Tack in Urethane Elastomers

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Synopsis

The phenomenon of tack has been studied in urethane–urea elastomers prepared from polyether or polyester prepolymers and 4,4′-methylenebis(2-chloroaniline). It is shown that tack at zero elongation is attained only in polymers in which the flexible chains, i.e., polyesters or polyethers, contain 50 chain links or more. This coincides with the requirements for the Gaussian vector function in elastomers. The results suggest that, in the absence of flexible chain ends in these polymers, tack is solely contributed by the flexible segments along the polymer chains, while the rigid blocks in the chains do not participate in the formation of tack.

I. Introduction

Tack (self-adhesion, autohesion) of polymers is generally defined as the ability of two polymer surfaces to adhere firmly to each other when brought into intimate contact at working temperatures. The term tack is normally used by the rubber chemist when two surfaces of the same type of polymer only are involved, while the adhesive chemist usually defines tack, tackiness, and stickiness as the ability of one polymer surface to adhere to a multitude of other surfaces. In this work we refer to tack only in the sense that two separate surfaces of one type of polymer are involved.

Previous studies have shown that variables affecting tack are: contact time,[1–4] rate of pull,[1,3,4] viscosity,[1,3–6] molecular weight,[2,3] degree of vulcanization,[2] contact pressure,[1,2,7] fillers and plasticizers,[1,8] chemical structure,[2,3,8] and temperature.[1,2,7,9]

The phenomenon of tack has not, however, been reported in urethane elastomers, although such polymers are excellently suited for the study of the nature of tack.

II. The Nature of Tack

The nature of tack is elucidated by the fact that the bond strength of two contiguous surfaces increases as the contact time is increased. The time effect can be described in principle by eq. (1):

$$1/A = af_0 + (b/t) \tag{1}$$

where a and b are constants, A is the tack strength, f_0 is an activation factor, and t is the contact time. Nearly all experimental results so far published appear to conform to this relation.

This fact has led to the general belief that a diffusion mechanism is involved in building tack strength. Diffusion of first chain segments or chain ends that are present in two contiguous surfaces permits the close molecular contact that is needed for the formation of secondary bonds. Chain diffusion and bond formation results in the growing together of the two contiguous surfaces into one body, i.e., coalescence. This concept of diffusion and coalescence as a condition for tack is now generally accepted by most researchers.

In view of the dependence of tack on both the temperature and the depth of diffusion, tack strength must be dependent upon the energy required for a chain end or chain segment to enter the polymolecular matrix of the "other" surface. Such an activation energy can be calculated by making use of the Arrhenius equation, eq. (2):

$$A = J_0 e^{-E/RT} \qquad (2)$$

where A is the tack strength, J_0 is an activation factor, E is the activation energy of the diffusion process, R is the gas constant, and T is the absolute temperature. From eq. (2), a plot of the logarithm of tack strength versus the reciprocal of the absolute temperature should result in a straight line. It has been shown by Voyutskiĭ and Shtarkh[2] that this is actually the case.

Another experimental contribution to the diffusion theory is the finding that the tack of 1,4-polybutadiene is decreased as the proportion of 1,2-polybutadiene in copolymers is increased. This response has been attributed[2] to the hindrance in the diffusion process caused by pendant groups.

It has been reported that tack is decreased as the molecular weight of the polymer increases.[2,3] This phenomenon has been explained by the decrease in the number of chain ends in the higher molecular weight polymer, the argument being used that the mobility of the chain segments is not affected by the increased molecular weight,[2] and that therefore tack is largely due to the mobility of the chain ends. It will become evident from the work reported in this paper that, in contrast to these arguments, the chain segments are indeed most important in the formation of tack strength, and that high tack strength is obtained in polymers that do not contain flexible chain ends.

The activation energy involved in the diffusion process should be expected to be a material constant and independent of molecular weight, since the length of the operative chain ends and chain segments in high polymers is not a function of the length of the total polymer chain. This has been confirmed experimentally for a large spread of molecular weights on both butyl rubber[2] and natural rubber.[3] An activation energy of 2.39 kcal. had been recently reported[2] for butyl rubber.

While the various aforementioned factors influencing tack have been

dealt with in the literature, it appears that the effect on tack of prestressing the polymers has not been mentioned thus far. It will be shown on polyurethane elastomers that prestressing is essential in certain polymer types to attain tack of a significant magnitude.

III. Experimental Procedure

The materials tested were prepared from prepolymers of polypropylene glycol and also those of a saturated polypropylene adipate, cured with the diamine Moca (du Pont). Some of the specimens also contained a flexible epoxy resin, DER 732 (Dow). The prepolymer, or mixture of prepolymers, was heated to 82°C. and degassed in a vacuum chamber at about 3 mm Hg until bubbling ceased. When DER 732 was used, it was added to the prepolymer before degassing. The Moca was heated to 110°C. and stirred carefully into the prepolymer to avoid air entrainment. The mixture was then poured on plate glass molds, waxed and heated to about 80°C., to form slabs about $1/4$ in. thick. The slabs were cured in an oven for 3 hr. at 100°C., followed by 4 hr. at 150°C.

Test specimens were die-cut to approximately 0.250 × 0.125 in., conforming to ASTM die specification D412-51T, Type C. The average cross section over the gage length was measured by micrometer to the nearest thousandth of an inch. The specimens were preloaded and bonded in a TM Model Instron Universal Test Machine fitted with a D type 1000 lb. capacity load cell. The grips of the machine were used both to restrain the samples during prestressing and to support them during the bonding procedure.

The desired elongation (±0.1 in.) was produced by deformation of the specimen at 10 in./min. (it should be noted that the specimens begin

TABLE I
Molecular Weight, Number of Chain Links, and
Physical Properties of the Flexible Polymers

Sample number	Molecular weight of flexible chain segment		Number of chain links in flexible chain segment	Physical properties of cured sheets	
	Poly(propylene ether)	Poly(propylene adipate) ester		Tensile strength, psi	Elongation, %
1	430	—	22	7676	5
2	775	—	40	4149	425
3	—	790	42	4990	737
4	—	1000	54	3592	821
5	1060 (80%)	790 (20%)	53	2758	960
6	1060	—	57	1379	627
7	—	1300	70	2740	921
8	2000	—	103	547	865
9	—	2290	123	2011	696

to "flow" or stress relax as soon as crosshead movement ceases). Samples were cut with a stainless steel knife at mid-span. A certain minimal amount of elongation, probably several per cent, is present in specimens designated as zero elongation, since some tension is necessary to produce a clean cut.

The time lapse between severing the specimens and reuniting them, herein termed the open assembly time, was approximately 5 sec. for specimens at zero elongation and about 2–3 min. for samples elongated to permit relocation of the specimen in the jaws to allow about $^3/_{32}$ in. exposure. Specified times are given where open assembly time was a factor in the test.

The cut ends were pressed together by hand alignment of the supporting jaws at 20 psi pressure (except as specified when pressure was a test factor), and held together for 5 min. (except as specified when time was a test factor).

All specimens were remeasured with a micrometer at the bond cross section, and tested at a rate of deformation of 5 in./min. until the bond broke. Results are summarized in Table I.

IV. Results

The effect of elongation on the tack bond strength of various urethane polymers is shown in Figure 1. Sample 1, composed of very short polyether chains of 23 average chain segments, does not exhibit tack under any of the conditions tested. Sample 2, containing 40 average chain
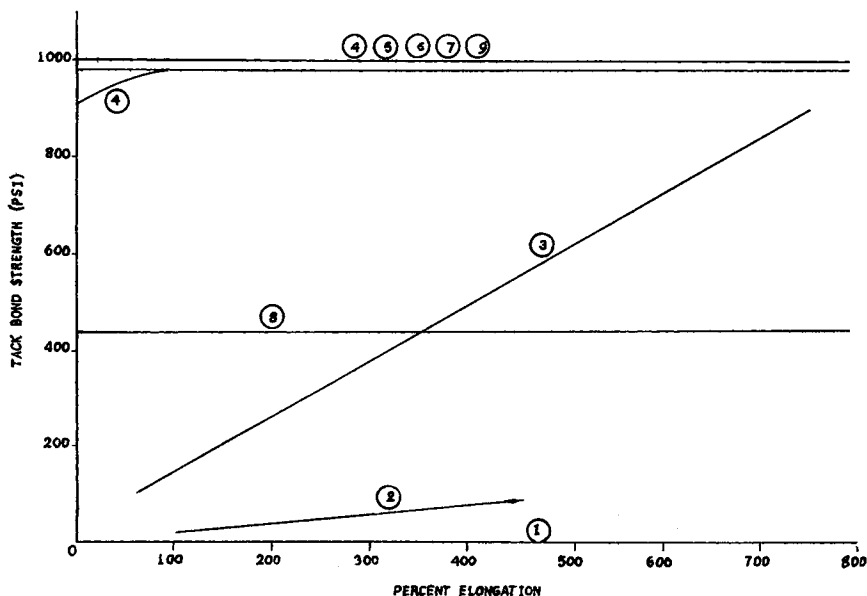

Fig. 1. Effect of per cent elongation at cut on tack tensile strength. Numbers refer to samples listed in Table I.
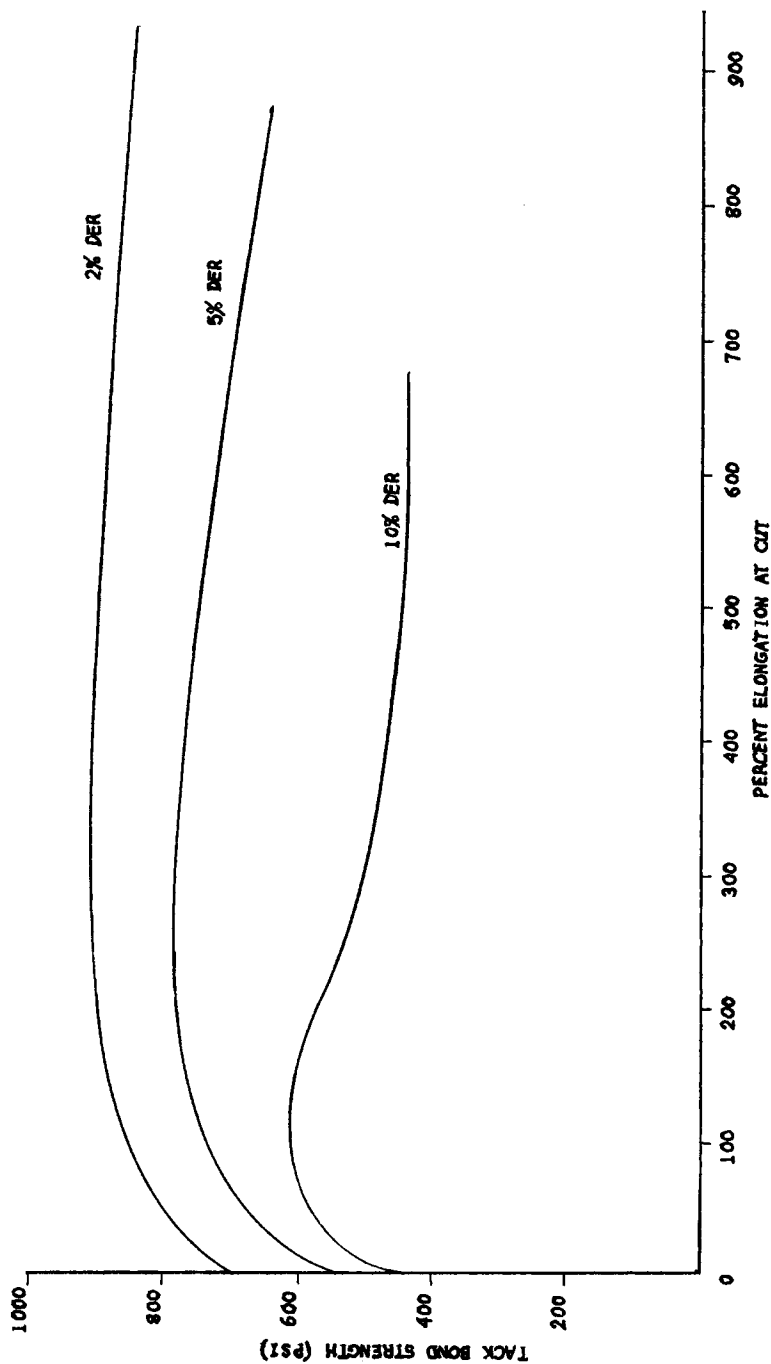
Fig. 2. Effect of Dow epoxy resin 732 (DER 732) on the tack tensile strength of sample 6.
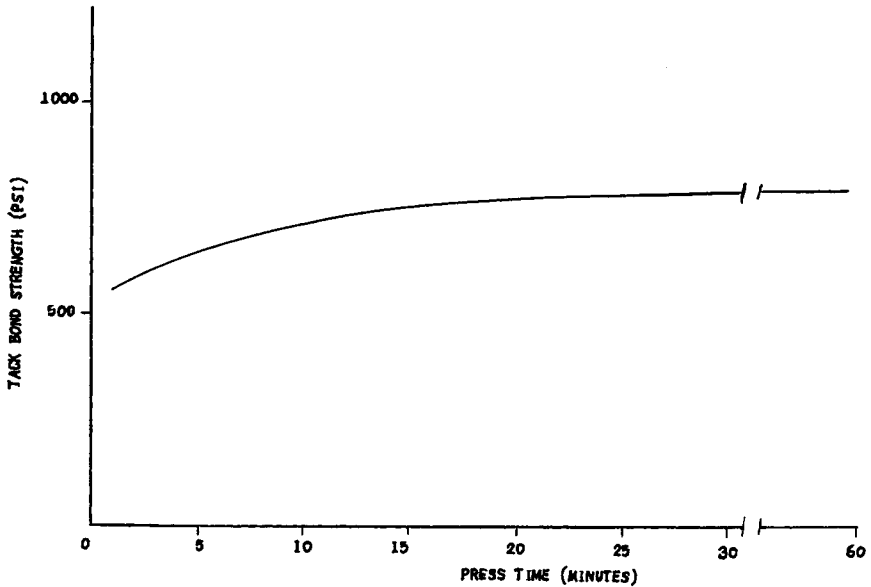
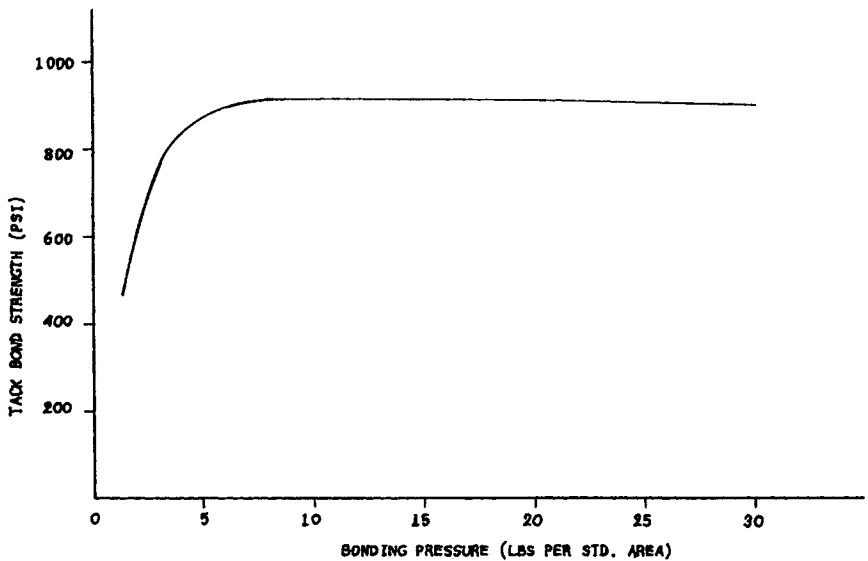Fig. 3. Effect of press time on the tack tensile strength of sample 6.

Fig. 4. Effect of bonding pressure on the tack tensile strength of sample 6.

links in the flexible segment, shows some tack when elongated.   Specimen 3, with 42 average chain links, displays considerable tack strength when sufficiently elongated.   Upon further increasing the average number of chain links, a high degree of tack is measured at zero elongation and the tack bond strength remains reasonably constant over the whole range of elongation.   The low, constant value of specimen 8 is due to the low
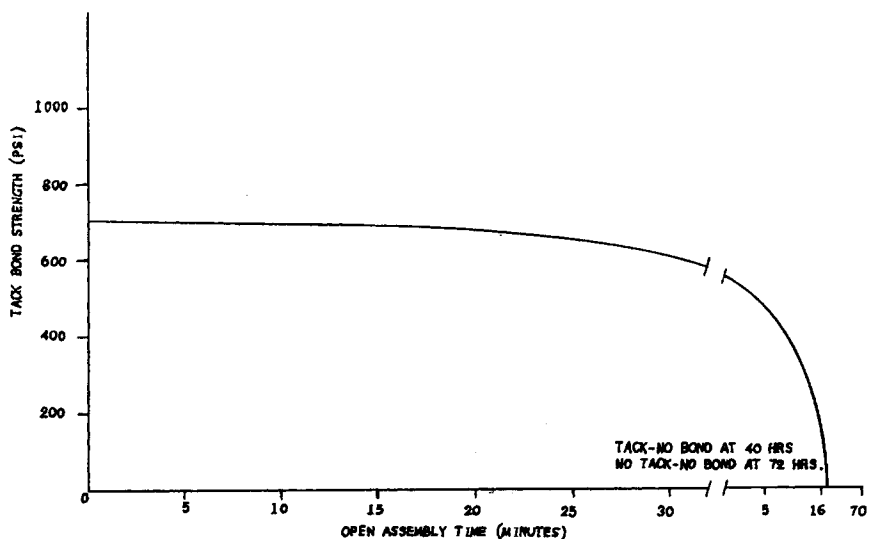
Fig. 5. Effect of open assembly time on the tack tensile strength of sample 6.

raw tensile strength of the polymer. It should be noted that, even at zero elongation, the surfaces of specimens have to be freshly cut to obtain the tack strengths indicated.

Addition of diepoxy resin reduces the tack strength, as shown in Figure 2. This is due to the additional crosslinks built up in the polymer which results in a reduction of the degrees of freedom of the polymer matrix.

The effect of contact time on tack bond strength under a given pressure is illustrated in Figure 3 for sample 6; this specimen exhibits maximum tack without requiring elongation. Evidently, most of the tack bond strength is built up within a few seconds.

Figure 4 shows that a minimum of about 5 psi pressure is required for highest tack bond strength. Higher pressures have no significant effect upon the tack strength. However, when a pressure of 2 psi is applied, the tack bond strength is found to be decreased by about one-third of the maximum value.

The freshly cut surface of a tacky urethane rubber (sample 6) retains its tack over a period of 30 min. (Fig. 5). The tack bond strength then decreases over a period of about 40 hr. to nearly zero.

These results indicated that the experiments should be extended to determine the effect of solvents on the uncut surface of the urethane polymers. Lap-joint shear samples, $4^1/_2 \times {}^1/_2 \times {}^1/_8$ in. thick, were prepared from specimen 6 and the surface cleaned with a cloth that had been sufficiently wetted with the solvent. After about 1 min. the surfaces of the ends of the test specimens were pressed together for 3 min. at 10 psi, forming a 1 in. overlap.

After a 24-hr. wait the samples were pulled apart by use of the Instron tester. The shear strength values are listed in Table II.

TABLE II
Effect of Solvents on Bond Shear Strength

Solvent used	Lap-joint shear strength, psi
Ethyl alcohol	117
Acetone	132
Methyl ethyl ketone	103
Benzene	76
Toluene	75
Dimethylformamide	88

It is evident that the bond shear strengths obtained are of a very significant magnitude.

Finally, the effect of the knife temperature during the cutting of the surfaces was studied (sample 6). Within the range from room temperature to 300°F. the tack tensile values were essentially the same, while the values decreased significantly when a knife with a temperature of 350°F. was used to cut the samples (Table III). This is evidently due to polymer breakdown.

TABLE III
Effect of Knife Temperature on Tensile Tack Strength
(Sample 6)

| Knife temperature, °F.	Tack tensile strength (aug.), psi
80	905
100	890
195	885
290	925
350	490

In these tests the tensile specimen was placed in the grips of the Instron tester and during cutting just enough tension was employed to maintain the vertical position of the sample. After 3 min. time, 20 psi pressure was applied for 5 min., the sample removed, and then left at room temperature for 24 hr. before measuring the tensile tack strength.

V. Discussion

The existence, *per se*, of tack in the urethane polymers tested indicates that the assumption of some researchers[2] that tack is due to the mobility of the chain ends and not due to the mobility of the polymer chain segments is in error. Since the polymers employed in this work are free from mobile endgroups, the tack measured is entirely due to the flexible chain segments.

It is important to note that tack at zero elongation is obtained only if the flexible chains possess or exceed a critical length of about 50 chain links. Below this critical chain length no tack is observed at zero elongation. The fact that this critical chain length is identical with that required by the Gaussian vector distribution for elastomeric chains[10,11] calls for comment.

In supporting the diffusion theory in the formation of tack, it has earlier been shown[2,7] that pendent groups reduce the tack bond strength, as do polar structures at room temperatures. The urethane polymer chains prepared and tested in this work are composed of two segmental species, i.e., the flexible polyether or polyester chains on the one hand and the rigid highly aromatic urea–urethane blocks of the type:
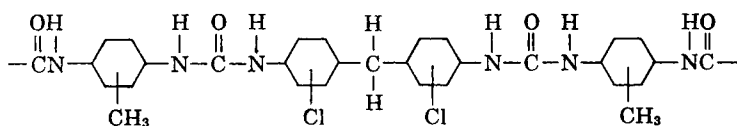
In these blocks rigidity, planarity, and polarity are augmented by resonance.

Thus the polymeric chains can be schematically described as consisting of flexible chains and rigid blocks (Fig. 6).

Figure 6.

Since such rigid building blocks along the polymer chains do not participate in the formation of tack,[3] the tack bond strengths measured in this work must be assumed to be originated solely by the action of the flexible chain segments.

TABLE IV
Molar Cohesive Energies

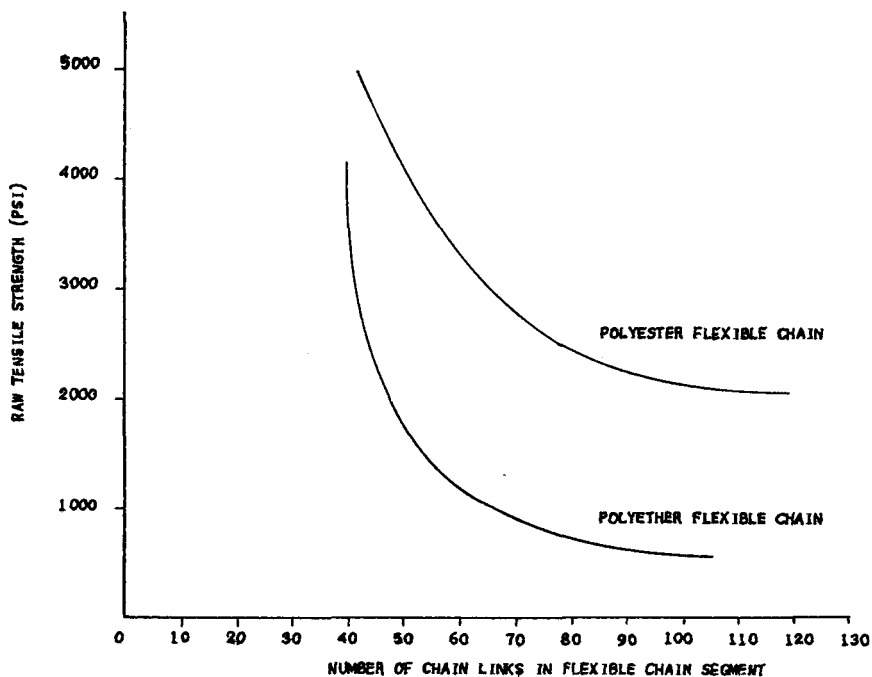| Group in polymer chain	Cohesive energy, kcal./mole[a]
—CH—	0.68
—O—	1.00
—COO—	2.90
—CH— (aromatic)	3.90
—CONH—	8.50
—OCONH—	8.74
—HN—CO—NH—	8.74

[a] Data of Beckwith et al.[1]

Fig. 7. Effect of number of chain links in flexible chain segment on the raw tensile strength of the polymers.

The results of this study indicate that the tack strength of the urethane polymers having 50 or more links in the flexible chain segments is independent of the frequency of the highly polar blocks along the chains. This must be interpreted as evidence that these polar blocks do not participate in the formation of tack.   If the polar blocks contributed to the diffusion process in any way, the tack bond strength should increase with the frequency of such blocks.

The cohesive energies contributed by such polar groups are 8 to 10 times greater than the energies imparted by ether and methylene linkages (Table IV).

In agreement with this, the inherent tensile strength values of the polymers employed in this study show that the raw strength increase of these polymers with increasing concentration of the polar blocks is indeed significant.   This is illustrated in Figure 7, in which the number of chain links between the rigid blocks is plotted against the raw tensile strength.

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Résumé

On a étudié le phénomène d'adhérence des élastomères uréthanne-urée, préparés à partir des prépolymères de polyéther ou de polyester et de 4,4'-méthylène-bis-(2-chloro-aniline). On a démontré que l'adhérence est obtenue à l'élongation zéro uniquement pour les polymères dans lesquels les chaînes flexibles, c.a.d. polyester ou polyéther, contiennent au moins 50 segments. Ceci est en accord avec les exigences de la fonction vectorielle de Gauss pour les élastomères. Les résultats suggèrent qu'en absence de fins des chaînes flexibles dans ces polymères l'adhérence doit être uniquement attribuée aux segments flexibles le long de la chaîne polymérique, tandis que les parties rigides dans la chaîne ne participent pas à la formation de l'adhérence.

Zusammenfassung

Die Erscheinung der Klebrigkeit wurde an Urethan-Harnstoffelastomeren aus Poly-äther- oder Polyestervorpolymerisaten und 4,4'-Methylen-bis(2-chloranilin) untersucht. Klebrigkeit bei Elongation Null wird nur bei Polymeren erreicht, bei welchen die biegsamen Ketten, d. h. die Polyester- oder Polyätherketten 50 oder mehr Kettenglieder enthalten. Das entspricht der Vorbedingung für die Gauss'sche Vektorfunktion bei Elastomeren. Die Ergebnisse zeigen, dass bei Fehlen flexibler Kettenenden in solchen Polymeren die Klebrigkeit nur durch Beiträge der flexiblen Segmente entlang der Polymerkette zustande kommt, während die starren Blöcke in der Kette nicht zur Klebrigkeit beitragen.