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# Influence of properties of materials for solventless lamination on the bonding strength of multilayer packaging

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## Abstract

The article presents the study of the bonding strength of multilayer polymeric packaging films, the use of which is one of the directions of development of the flexible packaging technology to ensure high barrier properties and strength of packaging. The dependence of the viscosity of two-component polyurethane adhesive on temperature and time has been studied. During the research, polymer films of the different chemical structures have been selected: polyethylene terephthalate, polypropylene, including the metalized one, and polyethylene. The wetting of the selected polymer film surface with polyurethane adhesive has been studied, the value of their surface energy has been determined, and multilayer systems (laminates) have been formed in production conditions. It has been found that the value of surface energy has a great influence on the formation of laminates with high bonding strength. The surface energy components have been identified according to the Owens–Wendt method to study the nature of the intermolecular interaction in the adhesive bonding. The correlation dependence between the surface energy and its components has shown that the adhesive bonding strength increases as the polar component increases. In general, it has been found that all the systems under study have provided the sufficient strength for laminates (multilayer packaging).

**Keywords:** film, adhesive, viscosity, packaging strength, surface energy

## 1. Introduction

High requirements for food safety and quality, in turn, place high demands on the packaging quality. Various analytical forecasts show that more than 75 % of the world's flexible packaging materials are consumed in food packaging. In particular, in the countries of Central and Eastern Europe, their annual utilization is 1960 thousand tons, and the annual increase is 3.5 %; in Ukraine, the volume of production and consumption of flexible polymer packaging is approximately 140 thousand tons per year with an annual growth of 2 % (Alexandrov, 2017). The worldwide market for lamination adhesives for flexible packaging is expected to grow at a compound annual growth rate of roughly 0.9 % over the next five years, reaching 3 000 million US$ in 2024, from 2 850 million US$ in 2019, according to a new study (360marketupdates, 2019).

One of the priority areas for the development of flexible packaging technology is the use of multilayer polymeric materials – laminates. Among the wide range of manufacturing technologies, the most popular is solventless lamination technology, which provides a number of significant technological and economic benefits (NIIR Board, 2010). Thorough studies of the processes and materials of solventless lamination make it possible to understand the essence of the physicochemical processes underlying the technology and thus to influence their efficiency and quality of the finished packaging.

## 2. Literature review

The studies in which the authors examine the features of a particular lamination technology, their advantages and disadvantages, and particularities of their application in detail are of considerable practical interest. Such studies

(Wolf, 2010; Schetschok and Kupsch, 2011; Anjani and Annu, 2015) may serve as a guideline when selecting the lamination technology for a particular packaging segment.

The properties of the basic materials used in the technological process, in particular the properties of polymer films and adhesives, have a decisive influence on the operating characteristics of the finished laminate. The knowledge about the range of adhesives (Petrie, n.d.), their composition (Ardman, 2014), as well as the specifics of systems for their application (Ling, Wencai and Guangshen, 2010) is an important basis for further improvement of the technology and the study of immediate practical properties (Singh, 2017).

The adhesive bonding of objects occurs mainly under the influence of intermolecular interaction forces in the boundary layer between the substrate and the adhesive, and its strength depends on the nature and the number of functional groups, the structure of materials, and the interphase surface energy. It is appropriate to mention that a functional group (e.g., carboxyl –COOH, hydroxyl –OH, aldehyde –CHO, amino $-NH_2$, nitrile $-C\equiv N$, thio –SH, etc.) is a fragment of an organic molecule that determines its physical and chemical properties and it is a criterion for assigning this molecule to a certain class of organic substances – acids, alcohols, phenols, aldehydes, etc., respectively (Shibanov, 2016). Due to the wide variety of properties of adhesives, one can create materials that have brand new, often unexpected, but sometimes predictable functional parameters and characteristics.

In the bonding process, as a rule, there is a change in the aggregate state of the adhesive from a liquid (which provides better contact between the adhesive and the substrate) to solid. This greatly increases the viscosity (physical viscous state) and the melting point of the adhesive. Obviously, the hardening mechanism of adhesives that contain and do not contain solvents will be different. In the first case, the solid phase in the adhesive layer appears due to the evaporation of the solvent or dispersion medium (often water) and an increase in the concentration of the main component – a film-forming agent. In the other case, the adhesive hardening is due to chemical reactions leading to a multiple increase in the molecular weight of the main component of the adhesive composition in the chemical process, in its polymerization, polycondensation, polyaddition, three-dimensional crosslinking.

During hardening, the cohesive strength of the adhesive increases significantly. Cohesion is known to express the bonding power between molecules (atoms, ions) inside the object within a single phase and it characterizes the body strength. The destruction of the adhesive bonding under the action of external forces can occur either at the boundary between the adhesive and the substrate (there is adhesive destruction then), or on the adhesive seam or the substrate itself (cohesive destruction). The adhesive must have such adhesion to the substrate that the mechanical action on the adhesive bonding can cause cohesive destruction.

Previous works (Cheruvathur, 2009) have shown that the type, thickness, and surface properties of polymer films and the adhesive type and conditions of its application (its viscosity, and temperature) play an important role in determining the durability parameters, such as the bonding strength of laminates. The thickness and characteristics of the ink layer applied to the laminated films also have a significant effect on the bonding strength (Izdebska, Żołek-Tryznowska and Wirtek, 2015).

Studies of the properties of basic materials and solvent-free lamination modes provide not only additional information for improving the efficiency of the technological process, but also create a certain theoretical basis for further deeper analysis of the quality factors of the processes of forming flexible multilayer materials.

## 3. Methods

One of the important factors that significantly affect the lamination process is the properties of the two-component adhesive composition. It is known that in addition to the surface energy ratios of the substrates, the viscosity plays an important role in the liquid spreading over the material surface. The process of solventless lamination occurs at a raised temperature; the adhesive components are mixed in the laminator head just before being applied to the opening. The multilayer laminates were formed on solventless laminator Laminastar 2 (DCM); the amount of adhesive applied was 2 g/m$^2$. Mor-Free L75-300/C79 (Dow) adhesive was used in the process of solventless lamination. It is a two-component solventless polyurethane adhesive system for high speed operation (up to 400 m/min).

Polymer films with different chemical structures and different storage times from the date of manufacture were selected for this study. Their characteristics are shown in Table 1. Table 2 shows the characteristics of solvent-based

flexographic inks, which were used to print polymer films before the lamination operation. When studying the effect of the ink layer on the adhesive bonding strength of the films, the relative dot area of the CMYK image was 95 %. The apparent viscosities of printing inks were determined by measuring of efflux time with 4 mm DIN cup (Deutsche Institut für Normung, 1987). The viscosity of the adhesive was determined with the Brookfield RVT viscometer, rotor No 5.

The surface energy of the polymer films was determined according to ASTM D 5946–09 standard (American Society for Testing and Materials, 2009) by the contact angle of their surface with a drop of distilled water. The contact angles of the substrate by liquid were determined according to the methodology described in Repeta (2013), by digital registration of drop profiles. Small droplets of test liquid and ink 7.5 ± 0.5 µl were placed on the substrate with a micropipette. The drop images were captured with a CCD camera (1280 × 720 px) attached to the microscope, and then recorded by a computer. The spreading of liquids was evaluated 1 min after application on the substrate at temperature of 20 ± 0.5 °C and 82 % relative humidity.

*Table 1: Characteristics of polymer films*

| Film name | SHD | SVD | MLD | CMVV.M | FBW | F-CHE-0.12 |
|---|---|---|---|---|---|---|
| Producer | Treofan | Treofan | Treofan | Biaxplen | Technologia JSC | Flex P.Films |
| Type | Polypropylene | Polypropylene | Polypropylene | Metallized polypropylene | Polyethylene | Polyethylene terephthalate |
| Thickness [µm] | 28 | 28 | 20 | 30 | 50 | 12 |
| Orienting type | monoaxial | monoaxial | biaxial | / | / | / |
| Surface activation | physical | physical | physical | physical | physical | chemical |
| Roll width [mm] | 520 | 520 | 540 | 540 | 820 | 600 |
| Grammage [g/m$^2$] | 21.5 | 21.0 | 18.2 | 27.3 | 50.0 | 16.8 |

*Table 2: Characteristics of printing inks*

| Ink | Ink name | Producer | Apparent viscosity (DIN 4 cup), s |
|---|---|---|---|
| Yellow | Polistar Process Yellow | FlexoRes | 40 |
| Magenta | Polistar Process Magenta | FlexoRes | 32 |
| Cyan | Polistar Process Cyan | FlexoRes | 34 |
| Black | Polistar Process Black | FlexoRes | 34 |

The polar and dispersive components of the surface energy are determined by Owens–Wendt method for contact angle of test liquids (Owens and Wendt, 1969):

$$0.5\,\gamma\,(1+\cos\theta)\,/\,(\gamma_d)^{0.5} = (\gamma_d^s)^{0.5} + (\gamma_p^s)^{0.5}\,(\gamma_p\,/\,\gamma_d)^{0.5} \quad [1]$$

where $\gamma$ is a surface tension of the liquid; and $\gamma_d$ and $\gamma_p$ are dispersive and polar components of the surface energy that characterize solid body marked by index S, or liquid (no index).

For the calculation of the results of Equation [1], which lies in the intersection of the coordinates $0.5\,\gamma\,(1+\cos\theta)\,/\,(\gamma_d)^{0.5}$ and $(\gamma_p\,/\,\gamma_d)^{0.5}$ represented as a straight line with a slope of $(\gamma_p^s)^{0.5}$, and the point of intersection of this line with the axis value of ordinates $(\gamma_d^s)^{0.5}$, the developed program was used, which interface is shown in Figure 1. Liquids with known surface tension and polar and dispersive components such as distilled water and ethylene glycol have been used for testing.

Adherent interaction of the adhesive with the surface of the polymer films and the ink layer is of particular importance both for the printing and the lamination quality. Accordingly, the value of the surface energy of the selected films has been studied and the value of the contact angles of their surface with the adhesive has been determined.

The resultant indicator of the lamination quality of multilayer polymer materials is the bonding strength of the laminated materials. The preparation of samples and the determination of adhesive strength were carried out in

accordance with ASTM F904-16 (American Society for Testing and Materials, 2016) and DIN EN 868-5:2019 standards (Deutsches Institut für Normung, 2019). At the beginning of preparation before measuring, strips in dimension of 25 mm × 310 mm were cut from the finished laminate in the transverse direction and immersed in ethyl acetate (the immersion depth 70–80 mm) for 15 min to 20 min in a sealed container. Subsequently, the strips were removed, wiped, and stratified to form a T-shape. Tearing the laminates and testing the adhesive strength was carried out on the equipment shown in Figure 2.

The laminated material is considered to be of good quality according to the standard DIN EN 868-5:2019, if the bonding strength of the non-medical packaging is not less than 1.2 N (Deutsche Institut für Normung, 2019).

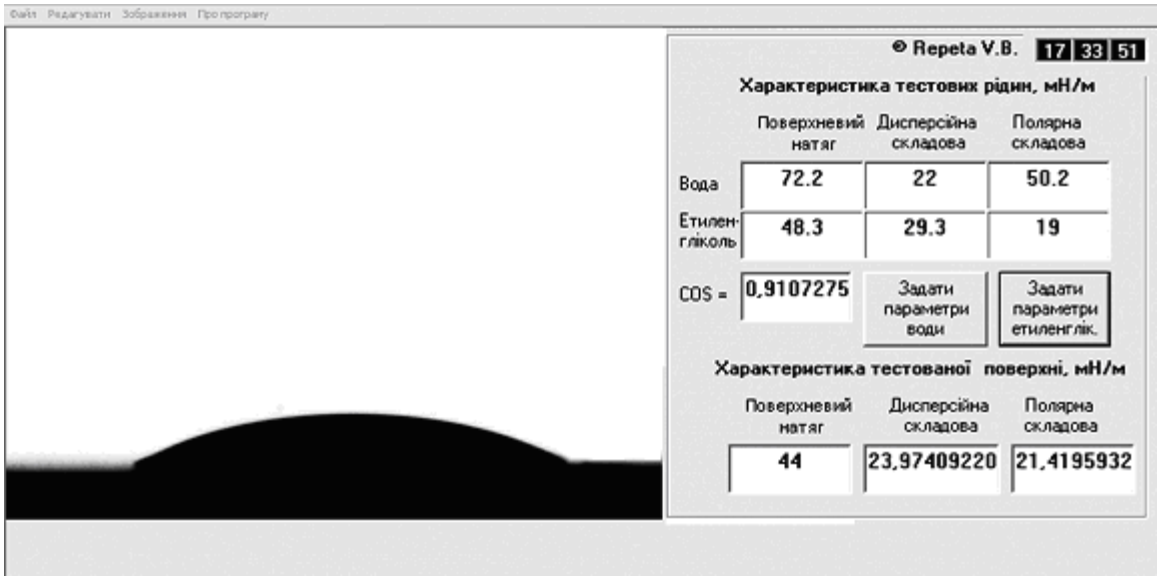


*Figure 1: The program interface for determining the cosine of the wetting angle and the substrate surface characteristics*

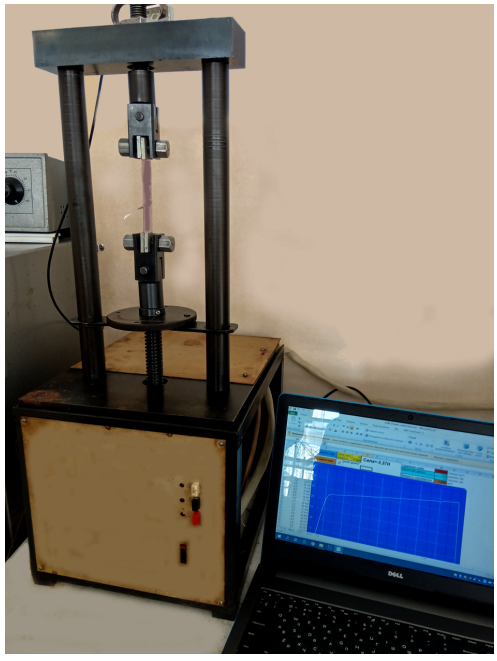

*Figure 2: The equipment for testing the adhesive strength of laminates*

## 4. Results and discussion

The process of chemical inter-component interaction begins immediately after mixing, so the open time of the adhesive is 20–30 min. During this time, the adhesive hardens; this is accompanied by the change in its viscosity, which is temperature dependent in its turn. Therefore, the dependence of the viscosity of the two-component adhesive on temperature (Figure 3) and time (Figure 4) has been analysed. The results obtained show that when the adhesive is heated to the temperature of 35–40 °C, its viscosity decreases very significantly – almost 10 times, which positively affects the parameters of its spreading and the ability to form a thin uniform film on the surface of the polymer film.

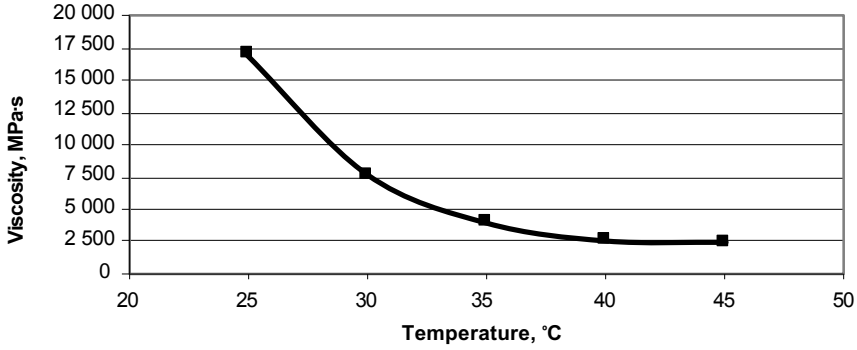


*Figure 3: The dependence of the viscosity of Mor-Free L75-300/C79 adhesive on temperature (the viscosity is determined just after the heated components mixing)*

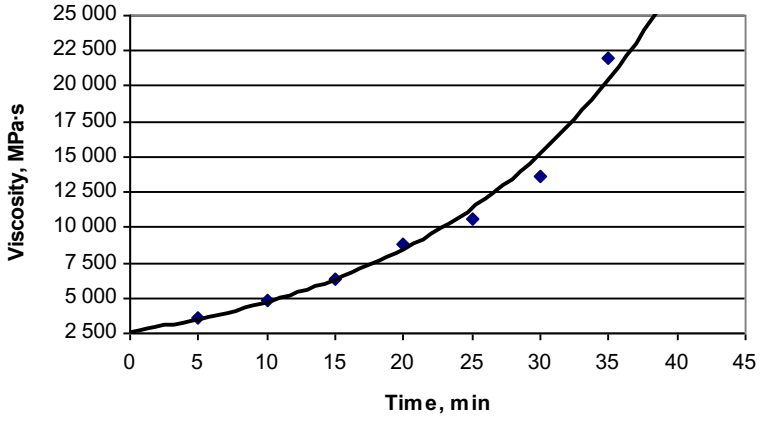


*Figure 4: The dependence of the viscosity of Mor-Free L75-300/C79 adhesive on time after the component mixing*

The results of the measurements of adhesive contact angles with polymer films, including four-color printed SVD marked as SVD+CMYK, used in this study are shown in Table 3.

*Table 3: The surface energy of polymer films and the cosine of the wetting angle with the adhesive*

| Materials | Surface energy (ASTM D5946-09), mN/m | Surface energy (Ovens–Wendt), mN/m | | | Cosine of the adhesive wetting angle |
|---|---|---|---|---|---|
| | | Dispersive component $\gamma_d$ | Polar component $\gamma_p$ | Total surface energy $\gamma_s$ | |
| SVD | 43 | 28.5 | 14.6 | 43.1 | 0.651 |
| SHD | 47 | 26.3 | 19.8 | 46.1 | 0.808 |
| F-CHE-0.12 | 46 | 28.4 | 17.5 | 45.9 | 0.798 |
| FBW | 43 | 27.2 | 16.1 | 43.3 | 0.677 |
| MLD | 45 | 24.8 | 19.9 | 44.7 | 0.768 |
| CMVV.M | 42 | 27.7 | 15.5 | 43.2 | 0.632 |
| SVD+CMYK | 40 | 31.3 | 10.4 | 41.7 | 0.683 |

Over time, the adhesive viscosity (Figure 4) increases quite rapidly – in 10 min twice, and in 20 min almost four times. These data correlate with the recommendations received from the manufacturer, according to which the open time of the adhesive is 20–30 min. The data obtained give the additional information about the essence of the technological process and will allow to regulate it more precisely, which will provide a laminated product of appropriate quality. According to the results, in the study of the process of spreading the adhesive compositions, their application was carried out 10 min after the component mixing.

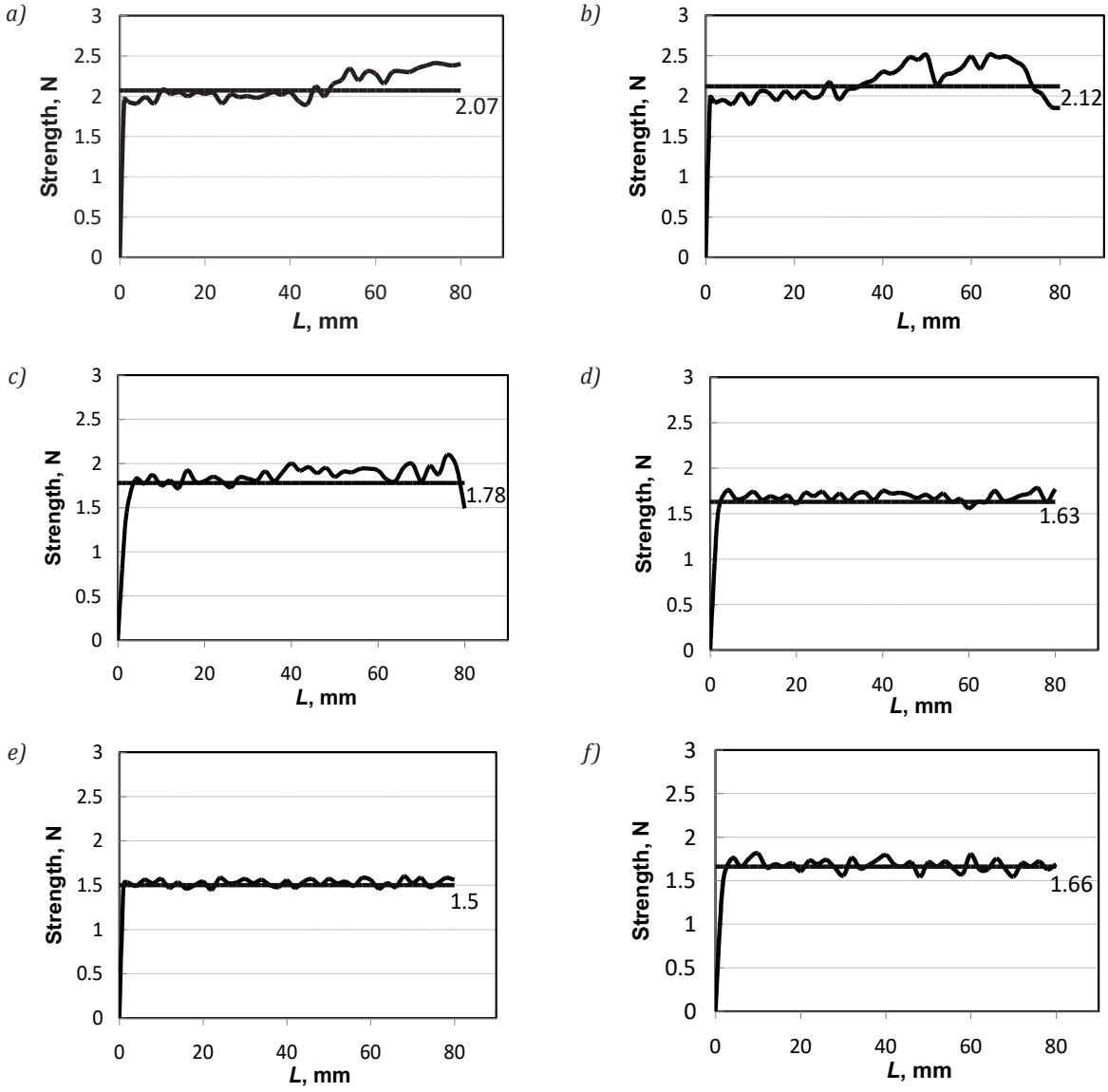


*Figure 5: Bonding strength of the MLD film system with the film: (a) F-CHE-0.12; (b) SHD; (c) FBW; (d) SVD; (e) CMVV.M; (f) SVD+CMYK; L is the length of the measured sample*

The bonding strength of various polymer films, including the printed surface, was determined on the bursting machine; the results are shown in Figure 5. MLD film was used for laminating in all cases. The results clearly show similar dependencies of the applied bursting force on the passed way. For SHD laminated polypropylene and F-CHE-0.12 polyethylene terephthalate, one can see some non-uniformity of the tensile force (Figure 5b), which can probably be caused by fluctuations in the distribution of the surface energy of the films. The analysis of the experimental dependencies obtained allowed one to determine the average bursting force for different types of laminates. The results indicate that MLD-F-CHE-0.12 and MLD-SHD films, have the highest strength (Figures 5a, and 5b), about 2.07 N and 2.12 N on average, respectively.

The bonding strength in MLD laminated on FBW systems, and MLD laminated on SVD+CMYK is somewhat lower, in the range of 1.66 N to 1.7 N. The lowest strength values of 1.5 N are for laminated material based on CMVV.M. It should be noted that all the studied laminates meet the requirements for laminated polymer films by the adhesive strength. The obtained values of the bonding strength of the films (Figure 5) correlate with the results obtained in the study of the surface properties of the polymers (Table 3). Higher surface energy films logically provide better orientation of the molecules when wetted with the adhesive and, accordingly, higher bonding strength of the laminate for multilayer packaging. It is clear that the surface characteristic of the MLD film is decisive for the bonding strength. An interesting pattern has been found for films with the highest surface energy, for which much larger variations of the sampling force data are observed (the difference between the maximum and minimum is 0.3 N on average). First of all, this indicates the heterogeneity of the distribution of active centers on the surface of the film formed in the modification process, which in general is not significant because of the high value of their surface energy. A similar situation is observed in the case of lamination of the printed film, which is explained by the unevenness of the ink layer.

The components of the surface energy of the substrates have been determined for a more detailed study of the nature of the intermolecular adhesion interaction (Table 3). The results have shown that the surface of all film samples has a high polar component, which lies in the range of 14.6 mN/m to 19.8 mN/m. We see a different situation for the ink layer, for which the polar component is the smallest and the dispersive component is high. Nevertheless, the ink layer surface provides high adhesive parameter of the bonding strength (1.66 N), which indicates a slightly different intermolecular interaction.

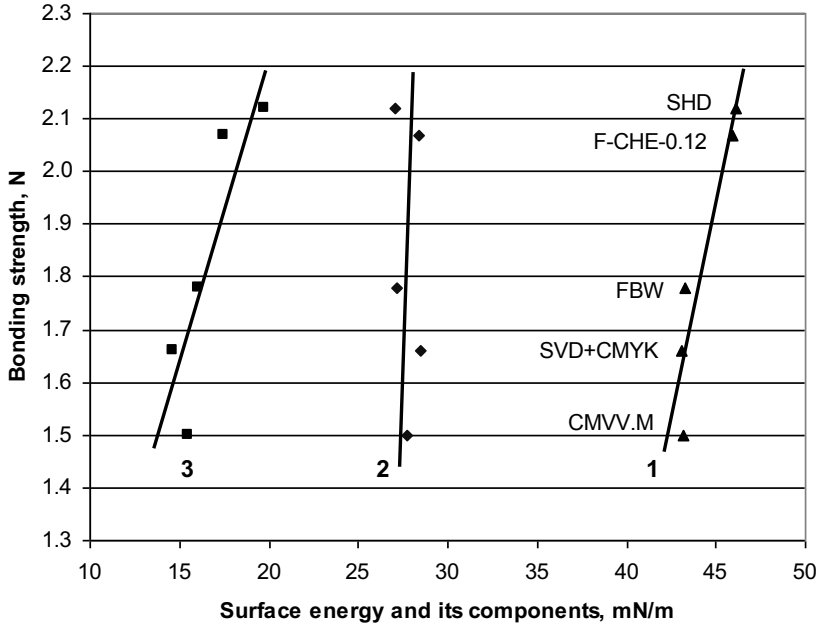


*Figure 6: The relationship between bonding strength and surface energy with its components: 1 – total surface energy; 2 – dispersive component; 3 – polar component*

Figure 6 shows the relationship between the bonding strength and the surface energy components. The analysis of the experimental data shows that the increase in the adhesive bonding strength is proportional to the increase of the polar component of the surface energy, which indicates that there are more functional polar groups on the surface involved in the intermolecular interaction.

## 5. Conclusions

In the paper, the compliance of the open time of the adhesive composition to the manufacturer's recommendations has been confirmed and the change in its viscosity with the temperature has been studied, which makes it possible to apply the adhesive in the lamination process and to form a thin layer. The results of the research have shown the influence of the surface energy of the substrates on the formation of adhesive bonding in the system of polymer

film–adhesive–polymer film, which determines the future operating parameters of such multilayer packaging. For films with the highest surface energy, larger differences between the maximum and minimum of the sampling force data are observed. This indicates, the heterogeneity of the distribution of active areas on the surface of the substrate.

The observed dependence between the surface energy and its components suggest that the increase in the adhesive bonding strength is due to the increase in the polar component of the surface energy. The ink layer of solvent-based inks of Polistar series (FlexoRes), applied on polymer films, does not cause the change in the bonding strength of the laminates.

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