

Evaluation of protective coating and inert surfaces adhesion

L.Yu.Vergun, Yu.F.Zabashita, T.T.Todosiychuk^{},
L.F.Kosyanchuk^{*}, O.A.Zagorodnia*

Department of Molecular Physics, Faculty of Physics, T. Shevchenko
National University of Kyiv, 60 Volodymyrska Str., 01033 Kyiv, Ukraine
^{*}Institute of Macromolecular Chemistry, National Academy of Sciences of
Ukraine, 48 Kharkiv Road, 02160 Kyiv, Ukraine

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The physical mechanisms of interaction between the substrate and the inert polymeric material have been studied. It has been showed that during such interaction the structures of oriented chains are formed. While the bounds are breaking in these areas the strands which can attributed to structural features called "silver cracks" occur.

Исследованы физические механизмы взаимодействия между инертной подложкой и полимерным материалом. Показано, что во время такого взаимодействия происходит образование структур, которые являются ориентированными цепочками. Во время разрыва в отмеченных областях образуются дефекты, которые могут быть отнесены к структурным особенностям под названием "трещин серебра".

*Оцінка адгезії розроблених захисних покриттів до інертних поверхонь.
Л.Ю.Вергун, Ю.Ф.Забашита, Т.Т.Тодосійчук, Л.Ф.Косянчук, О.А. Загородня.*

Досліджено фізичні механізми взаємодії між інертною підложкою та полімерним матеріалом. Показано, що під час такої взаємодії відбувається утворення структур, що являють собою орієнтовані ланцюги. Під час розриву у зазначених областях утворюються тяжі, які можна віднести до структурних особливостей під назвою "тріщин срібла".

1. Introduction

Currently, the technique of semiconductor devices production is based on the use of silicone compositions with polymer protective films [1]. For these films, as well as for other insulation coatings the defects related to broken adhesive cohesion between the system layers are likely to occur [2]. It is a well-known fact [3] that when applying the polymer coating the requirements for homogeneous properties across the plane of silicon plate must be met. This homogeneity is determined by the physical mechanism of organic silicon composition formation. When establishing these mechanisms it is necessary to take into account the role of

surface phenomena in the formation of this system, which is determined by the presence and concentration of active centers. Change in concentration of the latter is related to adhesion strength [4, 5].

For such coatings while they are contacting with the substrate the self-organization processes are likely to take place. They result in changing the rheological and mechanical properties [6]. In the modern approach of testing the polymeric structural materials there are some drawbacks related to mechanical properties determination. There is a lack of dynamic mechanical analysis techniques which would help determine the relationship between the reversible and the irreversible changes in mechanical

properties under the influence of external factors [7–9]. In this regard, the paper contributors propose a technique to evaluate the adhesive properties of polymeric materials under the process of formation of protective coating of silica-containing compositions. By definition [10] the nature of interaction between substrate and adhesive material may be either inert or active. The active interaction corresponds to the case when there are chemical bonds between the substrate and the adhesive materials. The inert interaction is characterized by absence of the chemical bonds [11].

The process of applying the protective polymer coating involves its interaction with the surface of substrate for which silicon is a raw material. It is a well-known fact [12] that crystalline silicon is an inert substance that affects the degree of chemical inertness of the substrate surface.

In this study, the substrate is laboratory glass. The presence of silicon atoms in glass allows us to suggest that interaction between the adhesive and the glass has the same character as interaction between the adhesive and the silicon substrate. The glass surface can be considered as inert. It is known [13, 14] that after applying the coating there it is started the physical and chemical processes resulting in growing cohesive strength. During formation of the "substrate-coating" system the solid and liquid phases interacting with each other, as well as with the surface are formed in adhesive [15]. The number of phases is determined by the elastic properties of the forming layer. The similar processes sometimes may occur later, while operating the joint. However, the strength asymptotically approaches a certain value which corresponds to the ultimate strength of the adhesive joint. The ultimate bond strength depends on the local values of strength, i.e. the strength in areas which are fractured earlier than the entire loaded plane. Under the action of breaking load not only the ultimate strength, but also the nature of fracture that can occur in the substrate, on the adhesive (glue), and in the coating — substrate interface are usually assessed. The coating technique is known to involve keeping the joint at a certain temperature. Therefore, it is necessary to determine the optimum temperature for providing the necessary operating and performance data of coating to be used in the operating environment. In accordance with these objectives the aim of this study is to determine the

Table. Strength properties of samples

Type of sample	Shear stress τ , 10^6 Pa	Time to rupture, min
A	2.18±0.04	1.7±0.2
B	2.31±0.06	1.7±0.2

mechanisms of interaction between the adhesive and the substrate, as well as to establish the optimal conditions for manufacturing the system of "inert substrate — polymer coating."

2. Experimental

The samples of two types (**A** and **B**) having different coating technique have been studied. After application of coating of **A**-type the samples have been kept within 8–10 hours at temperature of 333 K, while the **B**-type samples have been kept within 8–10 h at temperature of 353 K. The coating is polymer adhesive composition consisting of two components, the base and the hardener. The base is semi-polymer synthesized from polydiethylene-glycol-adipate (MM 800) and hexa-methylene-diisocyanate at a ratio of 1:2. The adhesive composition has been hardened with the use of trimethylolpropane (TMP).

According to the method described in [16] the strength of **A**- and **B**-type adhesive joints has been determined. The measurements have been carried out at temperature of 293 K. The results of measurements are given in Table.

As one can see from Table the strength of the **B**-type bond exceeds the strength of the **A**-type one. The intervals from the moment of application of the load to rupture of the samples (time to rupture) are the same for both types of the samples.

Structure of fracture surfaces of the samples of the both types has been studied using an optical microscope. Images of the fracture surfaces are given in Fig. 1 and Fig. 2. As one can see from the figures the adhesive joint fracture occurs along the adhesive.

Comparing Fig. 1 and Fig. 2 allows us to determine the fundamental difference between two types of the fracture patterns. The difference is that Fig. 2 shows the fracture surface looking like the highly elastic rupture, while Fig. 1 contains the areas which are typical for the brittle rupture (section **A**). Figure 3 shows images of cross-sectional fracture surfaces for the samples of type **A** and type **B**. According to Fig. 3

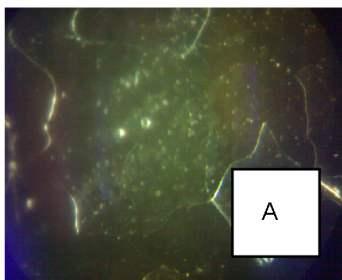


Fig. 1. Typical structure of the fracture surface for **A**-type sample (enlargement $\times 28$).

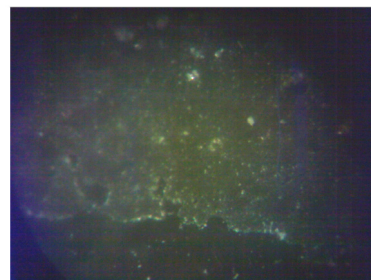


Fig. 2. Typical structure of the fracture surface for **B**-type sample (enlargement $\times 28$).

the cross section of fracture surfaces can be schematically represented as a schematic model given in Fig. 4. According to Fig. 3 and Fig. 4 the fracture surface can be represented as a set of shelves and hollows. Also, it is clear that for the shelves observed there is a hierarchy of sizes: there are two classes of shelves: the macro-shelves having a size of hundreds of microns and the micro-shelves with a size of tens of microns (in Fig. 4, the both types are marked 3 and 4, respectively).

According to Figs. 1 and 2 the micro-shelves form two types of the fracture surface. The first type corresponds to the coarse-grained structure with the large size of heterogeneity, while the second one corresponds to the fine-grained structure with small inhomogeneities. The both types of fracture surfaces are typical for the **A**-type samples. However, in Fig. 1a the coarse-grained structure prevails. The areas of fine-grained and coarse-grained structures are separated by cracks as showed in Fig 1b.

The **B**-type samples are characterized exclusively by the fine-grained structure.

3. Results and discussion

Having processed the images using the optical microscope the histogram of heterogeneities distribution by size (Fig. 5 and Fig. 6) has been built. There r (in microns) is size of heterogeneity; f is distribution function of heterogeneity by size.

Let us determine the nature of occurrence of heterogeneities observed. At temperature of $T = 293$ K the investigated polymer is highly elastic. This allows us to determine the nature of heterogeneity based on the modern concepts of destruction of highly elastic materials [16, 17].

It is known [18] that one of the features of destruction of highly elastic materials is appearance of specific cracks which, unlike the cracks formed during the brittle fracture, are cavity partially filled with the

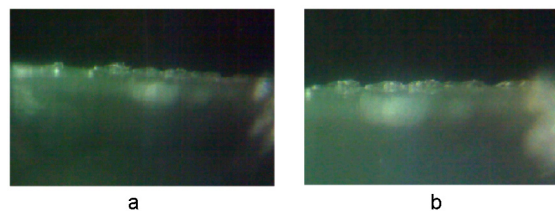


Fig. 3. Cross section of the fracture surface (a — type **A**, b — type **B**, enlargement $\times 40$).

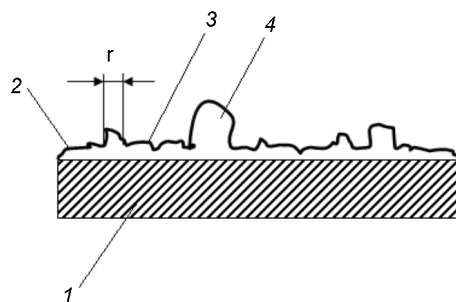


Fig. 4. Cross section of the fracture surface (1 — substrate, 2 — adhesive, 3 — micro-shelf, 4 — macro-shelf, r — size of micro-shelf).

strained material. The walls of these cracks appear to be interconnected by so-called strands consisting of oriented chains. These cracks are called "silver cracks", because for the first time they have been detected in strained PMMA to which these cracks add luster due to the light reflection.

Formation of the strands takes place in different scales. The formation of "silver cracks" deals with the order of hundreds of angstroms. The next step is the formation of strands whose diameter reaches micrometers. The formation of these strands is schematically presented in Fig. 7.

Existence of these strands allows us to determine the nature of micro-shelves observed on the fracture surfaces. As one can see from Fig. 7c the micro-shelves can be seen as a consequence of rupture of the strands of respective diameter. This fact allows us to determine the nature of occur-

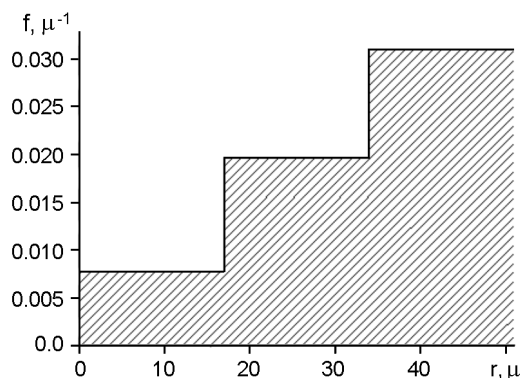


Fig. 5. Histogram of heterogeneities size distribution for the coarse-grained structure.

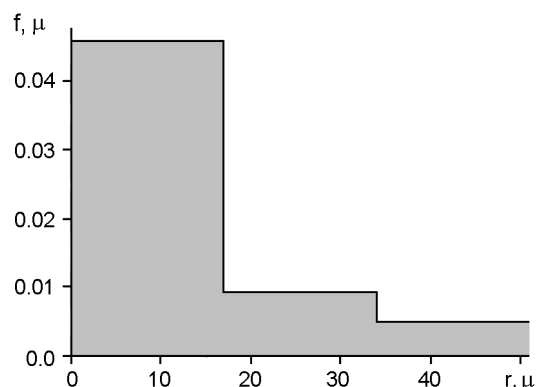


Fig. 6. Histogram of heterogeneities size distribution for the fine-grained structure.

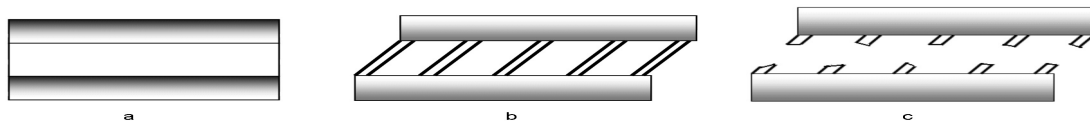


Fig. 7. Model of formation and rupture of the strands during fracture of adhesive joint (a — unstrained sample, b — strand formation, c — rupture of strands and formation of micro-shelves).

rence of various types of the fracture surface. As already mentioned, the fine-grained and the coarse-grained structures are differed by average size of micro-shelves. According to the proposed mechanism for the formation of such selves it can be concluded that the fine-grained structure is formed due to rupture of the small strands whereas the coarse-grained is formed by rupture of the strands with large diameter.

The formation of the strands of small diameter occurs when the chains have sufficient mobility. Where the chains have insufficient mobility there are formed the strands of the larger diameter. A factor that contributes to the immobilization of polymer chains is cross-linking. Therefore, we can say that during rupture the areas with low concentration of the cross-links there the strands of small diameter are formed. Conversely, high concentration of the cross-links promotes the formation of the strands of large diameter. For the strands of large diameter the probability of their brittle fracture is higher. These considerations allow us to suggest that two types of adhesive structures exist. There are the areas of the rare and the dense lattices. During fracture the rare lattice gives the fine-grained fracture surface, while fracture of the dense lattice leads to the coarse-grained fracture surface. Thus, we can conclude that in contrast to the B-type samples the A-type samples have the areas

of densely linked lattice. These areas generate the coarse-grained structures in the A-type samples and cause the brittle rupture.

4. Conclusions

One of the features during the formation of the "substrate-polymer coating" interface is rearrangement of the polymer chains at the surface of substrate with formation of the oriented structures. The nature of these structures depends on temperature of the "molten-lattice" transition. At low temperature the densely linked lattice is formed, as a result of which the adhesive strength of "adhesive — substrate" decreases. High temperature increases mobility of the chains during the cross-linking. As a result, the size of the oriented areas in disordered material grows. At the lower temperatures, the adhesive layer of latticed polymer contains the higher concentration of cross-links than the layer formed at the higher temperatures.

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