97	10.86	9.84
160°C/7 min.	11.63	7.28	11.83	7.94
160°C/10 min.	6.53	3.80	8.68	7.35
160°C/15 min.	7.13	4.38	9.11	7.40
180°C/1 min.	9.96	6.47	10.81	6.79
180°C/3 min.	9.59	5.95	15.05	13.00
180°C/5 min.	8.11	6.00	12.24	8.40
220°C/1 min.	13.30	9.22	14.89	13.58
220°C/3 min.	12.05	7.12	13.84	9.99
220°C/5 min.	8.31	4.82	7.93	6.08

Table XIII: The adhesion values measured at room temp. and at 90°C for nylon 6,6 (C_2) cord treated with RFL-1 dip and bonded to NR compounds R-1 and R-2.

Heat treatment conditions (°C/min.)	R-1		R-2	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.54	1.92	12.62	8.91
160°C/5 min.	8.87	6.59	15.75	13.49
160°C/10 min.	6.30	4.20	7.55	6.11
160°C/15 min.	6.24	3.68	8.52	6.51
180°C/3 min.	9.32	5.94	15.34	12.66
180°C/5 min.	6.60	4.29	10.42	7.70
220°C/1 min.	9.41	6.87	13.94	13.49
220°C/3 min.	6.21	3.91	9.87	7.32
220°C/5 min.	6.53	3.84	9.99	7.55

Table XIV: The adhesion values measured at room temp. and at 90°C for nylon 6,6 (C3) cord treated with RFL-1 dip and bonded to NR compounds R-1 and R-2.

Heat treatment conditions (°C/min.)	R-1		R-2	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	2.99	1.92	8.21	7.30
160°C/5 min.	6.79	4.54	13.56	11.37
160°C/10 min.	4.48	3.39	10.31	8.98
160°C/15 min.	5.63	3.64	9.75	8.47
180°C/3 min.	5.36	3.77	10.53	8.65
180°C/5 min.	5.93	3.56	10.48	9.58
220°C/1 min.	6.11	4.15	12.86	10.71
220°C/3 min.	5.74	4.08	7.18	6.22
220°C/5 min.	5.18	3.57	7.01	5.83

Table XV: The adhesion values measured at room temp. and at 90°C for polyester (P1) cord treated with RFL-1 dip and bonded to NR compounds R-1 and R-2.

Heat treatment conditions (°C/min.)	R-1		R-2	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.60	1.80	7.27	6.09
160°C/3 min.	6.69	4.24	7.11	5.40
160°C/5 min.	7.80	4.94	7.28	5.91
160°C/7 min.	8.36	5.26	8.75	6.06
160°C/10 min.	8.59	5.41	9.75	6.35
160°C/15 min.	6.25	3.89	6.65	4.89
180°C/1 min.	9.32	5.68	9.71	6.23
180°C/3 min.	5.74	3.68	7.02	5.25
180°C/5 min.	6.27	4.39	7.10	5.55
220°C/1 min.	10.15	6.60	8.88	7.05
220°C/3 min.	7.94	5.70	8.00	6.92
220°C/5 min.	6.79	4.03	6.90	6.55

Table XVI: The adhesion values measured at room temp. and at 90°C for polyester (P_2) cord treated with RFL-1 dip and bonded to NR compounds R-1 and R-2.

Heat treatment conditions (°C/min.)	R-1		R-2	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.52	1.74	8.18	7.55
160°C/3 min.	7.27	4.68	7.76	5.05
160°C/5 min.	7.36	4.73	7.78	6.82
160°C/7 min.	7.39	4.78	9.30	5.39
160°C/10 min.	8.15	5.29	8.46	5.38
160°C/15 min.	5.92	3.96	6.96	5.72
180°C/1 min.	8.36	5.12	8.77	5.57
180°C/3 min.	6.46	4.42	8.00	6.32
180°C/5 min.	6.60	3.95	7.18	5.53
220°C/1 min.	9.52	6.76	9.78	7.47
220°C/3 min.	8.38	5.62	8.72	7.76
220°C/5 min.	5.99	3.56	7.77	6.00

Table XVII: The adhesion values measured at room temp. and at 90°C for polyester (P3) cord reated with RFL-1 dip and bonded to NR compounds R-1 and R-2.

Heat treatment conditions (°C/min.)	R-1		R-2	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.63	1.63	9.25	8.96
160°C/3 min.	7.53	5.29	8.49	5.90
160°C/5 min.	7.40	5.33	8.31	6.69
160°C/7 min.	10.41	5.63	10.33	5.77
160°C/10 min.	9.92	5.57	9.43	5.52
160°C/15 min.	7.27	4.92	8.27	6.33
180°C/1 min.	9.75	5.73	10.82	6.11
180°C/3 min.	8.19	5.34	8.52	6.16
180°C/5 min.	9.09	5.86	8.38	6.25
220°C/1 min.	10.07	6.61	10.28	8.79
220°C/3 min.	9.10	6.76	10.52	8.83
220°C/5 min.	5.84	3.20	9.66	7.27

Table XVIII: The adhesion values measured at room temp. and at 90°C for polyester (P_1) cord treated with RFL-2 dip and bonded to NR compounds R-1 and R-2.

Heat treatment conditions (°C/min.)	R-1		R-2	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.60	1.80	7.27	6.09
160°C/5 min.	8.10	5.51	10.01	7.50
160°C/15 min.	8.33	6.03	10.81	8.40
180°C/3 min.	9.28	6.17	11.59	7.95
180°C/5 min.	9.89	6.21	11.20	7.79
220°C/1 min.	10.01	5.79	13.53	9.67
220°C/3 min.	12.90	8.81	12.02	9.33
220°C/5 min.	15.26	8.58	14.48	10.07

Table XIX: The adhesion values measured at room temp. and at 90°C for polyester (P_2) cord treated with RFL-2 dip and bonded to NR compounds R-1 and R-2.

Heat treatment conditions (°C/min.)	R-1		R-2	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.52	1.74	8.18	7.55
160°C/5 min.	7.00	4.52	8.37	6.48
160°C/15 min.	8.16	5.29	10.36	7.50
180°C/3 min.	9.98	6.66	11.40	8.45
180°C/5 min.	8.31	5.65	11.12	7.96
220°C/1 min.	8.49	5.37	11.05	8.30
220°C/3 min.	11.95	7.75	12.47	10.02
220°C/5 min.	10.74	6.05	12.41	8.55

Table XX: The adhesion values measured at room temp. and at 90°C for polyester (P3) cord treated with RFL-2 dip and bonded to NR compounds R-1 and R-2.

Heat treatment conditions (°C/min.)	R-1		R-2	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.63	1.63	9.25	8.96
160°C/5 min.	10.47	5.89	12.08	9.19
160°C/15 min.	8.39	5.57	11.94	8.60
180°C/3 min.	11.89	7.03	12.87	9.35
180°C/5 min.	12.76	7.28	14.65	9.54
220°C/1 min.	11.50	6.79	15.46	11.55
220°C/3 min.	13.90	9.55	18.43	12.38
220°C/5 min.	12.03	7.74	16.42	11.27

Table XXI: The adhesion values measured at room temp. and at 90°C for polyester (P_1) cord treated with RFL-2 dip and bonded to CR compounds R-3 and R-4.

Heat treatment conditions (°C/min.)	R-3		R-4	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	4.08	1.71	4.95	3.00
160°C/5 min.	10.68	6.56	7.96	4.74
160°C/15 min.	10.66	6.58	8.72	5.04
180°C/3 min.	12.38	6.55	8.61	4.99
180°C/5 min.	11.11	7.08	7.37	5.11
220°C/1 min.	9.67	6.07	8.55	5.53
220°C/3 min.	13.86	8.62	9.44	6.13
220°C/5 min.	13.09	7.39	10.00	6.83

Table XXII: The adhesion values measured at room temp. and at 90°C for polyester (P_2) cord treated with RFL-2 dip and bonded to CR compounds R-3 and R-4.

Heat treatment conditions (°C/min.)	R-3		R-4	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	2.95	1.32	5.59	3.53
160°C/5 min.	8.92	5.40	8.41	5.10
160°C/15 min.	10.20	5.66	9.00	5.68
180°C/3 min.	12.11	6.78	9.10	5.89
180°C/5 min.	10.40	6.20	9.61	6.01
220°C/1 min.	10.65	6.83	10.46	6.29
220°C/3 min.	11.70	7.49	9.22	6.15
220°C/5 min.	11.78	7.82	9.39	5.34

Table XXIII: The adhesion values measured at room temp. and at 90°C for polyester (P3) cord treated with RFL-2 dip and bonded to CR compounds R-3 and R-4.

Heat treatment conditions (°C/min.)	R-3		R-4	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.66	1.71	6.73	4.33
160°C/5 min. 160°C/15 min.	12.28 10.37	6.99 6.72	12.41 12.16	6.93 7.21
180°C/3 min. 180°C/5 min.	12.68 11.16	7.35 6.75	11.16 11.63	7.36 7.14
220°C/1 min. 220°C/3 min. 220°C/5 min.	14.36 15.02 13.78	8.83 9.27 8.84	12.33 12.39 13.52	7.91 7.54 7.94

Table XXIV: The adhesion values measured at room temp. and at 90°C for nylon 6,6 (C_1) cord treated with RFL-1 dip and bonded to CR compounds R-3 and R-4.

Heat treatment conditions (°C/min.)	R-3		R-4	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.62	1.96	7.37	3.82
160°C/3 min.	12.16	6.27	17.96	10.19
160°C/5 min.	14.30	8.13	18.34	11.49
160°C/7 min.	14.48	8.25	17.04	9.35
160°C/10 min.	6.78	3.47	9.90	6.01
160°C/15 min.	8.14	3.83	12.31	7.17
180°C/1 min.	14.72	7.94	18.06	9.86
180°C/3 min.	10.83	5.43	20.00	10.63
180°C/5 min.	7.33	3.58	14.68	8.50
220°C/1 min.	12.98	5.64	16.01	9.03
220°C/3 min.	12.80	6.86	17.63	9.91
220°C/5 min.	8.32	4.45	13.45	7.95

Table XXV: The adhesion values measured at room temp. and at 90°C for nylon 6,6 (C_2) cord treated with RFL-1 dip and bonded to CR compounds R-3 and R-4.

Heat treatment conditions (°C/min.)	R-3		R-4	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	4.44	2.28	5.26	3.13
160°C/5 min.	6.94	2.87	11.84	6.72
160°C/10 min.	6.09	2.45	8.47	5.25
160°C/15 min.	6.74	2.98	9.37	5.89
180°C/3 min.	5.80	3.33	12.82	7.16
180°C/5 min.	6.94	3.13	12.49	6.90
220°C/1 min.	5.32	2.36	9.74	6.55
220°C/3 min.	5.55	2.07	12.06	6.48
220°C/5 min.	6.40	2.43	13.88	7.99

Table XXVI: The adhesion values measured at room temp. and at 90°C for nylon 6,6 (C3) cord treated with RFL-1 dip and bonded to CR compounds R-3 and R-4.

Heat treatment conditions (°C/min.)	R-3		R-4	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.51	1.28	6.28	3.12
160°C/5 min.	5.50	2.50	11.07	6.69
160°C/10 min.	5.66	2.75	10.33	6.52
160°C/15 min.	5.30	1.85	11.61	6.75
180°C/3 min.	7.15	3.50	10.80	6.60
180°C/5 min.	6.57	2.95	12.28	7.15
220°C/1 min.	6.00	2.68	10.84	6.78
220°C/3 min.	7.29	3.67	10.82	6.83
220°C/5 min.	6.07	3.25	11.46	6.92

Table XXVII: The adhesion values measured at room temp. and at 90°C for polyester (P_1) cord treated with RFL-1 dip and bonded to CR compounds R-3 and R-4.

Heat treatment conditions (°C/min.)	R-3		R-4	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	4.08	1.71	4.95	3.00
160°C/3 min.	9.10	5.97	8.80	5.45
160°C/5 min.	8.50	4.66	8.77	5.43
160°C/7 min.	9.16	5.07	9.92	5.86
160°C/10 min.	10.08	5.41	8.82	5.56
160°C/15 min.	5.73	2.56	7.67	4.28
180°C/1 min.	10.60	6.18	11.09	7.56
180°C/3 min.	5.84	2.77	8.62	5.33
180°C/5 min.	8.74	4.46	9.36	6.55
220°C/1 min.	7.10	4.54	8.97	6.10
220°C/3 min.	10.50	5.81	9.64	6.24
220°C/5 min.	8.04	4.82	11.46	5.89

Table XXVIII: The adhesion values measured at room temp. and at 90°C for polyester (P_2) cord treated with RFL-1 dip and bonded to CR compounds R-3 and R-4.

Heat treatment conditions (°C/min.)	R-3		R-4	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	2.95	1.32	5.59	3.53
160°C/3 min.	8.20	3.82	8.43	5.17
160°C/5 min.	8.50	4.00	9.26	5.68
160°C/7 min.	8.33	5.09	11.27	6.28
160°C/10 min.	8.24	4.82	9.88	5.91
160°C/15 min.	8.01	4.26	8.43	5.71
180°C/1 min.	7.50	4.77	12.08	6.60
180°C/3 min.	4.31	2.51	8.18	5.14
180°C/5 min.	6.25	3.38	7.30	5.13
220°C/1 min.	6.04	2.59	8.41	5.05
220°C/3 min.	5.55	2.48	7.79	5.24
220°C/5 min.	5.44	3.32	8.13	5.01

Table XXIX: The adhesion values measured at room temp. and at 90°C for polyester (P3) cord treated with RFL-1 dip and bonded to CR compounds R-3 and R-4.

Heat treatment conditions (°C/min.)	R-3		R-4	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.66	1.71	6.73	4.33
160°C/3 min.	6.27	2.93	9.28	5.01
160°C/5 min.	6.36	2.97	9.50	5.30
160°C/7 min.	10.98	6.92	12.29	7.12
160°C/10 min.	10.19	5.79	13.18	7.90
160°C/15 min.	5.27	2.55	8.10	4.65
180°C/1 min.	11.29	6.84	12.32	8.30
180°C/3 min.	6.02	2.17	9.12	4.86
180°C/5 min.	7.38	3.28	10.10	5.96
220°C/1 min.	6.59	3.30	9.94	6.25
220°C/3 min.	7.98	3.86	9.31	5.90
220°C/5 min.	6.60	3.11	10.26	6.47

Table XXX: The adhesion values measured at room temp. and at 90°C for nylon 6,6 (C_1) cord treated with RFL-2 dip and bonded to NR compounds R-1 and R-2.

Heat treatment conditions (°C/min.)	R-1		R-2	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.75	1.77	11.22	9.44
160°C/5 min.	10.30	6.53	11.47	8.63
160°C/10 min.	9.39	6.27	11.94	8.11
160°C/15 min.	7.80	5.01	10.43	7.62
180°C/3 min.	12.02	7.19	12.63	8.38
180°C/5 min.	12.50	7.71	14.66	10.89
220°C/1 min.	16.71	10.69	16.15	11.54
220°C/3 min.	16.07	12.31	15.60	10.15
220°C/5 min.	8.48	6.38	15.18	10.80

Table XXXI: The adhesion values measured at room temp. and at 90°C for nylon 6,6 (C_1) cord treated with RFL-2 dip and bonded to CR compounds R-3 and R-4.

Heat treatment conditions (°C/min.)	R-3		R-4	
	pull-out force (dN/cm)		pull-out force (dN/cm)	
	at room temp.	at 90°C	at room temp.	at 90°C
undipped and untreated cord	3.62	1.96	7.37	3.82
160°C/5 min.	12.83	6.06	12.10	7.39
160°C/10 min.	14.04	7.35	13.35	6.75
160°C/15 min.	10.74	5.31	12.60	6.77
180°C/3 min.	14.08	7.34	14.28	9.06
180°C/5 min.	13.78	6.74	13.78	7.38
220°C/1 min.	19.17	8.29	19.23	9.72
220°C/3 min.	19.46	8.74	18.49	8.61
220°C/5 min.	16.33	8.07	17.77	9.53