Adhesiveness of Polyethylene Mixtures

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INTRODUCTION

In a previous paper[1] the lowering of the peeling tension of polyethylene adhints (= adhesive joints) by addition of oleic acid was reported.   This note summarizes our observations on butt joints in which a polyethylene wax or its mixtures with several simple organic compounds acted as the adhesive.   The problem studied by us was that of the relation between the composition of an adhesive and the breaking stress of an adhint made with the latter.

This relation is likely to be different according to whether the change in composition does or does not alter the type of the joint from proper to improper or improper to proper.[2]   Examples of these two type alternations are outlined below as well as an example in which a proper adhint remained proper on the addition of an impurity but its breaking stress varied because the tensile strength of the adhesive varied with composition.   The approximate relation, valid for proper joints,

$$f = \frac{1}{\alpha}\left(\frac{\xi}{\beta} - s\right) \tag{1}$$

in which f is the breaking stress, α the stress concentration factor due to the difference in the mechanical properties of adherend and adhesive, ξ the molecular cohesion of the adhesive, β the stress concentration factor due to the inhomogeneity of all solids, and s the shrinkage stress, indeed shows that, in favorable circumstances, breaking stress of an adhint varies similarly to the tensile strength of the adhesive because this strength is not very different from ξ/β.

EXPERIMENTAL PROCEDURE

A. Breaking Stress

This was measured as before:[3] Several stainless steel (Type 303) cylinders, approximately 5 cm. long and 1.90 cm. in diameter, were machined to form a pin, 0.3175 cm. tall and 0.635 cm. in diameter, in the center of one of the basis planes.   The cylinders were stood vertically, with the pin upwards.   Three steel spacers, each 0.3200 cm. tall, were placed around

the pin.   A grain of a solid polyethylene mixture (0.0020 g.) was put on the polished flat pin surface, and another cylinder, having no pin, mounted on it.   The adhesive was melted by means of a heating tape wrapped around the cylinders and permitted to cool.   After cooling, an adhesive film 0.0025 cm. thick remained between the pin and the flat surface of the upper cylinder.

The adhints were broken in tension in a tester of the "inclination balance" type, at room temperature and room humidity.   Particular attention was paid to the correct alignment of the holders.

B. Tensile Strength

The specimens employed for the determination of tensile strength had approximately the dumbbell shape and were cast in two distinct operations. First, polished and degreased aluminum foil, 0.005 cm. thick, was rolled to a hollow cylinder, about 12 cm. long and 0.62 cm. in diameter.   The hollow was filled with molten polymer, and more polymer added when the first portion solidified and shrank.   After cooling, the foil was dissolved away in 3% sodium hydroxide solution, and the remaining polymer rod washed, dried, and inspected for bubbles and other defects.

In the second operation, aluminum foil cups, about 2.5 cm. tall, 1.2 cm. in diameter, and with wall thickness of 0.008 cm., were made and strings inserted through holes in the cup bottom.   The cups were filled with molten polymer, and a pre-heated end of the above rod was inserted in the melt; after this end cooled, the other end was in the same manner inserted in another cup.

Thus, a dumbbell-shaped solid with strings sticking out at both extremities was obtained.   For the determination of the tensile strength, the strings were attached to the jaws of the "inclination balance" tester.   The correct alignment of the two strings was essential for meaningful results.

C. Materials

The adhesionable polyethylene wax was prepared as described earlier[4] from a material whose molecular weight is given by the manufacturer as 4000.   As impurities, the following compounds were used: (1) oleic acid, "Century 1050 LP" donated by Wallace & Tiernan Inc.; (2) ethyl palmitate, the purest commercial sample; (3) stearone, i.e., diheptadecyl ketone, donated by Argus Chemical Corporation; and (4) Ionol, i.e., 4-methyl-2,6-di-*tert*-butylphenol, donated by Shell Chemical Co.

EXPERIMENTAL RESULTS

The results are presented in six graphs.   In all instances, the concentration of the second ingredient (adhesionable polyethylene being the first) is plotted along the abscissa.   It is expressed in the percentages of the total; for instance, a mixture consisting of 30 g. of ethyl palmitate and 70 g. of polyethylene is designated as 30% ethyl palmitate.

The ordinate of Figure 1 represents the breaking stress of butt joints (curve *1*) and the tensile strength of 12 cm. long columns (curve *2*) of mixtures of polyethylene and oleic acid.   Figure 2 is analogous to Figure 1
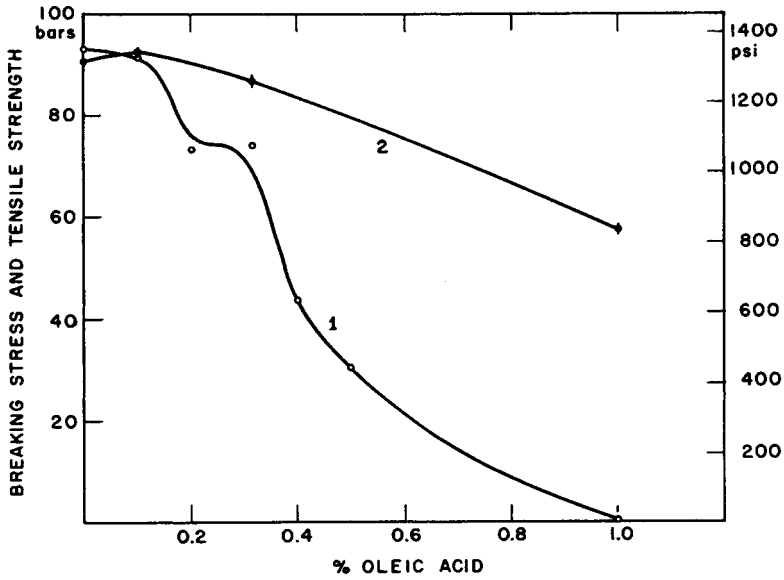

Fig 1. Breaking stress of butt joints (curve *1*) and tensile strength (curve *2*) in the polyethylene-oleic acid series.
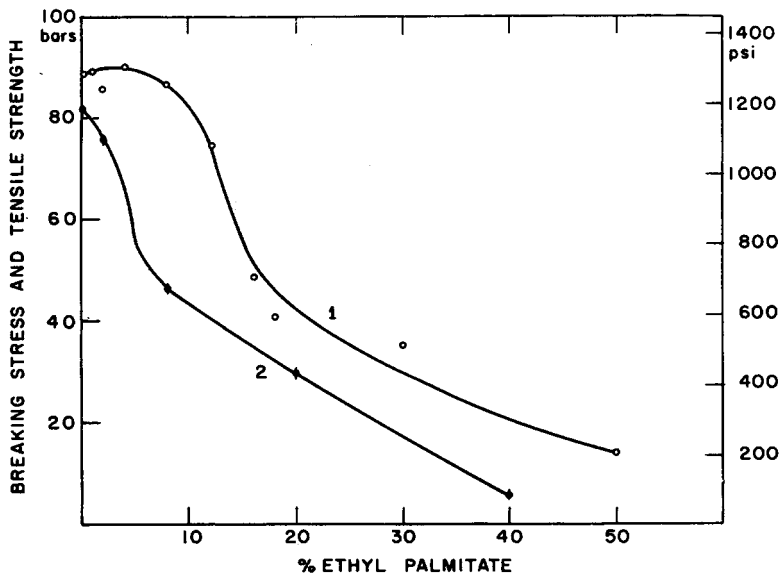

Fig. 2. Breaking stress of butt joints (curve *1*) and tensile strength (curve *2*) in the polyethylene-ethyl palmitate series.

but refers to polymers containing ethyl palmitate.   In Figure 3 the ordinate is the ratio of adhint strength to tensile strength; OA indicates oleic acid and EP, ethyl palmitate.   Total relative elongation (or maximum strain) is plotted along the ordinate of Figure 4.   Figure 5 is analogous to Figure 1
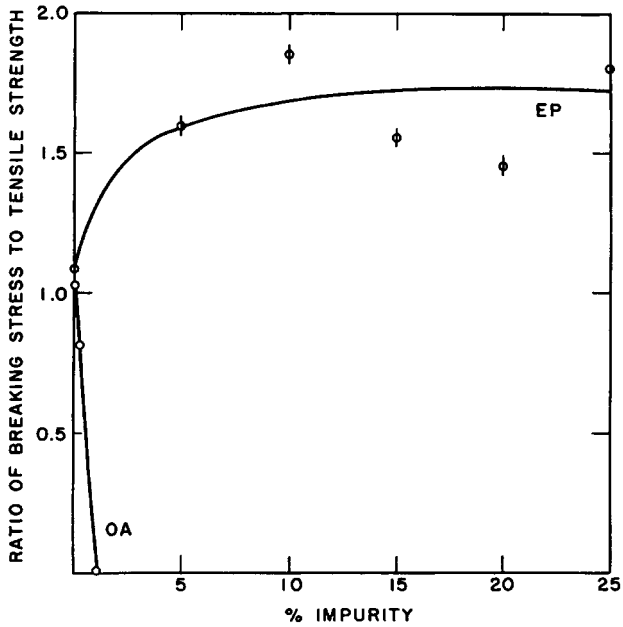

Fig. 3. Ratio of adhint strength to tensile strength for the oleic acid series (OA) and the ethyl palmitate series (EP).
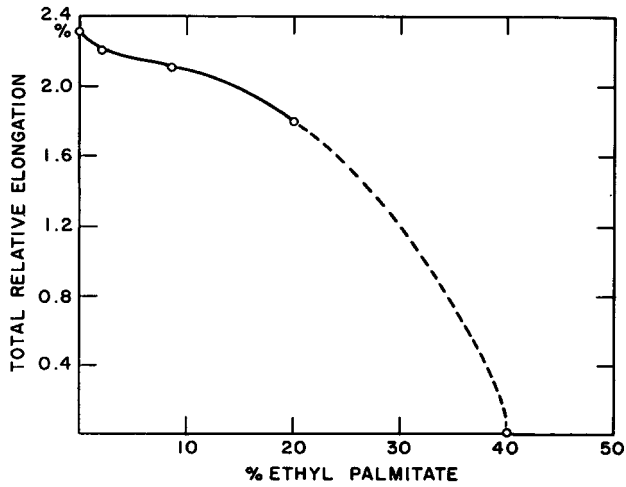

Fig. 4. Total relative elongation of mixtures of polyethylene and ethyl palmitate

and 2 but is valid for contamination with stearone.   Figure 6 presents the breaking stress of butt joints made with polyethylene + Ionol.

The points marked on the graphs are the average values.   The number of single experiments corresponding to one point varied from 52 (for the breaking stress of pure polyethylene adhints in the oleic acid series) to 4.
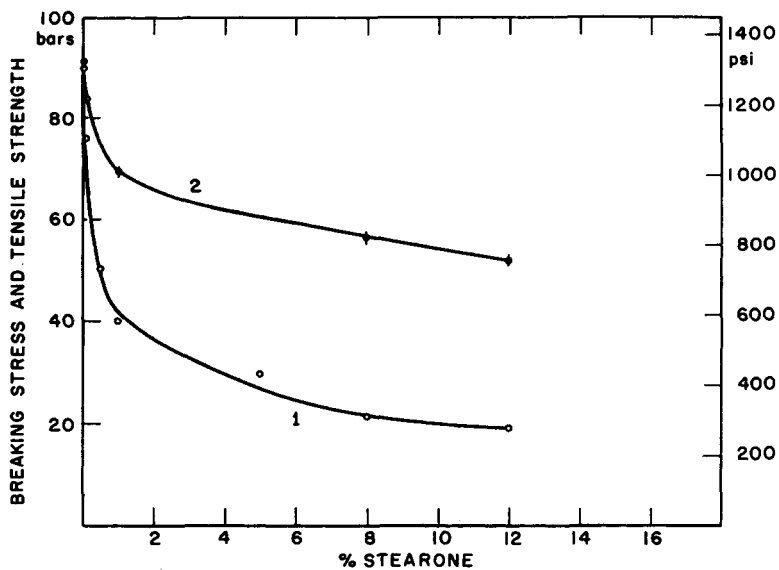

Fig. 5. Breaking stress of butt joints (curve *1*) and tensile strength (curve *2*) in the polyethylene-stearone series.
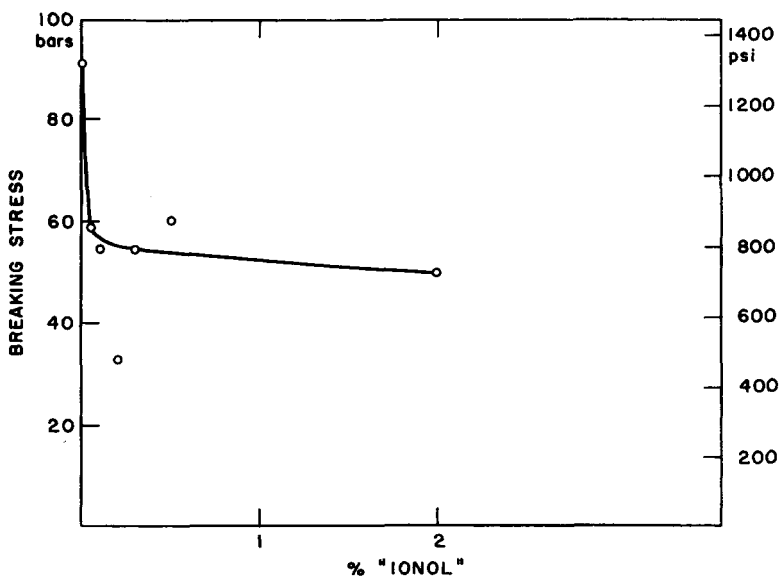

Fig. 6. Breaking stress of butt joints in the polyethylene-Ionol series.

MEANING OF THE RESULTS

A. Oleic Acid

The system of polyethylene wax plus oleic acid seems to be a perfect instance of transition from proper to improper adhints.   When the content c of oleic acid is less than 0.1% approximately, the breaking stress f remains equal to that of adhesionable polyethylene (Fig 1, curve 1).   When c increases beyond 0.2%, f decreases when c increases and becomes immeasurably small (i.e., smaller than about 1 bar or 10 psi) when c reaches the value of 1%.   The visible location of the rupture also changes near $c = 0.2\%$; at lower c values, polymer can be seen on both adherends with the unaided eye, while at higher c one of the adherends emerges after measurement with a metallic or oily gloss.

These effects are in accord with the assumption[4] that syneresis takes place in the system under consideration.   It appears that oleic acid is soluble in solid polyethylene wax (as used by us) to the extent of 0.1–0.2%. When this concentration is exceeded, the excess concentrates on grain surfaces, and oleic acid films along the polymer-adherend boundaries cause the adhint strength to be low.

The effect of oleic acid on the tensile strength f_m of polyethylene in small (Fig. 1, curve 2) and cannot account for the rapid decrease of f shown by curve 1.

Compounds related to oleic acid (e.g., stearylamide) sometimes are used as mold-release or parting agents.   Our experiments on oleic acid render it probable that these agents act mainly by forming weak boundary layers and that, when the shaped goods are taken out of the mold, both their surface and the inner surface of the mold remain coated with the agent. Thus, this effect also seems to belong to rheology rather than to surface chemistry.

B. Ethyl Palmitate

Although ethyl palmitate, chemically, is a close relative of oleic acid, its behavior is entirely different.   Its effects on f and f_m, see Figure 2, are very similar, and we may conclude that adhints made with polyethylene-palmitate mixtures are weaker than those containing pure polyethylene simply because the mixtures themselves are weaker than the pure material. Visual inspection corroborated this conclusion since, in all instances, some polymer was visible on both fracture surfaces.

The difference between oleic acid and ethyl palmitate is particularly striking when the ratio f/f_m is plotted as a function of the concentration of the contaminant, Figure 3.   Formation of a weak boundary layer lowers this ratio to almost zero, while in proper adhints the ratio remains above unity.

For unmixed adhesionable polyethylene the value of f/f_m was about 1.03 in the oleic acid series and about 1.09 in the palmitate series.   In an earlier

investigation,[3] the ratio of f of polyethylene wax adhints, 0.0025 cm. thick, to f_m was found to be greater than 2; it is now believed that the specimens which served for the previous measurements of f_m were less uniform than the new specimens and thus afforded too low values for the tensile strength. The new determinations of the adhint strength were in a satisfactory agreement with those reported in Ref. 3.

An attempt was made to account for the increase of f/f_m ratio with increasing concentration c of ethyl palmitate. As indicated by eq. (1), f would increase with c if a greater c means a smaller concentration factor α. Generally speaking, α decreases when the mechanical properties of the adherend and the adhesive become more similar to each other. The total relative elongation of stainless steel is greater than that of polyethylene wax (about 50% as against approximately 2%). If ethyl palmitate raises the extensibility of polyethylene, the increase of f/f_m with c can be attributed to this effect. In reality, see Figure 4, the total relative elongation of mixtures is less than that of adhesionable polyethylene alone, and α can not be made responsible for the observed relation between f/f_m and c.

Presumably, this relation is caused by factor β. The value of β is determined by the worst flaw in the specimen. The probability of a particularly bad flaw is smaller the more uniform the specimen and the smaller it is. The size effect is one of the reasons for the increase of f/f_m in thin adhints, but, at a constant adhint thickness, this ratio is likely to be greater the less uniform the sample. In other words, in a very uniform material the weakest spot in a short specimen may be only a few per cent stronger than in a long specimen, while a long specimen of a coarsely nonuniform material may contain a flaw only half as strong as the weakest spot in the short sample. Adhesionable polyethylene is a more uniform substance than its mixtures with ethyl palmitate and, hence, its β probably depends less on the sample dimensions than is the case in mixtures.

C. Ethyl Palmitate and Oleic Acid

We attribute the different effects of oleic acid and ethyl palmitate on f to the small solubility of the former and the easy solubility of the latter in solid polyethylene. If this explanation is correct, we may predict that polyethylene containing both oleic acid and ethyl palmitate in suitable amounts will give rise to proper joints.

To understand the reasoning, consider the example of water, benzene, and acetone. Benzene is almost insoluble in water but is soluble in acetone which is miscible with water in all proportions; and the solubility of benzene in water-acetone mixtures is greater than what it is in water alone. Substitute, in the foregoing sentence, oleic acid for benzene, polyethylene for water, and ethyl palmitate for acetone; we conclude that mixtures of polyethylene and palmitate should dissolve larger amounts of oleic acid than does pure polyethylene. Hence, the minimum concentration of oleic acid, at which syneresis occurs and a weak boundary layer forms, should be greater in the presence of palmitate.

Only one experiment (repeated several times) was performed to test this conclusion. A mixture of polyethylene 94, ethyl palmitate 5, and oleic acid 1 part by weight gave proper joints which broke at 73–94 bars (1060–1360 psi), i.e., had practically the breaking stress of polyethylene adhints. Thus, the minimum concentration for syneresis was shifted from 0.1–0.2% to >1% of oleic acid.

A commercial polyethylene wax, which showed immeasurably small breaking stresses, also was made "adhesionable" by the addition of 5 parts ethyl palmitate to 95 parts wax. Apparently, the impurities in this product also were soluble in the palmitate.

According to one of the older theories, adhesion intensity should increase with the polarity of the adhesive. It is instructive to compare this conclusion with our experimental results. Both oleic acid and ethyl palmitate are, and polyethylene is not, polar. In Figure 1, polar addition drastically lowers f; in Figure 2, polar addition has a small effect on f; and when ethyl palmitate is added to impure polyethylene, it strikingly increases f. Polarity can have a positive or a negative, a negligible or a marked effect on breaking stress of adhints, depending on solubilities. Solubility is important, not polarity.

D. Stearone

$CH_3(CH_2)_{16}CO(CH_2)_{16}CH_3$ was selected as contaminant because oxidation of polyethylene in air is likely to give rise to long-chain ketones. Thus, mixtures with stearone may be considered as model materials for partly oxidized polyethylene.

The effect of stearone (Fig. 5) is greater than that of ethyl palmitate but less than that of oleic acid. Because f_m is consistently and markedly greater than f, formation of a weak boundary layer is probable. This formation could not be confirmed by visual inspection of broken adhints because, for the unaided eye, stearone was indistinguishable from polyethylene. However, some observations supporting the hypothesis were made during the preparation of bulk samples of the polyethylene-stearone series. The 1% and 8% mixtures did not adhere to the aluminum tube into which they were cast.

It was tempting to explain the difference between curve 1 of Figure 1 and curve 1 of Figure 5 by the fact that stearone is solid at room temperature (it melts at 88°C.); if stearone separates as a thin film between polyethylene and steel in the adhints, the breaking stress of the adhint would be related to the tensile strength of stearone and, consequently, would be greater than in the system with oleic acid which is a liquid. To test this concept, adhints in which stearone alone was the adhesive were prepared and tested. Their breaking stress was very small (near 1 bar or 10 psi) in two experiments, i.e., not sufficient to account for the adhint strength. Usually, the adhints were broken a few hours after the preparation; perhaps this time was not sufficient for stearone to complete its migration to the surface. Further experimental work is indicated.

E. 4-Methyl-2,6-di-*tert*-butylphenol

No results significant for understanding adhesion were obtained with this compound because it decomposed (forming a greenish-yellow liquid) when heated above 120°C. and, at this and higher temperatures, apparently chemically reacted with stainless steel. The liquid was easily supercooled but crystallized at room temperature when touched with a grain of fresh Ionol. Thus, it was impossible to know whether, during the tensile test, the boundary layer (if any) consisting of Ionol was solid or liquid. The reaction with steel rendered restoration of a clean steel surface very difficult; a cylinder once heated in contact with a polyethylene-Ionol mixture required several polishing treatments and several heatings with adhesionable polyethylene before the f for the latter reached its usual value.

The poor reproducibility of the results, due to the above (and perhaps other) causes is visible in Figure 6.

4-Methyl-2,6-di-*tert*-butylphenol is used as an antioxidant in industry. Its exceptional ability to ruin the adhesiveness of polyethylene calls for caution when incorporating it into materials which are to be glued or to be employed as adhesives.

References

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Synopsis

The effect of additions to polyethylene wax on the breaking stress f of butt joints between two steel cylinders depended on the nature of the addition. Oleic acid lowered f in concentrations as small as 0.2%, and in presence of 1% oleic acid f was immeasurably small. Ethyl palmitate slightly diminished f (to about $^1/_5$th of the initial value when the amounts of polyethylene and palmitate were equal), but this decrease was wholly due to the weakening of the polymer itself, and the ratio of f to the tensile strength of polyethylene-palmitate mixtures was >1 at all compositions. Thus, with oleic acid above 0.2% improper, and with ethyl palmitate at all percentages, proper adhints were obtained. Stearone apparently formed a weak boundary layer and 4-methyl-2,6-di-*tert*-butylphenol gave erratic results as it decomposed on heating and apparently reacted with steel. Addition of ethyl palmitate to polyethylene contaminated with oleic acid made the mixture adhesionable. The solubility of the contaminant in solid polyethylene was more important than polarity. The relation between the composition of an adhesive and the breaking stress of its adhints can be understood if the distinction between proper and improper joints is kept in mind.

Résumé

L'effet produit par des additifs incorporés au cire de polyéthylène entre deux cylindres d'acier sur la résistance à la traction f de joints (bout-à-bout) dépend de la nature de

l'additif. L'acide oléique abaisse f en concentration aussi faible que 0.2%, et en présence de 1% d'acide oléique f était non-measurable. Le palmitate d'éthyle diminue f faiblement (jusqu'au $1/5$ ème de la valeur initiale lorsque les quantités de polyéthylène et de palmitate sont égales) mais cette diminution est complètement due an ramollissement du polymère lui-même, et le rapport de f à la résistance à la traction des mélanges polyéthylène-palmitate était >1 pour toutes compositions. Ainsi, on a obtenue des joints de la classe "impropre" avec l'acide oléique au dessus de 0.2%, et ceux de la classe "propre" avec le palmitate d'éthyle à tout pourcentage. La stéarone forme apparemment une couche interfaciale faible, et le 4-methyl-2,6-di-*tert*-butylphenol a donné des résultats non-reproductibles vu qu'il se décompose par chauffage et réagit apparemment avec l'acier. L'addition de palmitate d'éthyle au polyéthylène contaminé avec de l'acide oléique rend le mélange adhésif. La solubilité de l'agent contaminant dans le polyéthylene solide est plus importante que sa polarité. La relation entre la composition d'un adhésif et la résistance de rupture de ses joints peut être comprise, si la distinction entre les joints propres et impropres est gardée à l'esprit.

Zusammenfassung

Der Einfluss von Zusätzen zu Polyäthylenwachs auf die Bruchspannung f von Stossfugen zwischen zwei Stahlzylindern hängt von der Natur des Zusatzes ab. Ölsäure setzte noch bei Konzentration von 0,2% f herab und in Gegenwart von 1% Ölsäure war f unmessbar klein. Äthylpalmitat gab eine schwache Verringerung von f (auf etwa 1/5 des Anfangswertes bei gleicher Menge Polyäthylen und Palmitat); diese Verringerung rührte aber zur Gänze von der Erweichung des Polymeren selbst her und das Verhältnis von f zur Zugfestigkeit von Polyäthylen-Palmitatmischungen war bei allen Zusammensetzungen 1. Es wurden daher mit Ölsäure oberhalb 0,2% ungeeignete und mit Äthylpalmitat bei allen Prozentgehalten brauchbare Verbindungen erhalten. Stearone bildete offenbar eine schwache Grenzschichte und 4-Methyl-2,6-di-*tert*-butylphenol lieferte stark streuende Ergebnisse, da es sich beim Erhitzen zersetzte und mit Stahl reagierte. Zusatz von Äthylpalmitat zu Polyäthylen, das mit Olsäure verunreinigt war, machte die Mischung adhäsionsfähig. Die Löslichkeit der Verunreinigung in festem Polyäthylen besass grössere Bedeutung als die Polarität. Die Beziehung zwischen der Zusammensetzung eines Klebestoffes und der Bruchspannung seiner Verklebungen ist verständlich, wenn der Unterschied zwischen geeigneten und ungeeigneten Verbindungen beachtet wird.