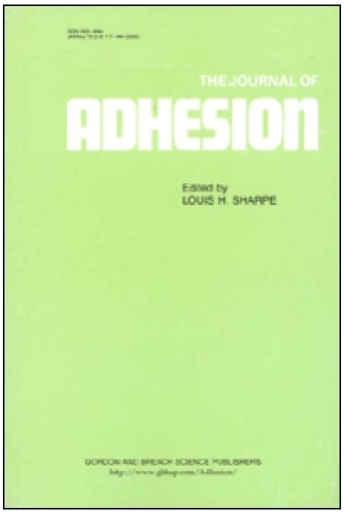

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Lipatov, Yu. , Kuskin, A. N. and Sergeeva, L. M.(1974) 'An Investigation of the Relation Between the Adhesion of Polyurethanes to Solid Surfaces and Network Structure', The Journal of Adhesion, 6: 3, 259 — 273
To link to this Article: DOI: 10.1080/00218467408075030
URL: http://dx.doi.org/10.1080/00218467408075030

J. Adhesion, 1974, Vol. 6, pp. 259–273

Printed in Scotland

An Investigation of the Relation Between the Adhesion of Polyurethanes to Solid Surfaces and Network Structure†

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INTRODUCTION

It is known that polymer interaction with solid surface limits the mobility of the polymer chain and this consequently affects the physico-chemical properties of the polymer.[1] In the course of polymer lattice formation, the presence of a solid surface leads to the formation of more defective spatial network.[2]

Our previous investigations have shown[3] that macromolecular interaction with the substrate has a definite contribution to the effective network density of polyurethane coatings formed on a metal surface. This was established in the course of the determination of crosslinking density using the Flory–Reiner method for polyurethane films formed on tetrafluoroethylene, i.e. at minimal interaction with the surface (so called "free" films) and coatings formed on aluminum foil. In the latter case an increase in crosslinking density of the polyurethane coating was found by comparison with free films which was ascribed to the formation of additional bonds between the polymer and substrate.

Obviously, the number of contacts at polymer-solid surface and subsequently adhesion will depend to a great extent on the mobility of chain segments between lattice nodules which in turn is governed by the chemical structure of the polymer.

The purpose of this paper is to establish a relationship between polyurethane adhesion to solid surfaces and the structure of the network on the substrate as well as their mutual influence.

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† The translation of this paper by Dr. Ahmed El-Shimi, Lever Brothers Company, Edgewater, New Jersey, is gratefully acknowledged.

EXPERIMENTAL

The polyurethane coatings studied were based on oligodiethylene—ODA—having molecular weights 600 and 1200 respectively and a copolymer of tetrahydrofuran with 25% oxypropylene (THF—25%, OP—1200), and also an adduct toluene diisocyanate with trimethyl propane (TDI—TMP).[4] For adduct synthesis TDI was used having ratios 2.4 and 2.6 of isomers equal to 65 : 35. The density of the lattice structure was controlled by changing the mole ratio of the isocyanate to hydroxylic groups.

The adhesion properties of the coatings were studied with the help of our previously described method for the determination of the quasi-equilibrium work of adhesion using a roller adhesion meter.[5] The films were cast on the test roller from cyclohexanone solution, followed by drying the films at 80–100°C with continuous rotation of the roller which was made of steel, brass, glass or an aluminum alloy.

The effective crosslinking density, characterized by the value of average molecular weight between lattice nodules M_c, was determined by the Flory–Reiner method in the presence of the solid surface (metal and glass) using thin foil on which the polymer film was cast. The results thus obtained were compared with network density of free films. The latter was obtained by pouring polyurethane composition on the fluoroplastic from which the films were detached upon hardening.

The superamolecular structure of polyurethanes was investigated by electron microscopy using carbon replicas of surfaces which were subjected to etching by gas discharge in the presence of oxygen according to a method described in Ref. 6.

RESULTS AND DISCUSSION

We have pointed out earlier that the solid surface influences the polymer structure. It was therefore found necessary to study the effective distance to which the substrate could extend its effect. For this purpose we have determined the effective crosslinking density of free films and films cast on glass and metallic substrates. The thickness of these films (coatings) ranged from 10–300 μ.

Figure 1 shows the dependence of M_c on coating thickness of ODA–1200. As can be seen, the effective crosslinking density of free films, i.e. films obtained under conditions where polymer–solid interaction is practically nonexistent, does not depend on the thickness in the range studied. However, the value of M_c of films on substrates decreases with decrease in film thickness.

As the film thickness increases, the difference between the values of M_c for free films and films on substrates decreases and at thickness equal to 120 μ and higher, the values of M_c in both cases become equal.

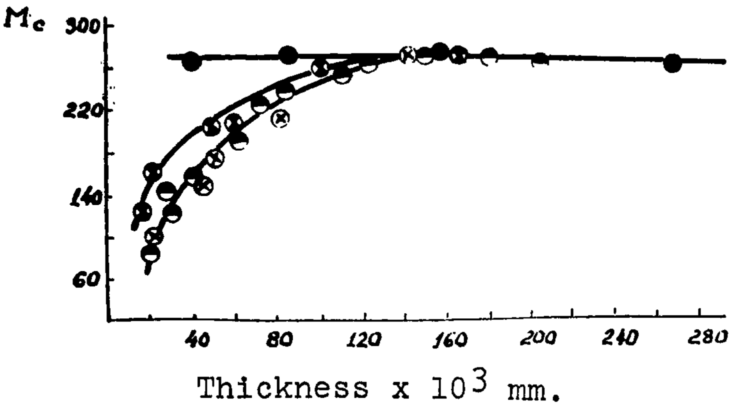


FIGURE 1 Effect of coating thickness—ODA-1200—on M_c. ● Free film, ⊗ coating on steel, ◓ on brass, ⨂ on duralumin.

These results confirm our earlier conclusions[1] that the influence of the substrate has an important bearing on the structure of linear as well as crosslinked polymers and extends to an appreciable distance in the polymer depending on the nature and physical state of the given polymer.

We have therefore proceeded to use films of equal thickness for the determination of M_c in order to obtain comparative results.

Figure 2 is a plot of M_c versus initial ratio of isocyanate to hydroxyl groups which characterizes the "chemical" crosslinking density of polyurethane coatings obtained from oligoesters. The graph shows that the curves exhibit some minimum in the interval where the isocyanate groups are twofold in excess. Obviously, initially the increase in the excess of isocyanate groups leads to an increase of the effective crosslinking density, and further increase in this ratio in excess of two leads to the decrease in effective network density resulting from a decrease in the number of chemical and physical nodules: firstly—formation of defective chemical network resulting from extreme limitation in the course of the final stages of the crosslinking reaction on the chain mobility at high NCO/OH ratios[3]; secondly—decrease in chain flexibility at high concentration of polar groups. The decrease in segment flexibility of the chains makes it more difficult for the chains to adapt to the surface and consequently decreases the number of contacts at the polymer–substrate interface. The maximum effective crosslinking density is observed at a ratio NCO/OH = 2 : 1. This is reflected on the value of the quasi-equilibrium work of adhesion.

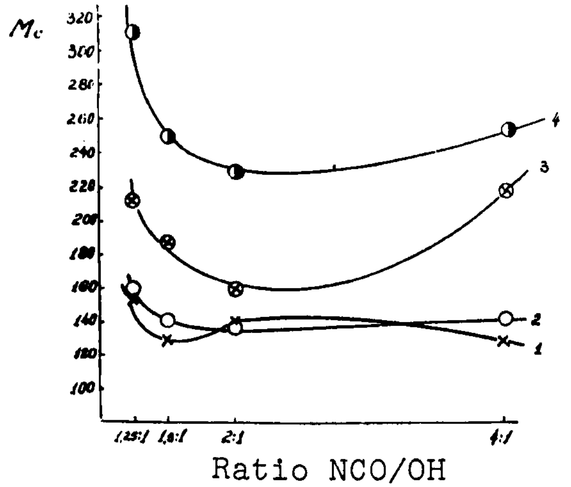


FIGURE 2. Effect of NCO/OH ratio for coatings based on ODA-1200 on M_c: 1-steel, 2-brass, 3-duralumin, 4-"free" films.

Figure 3 shows the experimental results as a plot of adhesion versus "chemical" crosslinking density. Maximum adhesion is observed at a ratio NCO/OH = 2 (minimum M_c). If we consider the dependence of adhesion on effective crosslinking density as the sum total of chemical and physical nodules (links) the resultant function is presented in Figure 4.

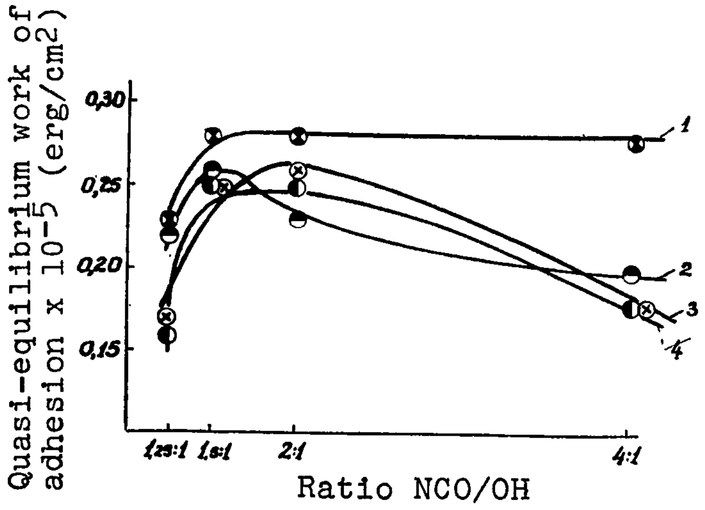


FIGURE 3. Effect of NCO/OH ratio for coatings based on ODA-1200 on the quasi-equilibrium work of adhesion.

The experimental dependence of adhesion on polar groups concentration indicates that the normally observed increase in adhesion bonding in the adhesive–substrate system resulting from introduction of functional groups in the adhesive macromolecule cannot be infinite.[7, 8] This confirms the conclusions expressed in,[9] that for every adhesive–substrate system there exists an optimum content of functional groups leading to maximum adhesion.

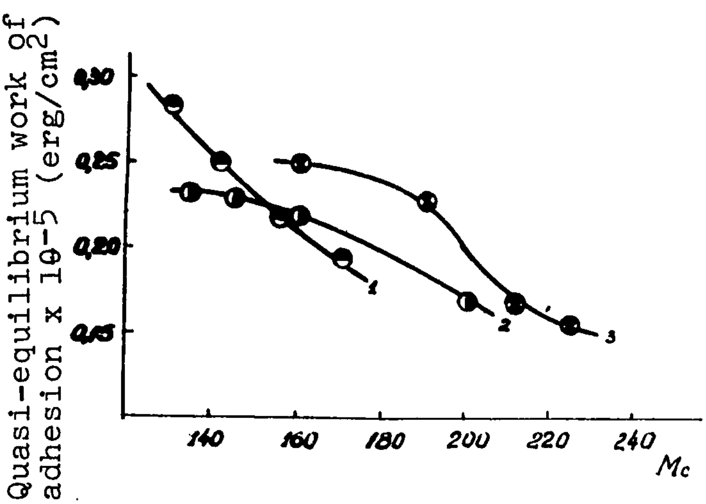


FIGURE 4 Effect of M_c for coatings based on ODA–1200 on the quasi-equilibrium work of adhesion. 1—steel, 2—brass, 3—duralumin.

Inspection of Figures 3 and 4 shows that in our systems adhesion decreases in the following order according to the nature of the substrate: steel > brass > duralumin > glass. The same sequence was observed also in the case of TFH–25% OP–1200 on the same substrates. It should be noted that the surface tension of the substrate materials decreases in the same sequence as the work of adhesion determined by us for the same surfaces. It is possible that this may reflect stronger interaction between the investigated polymers and metals which is higher than glass.

It is interesting to compare the results for the adhesion of coatings based on oligoethers and esters with the same molecular weight. Table I shows the data for the quasi-equilibrium work of adhesion of polyurethanes based on ODA–1200 and THF–25% OP–1200. As can be seen, the change in the value of the work of adhesion is in the same order for all substrates. Furthermore, adhesion in the case of oligoether is higher than oligoester with the same molecular weight. This can be ascribed to the difference in the interaction energy between polymeric chains in both cases. It is known that intermolecular attraction in polyurethanes based on esters is significantly higher than those based on oligoethers.[10] Consequently, the segment flexibility between chain links in the case of esters is low. This leads to less attachment to the surface than in the case of polyurethanes segments based on oligoethers. In addition, the number of contacts between the polymer and surface will be less in the case of coatings based on oligoesters compared to oligoethers which results in decreased adhesion. Besides the aforementioned reasons, it is also necessary to consider the difference in reactivity between oligoethers and esters, which bears on the network structure in polyurethanes and their adhesion to various surfaces.

TABLE I

Quasi-equilibrium work of adhesion of polyurethane coatings as a function of oligoether type, ratio of NCO/OH groups and nature of solid surface

Oligoether	ODA-1200				THF-15% PO-1200	
Ratio NCO/OH	1.25 : 1	1.5 : 1	2 : 1	4 : 1	2 : 1	4 : 1
Substrate	Quasi-equilibrium work of adhesion × 10^{-5} erg/cm^2					
Steel	0.23	0.28	0.28	0.28	0.47	1.97
Brass	0.22	0.26	0.23	0.20	0.34	1.50
Duralumin	0.16	0.25	0.25	0.18	0.34	0.75
Glass	0.17	0.25	0.26	0.18	0.27	0.30

TABLE II

Effect of molecular weight on the quasi-equilibrium work of adhesion of polyurethane coatings based on oligoesters

		[NCO] 10^{-3} mole cm^{-3}	Quasi-equilibrium work of adhesion × 10^{-5} erg/cm^2			
Oligoether	NCO/OH		steel	brass	duralumin	glass
ODA-1200	1.25 : 1	1.17	0.23	0.22	0.16	0.17
	1.5 : 1	1.24	0.28	0.26	0.25	0.25
	2 : 1	1.58	0.28	0.23	0.25	0.26
	4 : 1	2.16	0.28	0.20	0.18	0.18
ODA-600	1.25 : 1	1.85	0.64	—	0.38	0.63
	1.5 : 1	1.85	1.24	0.59	1.24	1.18
	2.0 : 1	2.22	1.45	1.24	1.27	1.38

In order to study the molecular weight effect of starting oligoesters on adhesion we have prepared coatings based on oligodiethylene adipinate with molecular weights 600 and 1200.

The results of the values of the quasi-equilibrium work of adhesion of coatings based on ODA–600 and ODA–1200 are represented in Table II. It can be seen that the work of adhesion in the case of ODA–600 in all cases is greater than coatings based on ODA–1200. It is probable that the reason for the observed trend is the increase of the concentration of polar groups, specifically the urethane groups in unit volume due to the decrease in molecular weight of the oligoether giving rise to an increased possibility of polymer-surface bond formation.

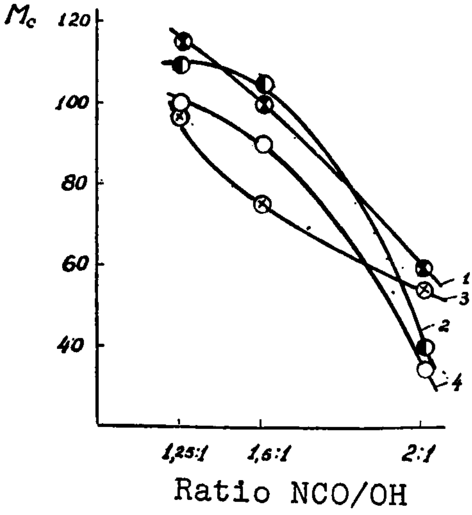


FIGURE 5 Effect of NCO/HH ratio for coatings based on ODA–600 on M_c. 1—brass, 2—duralumin, 3—glass, 4—"free" film.

Figure 5 shows the plot of experimental M_c values as a function of the molar ratio of isocyanate to hydroxyl groups for coatings based on ODA–600 in the presence of different substrates. Figure 6 represents relationships between the quasiequilibrium work of adhesion and the effective crosslinking density as expressed by the value of the average molecular weight between the network links (M_c).

The results presented in Figure 5 indicate that the effective crosslinking density of free films in most cases is higher than in films on solid surfaces.

The decrease in the effective network density of polymers based on molecular weights of oligoesters in the presence of solid surfaces as compared to free films has been described by us in Ref. 3. The observed phenomenon may be related to the effect of the solid surface on the polymerization process, leading to the formation of a more defective network. It could also be related to the increase of polymer chain stiffness with decrease in molecular weight of oligoethers leading to a lower number of contacts with the surface.

Also, adhesion has a maximum value which corresponds to the lowest M_c values.

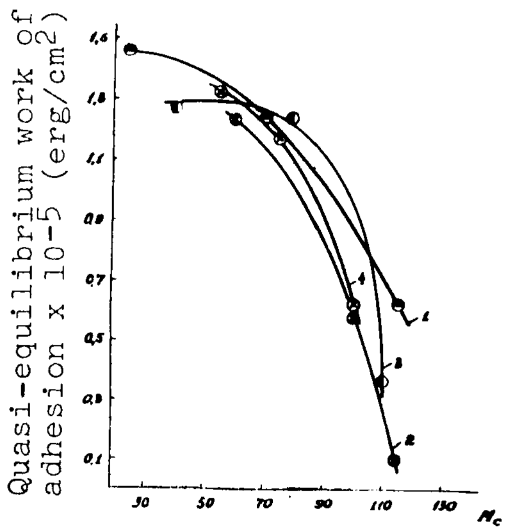


FIGURE 6 Effect of M_c on the quasi-equilibrium work of adhesion for coatings based on ODA-600: 1—steel, 2—brass, 3—duralumin, 4—glass.

Thus, the above results indicate that the network structure of polyurethane coatings, chain segment flexibility between nodules (links), and concentration of polar groups in unit volume are determined in many instances by the nature and molecular weight of the oligoether and subsequently the degree of polymeric chain interaction with the solid surface. Obviously all these factors affect the adhesion of the coating to the surface.

As expected the superamolecular structure of the coatings was found to depend on the above described factors.

Electron microscopic investigations of free polyurethane films, within the limit of experimental resolution (100 Å), have shown that their morphology bears a globular character which is usually observed for crosslinked polymers.[11, 12] An example for this type of structure is shown on Figure 7. The value of structural formations and their packing density, which are the basis for our assessment of the quantity of globules per unit area, is determined by the consistency of the spatial network, and the nature and molecular weight of the oligoether blocks for those coatings studied. Thus, on the one hand an increase in the consistency of the spatial network leads to finer

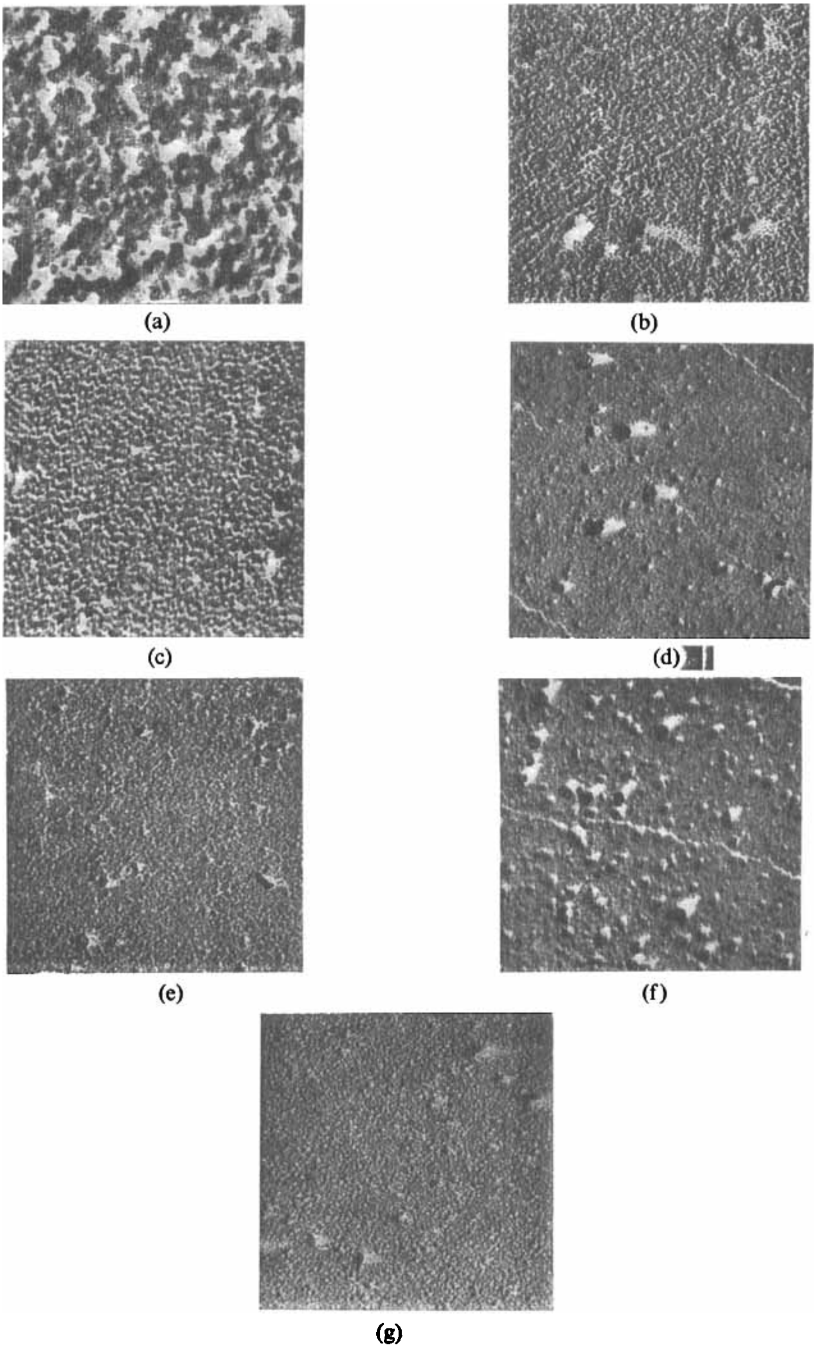


FIGURE 7 Structure of "free" polyurethane films of different oligoether nature and spatial network density. × 1200. (a) ODA–600 at NCO/OH ratio = 1.25 : 1, (b) ODA–600 at NCO/OH ratio = 1.5 : 1, (c) ODA–600 at NCO/OH ratio = 2 : 1, (d) ODA–1200 at NCO/OH ratio = 1.5 : 1, (e) ODA–1200 at NCO/OH ratio = 2 : 1, (f) THF–25% OP–1200 NCO/OH = 2 : 1, (g) THF–25% OP–1200 NCO/OH = 4 : 1.

globular formations (Figures 7a, 7d, 7f as compared with 7c, 7e, 7g respectively) and on the other hand an increase in the packing density of the structural elements occurs. A similar effect is also observed upon decreasing oligoether molecular weight (see Figures 7e and 7c).

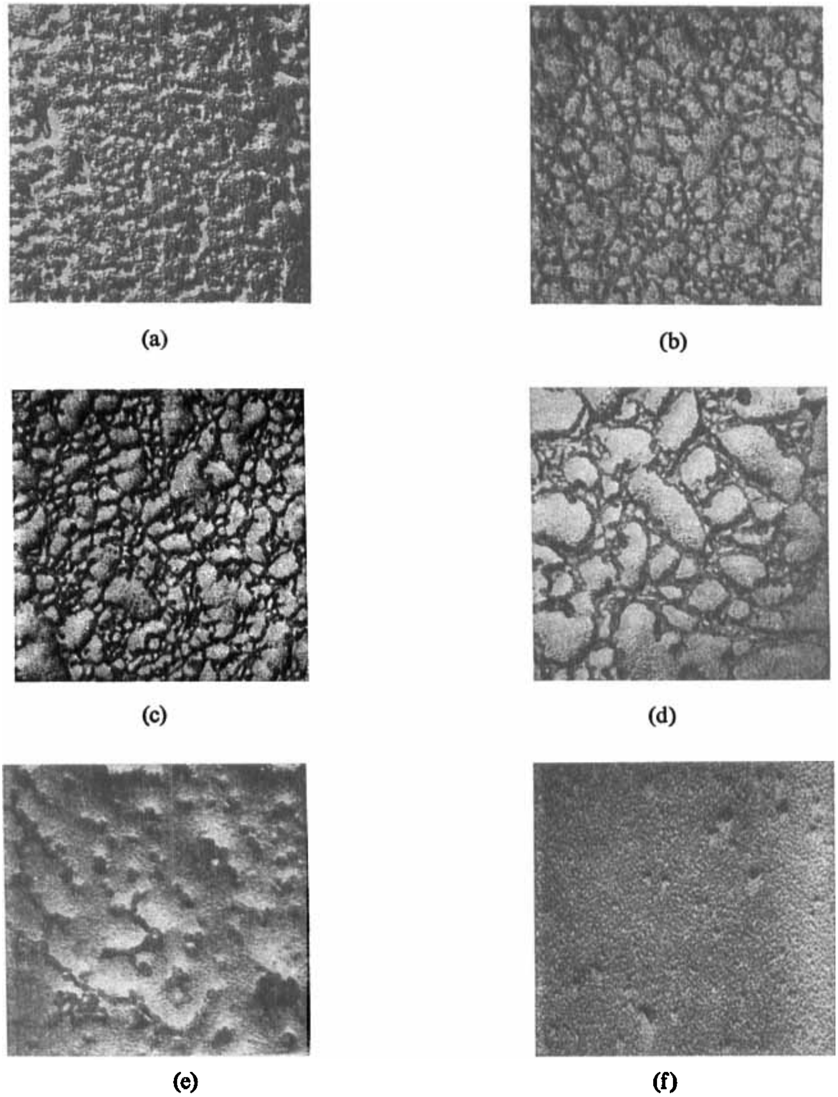


FIGURE 8 Polyurethane structure (ODA-600 NCO/OH = 1.5 : 1) at different separations from the solid (steel) surface. ×1200. (a) At polymer–solid interface, (b) at a distance of separation 20–25 μ from solid surface, (c) 45–50 μ separation, (d) 150 μ separation, (e) 160 μ separation, (f) >200 μ.

We think that this effect is due to the following: as the molecular weight increases, the flexibility of the chains also increases resulting in the formation of smaller globules.

As remarked earlier, the solid surface influences the effective crosslinking

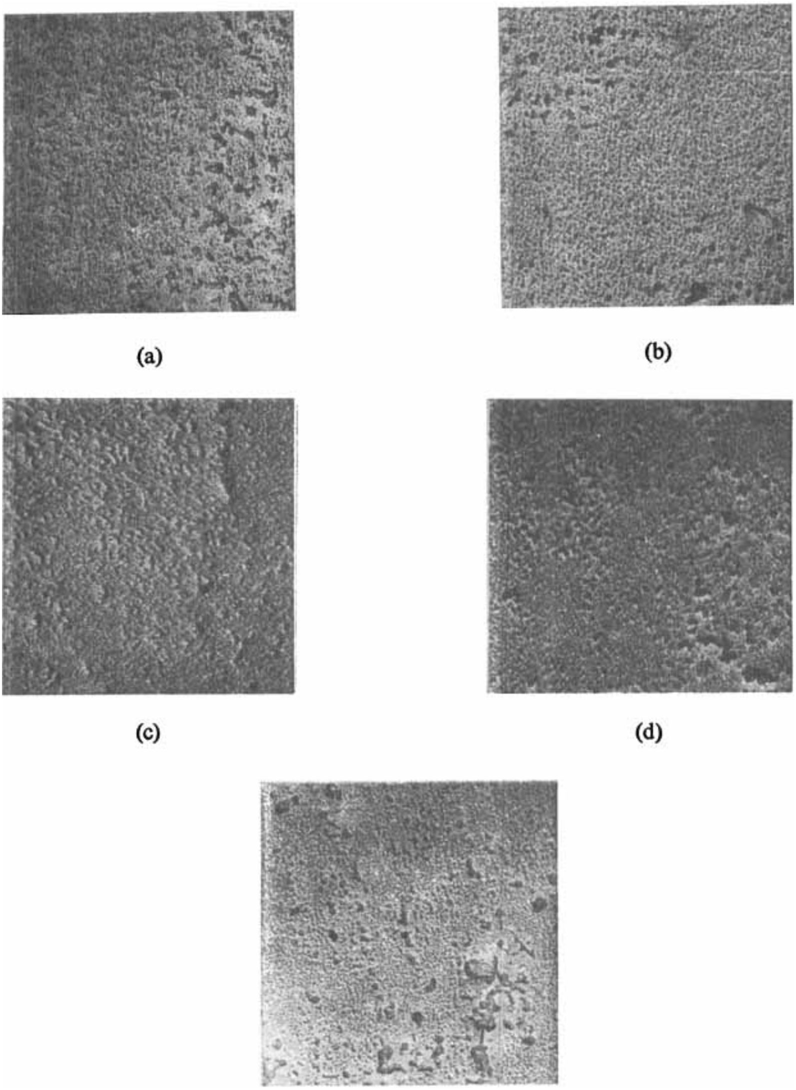


FIGURE 9 Polyurethane structure (ODA-1200 NCO/OH = 2 : 1) at polymer–air interface. Coatings prepared at different surfaces with thickness 200 μ: (a) steel, (b) brass, (c) duralumin, (d) fluoroplastic. × 1200.

density of the polymer and this effect could extend to considerable depth. In this respect, a question arises concerning the change in superamolecular structural layers of polyurethanes as a function of distance from the surface. Figures 8(a–e) show superamolecular structures of polyurethane based on ODA-600 in the presence of steel. It can be seen that at the interface there is a continuous network of secondary globular formations with densely packed miniglobular structures present in between the cells (Figure 8a). As the film thickens, an increase in the cell size of secondary formations is observed until a thickness of 160 μ is reached. Above 160 μ the structure of films formed on solid surface becomes similar to the structure of free films (see Figure 7e) and does not depend on the nature of the substrate (Figures 9a–e).

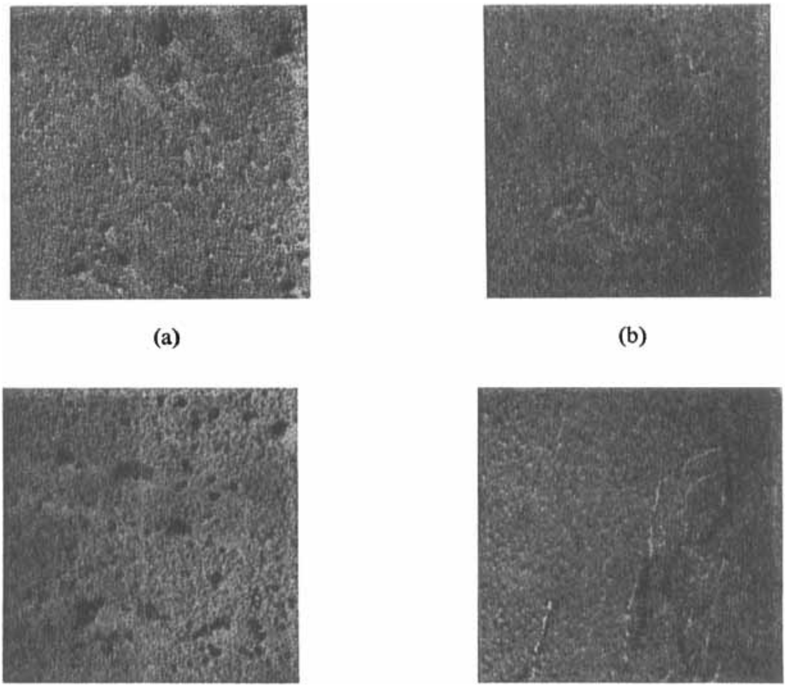
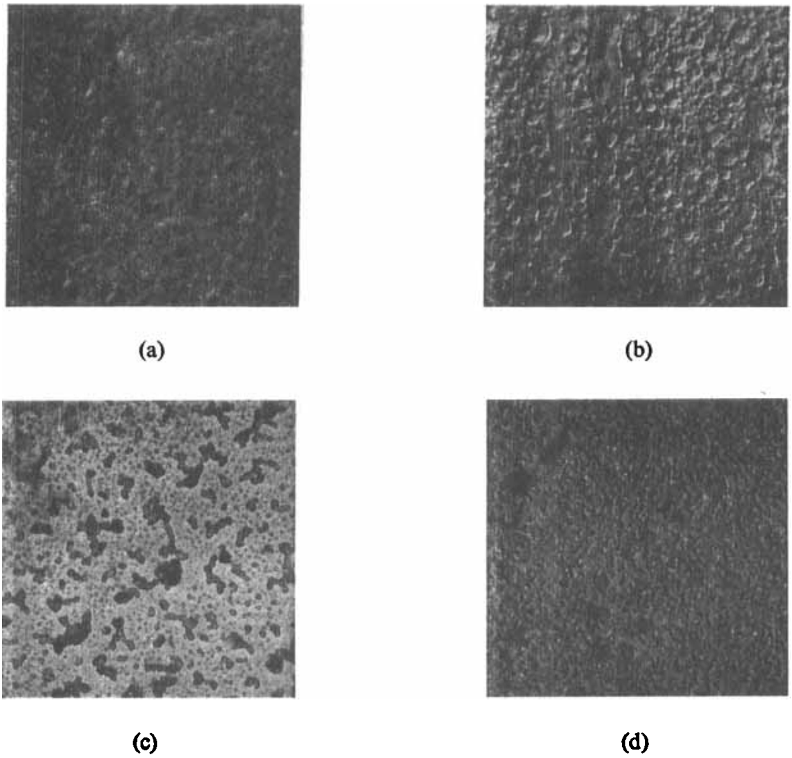

(a) (b) (c) (d)

FIGURE 10 Structure of polyurethane coatings based on THF–25% OP–1200 at a ratio NCO/OH = 2 : 1 at solid–polymer interface: (a) steel, (b) brass, (c) duralumin, (d) glass. ×1200.

Investigation of coating superamolecular structure at the boundary with different surfaces reveals that the character of structure formation in many cases is related to the magnitude of molecular interaction at the interface giving rise to different packing density of the globular structure. Thus, examination of Figures 10a–d shows that the structure of coatings based on oligoethers are characterized by dense globular packing at the interface with steel and brass to which these coatings have higher adhesion than in case of duralumin and glass, where large globules are observed to form at the interface. Furthermore, in the case of polyurethanes based on oligoesters with the same molecular weight and which exhibit lower adhesion than polyurethanes based on oligoethers are characterized by random arrangement of globular formation with different sizes and less packing density. This can be observed by comparing Figures 10 and 11.



(a) (b)

(c) (d)

FIGURE 11 Structure of polyurethane coatings based on ODA–1200 at a ratio NCO/OH = 2 : 1 at solid–polymer interface: (a) steel, (b) brass, (c) duralumin, (d) glass. × 1200.

The highest adhesion value of all studied coatings was observed in the case of polyurethane based on ODA–600 which is characterized by chain aggregation of globules forming what appears to be a continuous network (Figure 12), which is more sparse in the case of duralumin (Figure 12b). The unit cells of this network are filled with densely packed globules of different sizes. This regularity, however, is not observed on the glass substrate

(Figure 12c); in addition to densely packed minute globules there are secondary globule formations which do not give rise to a secondary network structure. On the brass surface (Figure 12d), a less densely packed, randomly arranged globular formation with different sizes can be observed. Such a structure corresponds to minimum adhesion bond strength (see Table II).

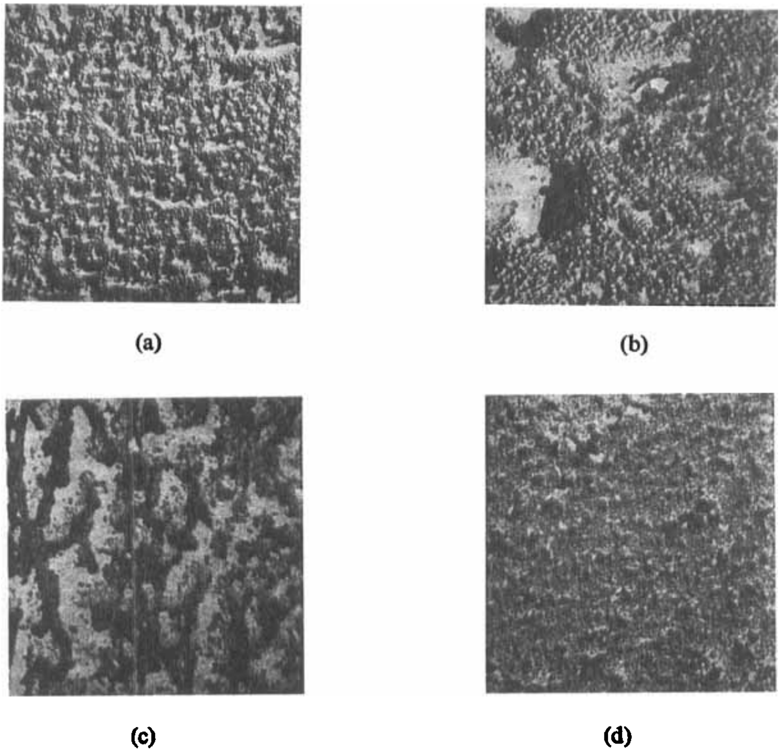


FIGURE 12 Structure of polyurethane coatings based on ODA-600 at a ratio NCO/OH = 1.5 : 1 at solid-polymer interface: (a) steel, (b) brass, (c) duralumin, (d) glass. × 1200.

The above results indicate that globular size and their packing density (influencing the real contact area with the surface) determine the number of functional groups interacting with the surface which in turn bears on the adhesion bond strength.

However, it should be noted that in addition to structural elements taking part in the interaction at the polymer-substrate interface and exposed during etching, there exists a structureless part which is separated during etching in oxygen gas discharge. It is obvious that the latter part plays the part of a builder with respect to superamolecular formation, and is similar to the builder role in reinforced and filler systems. Hence, it has to be taken into account when evaluating the effect of superamolecular structures on the physical mechanical properties.

Thus, the reported results clearly point out that the chemical structure of polyurethanes (nature of the oligoether block and its molecular weight) and the degree of interaction with the surface affects the structure of polyurethane coatings, changing the character of the superamolecular structures and effective crosslinking density. The change in effective network density bears on the flexibility of chain segments between links and these in turn determine the number of contacts at the polymer–substrate interface and subsequently adhesion of polyurethane coatings to solid surfaces.

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