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DEFECTS IN LAYERED MATERIALS

Layered polymeric materials are widely used when receiving thermomoulded articles from thermolayers. Often in such products materials with addition of secondary polymer, and also mixtures polymeric compositions are used. It is connected with that increase in production of plastic products causes need of utilization of the fulfilled products from them.

In this work such defects as peelings and cracks, layered products of practical use, namely bathtubs made by a combination of methods of thermoforming sheets of coextruded ABS plastic to polymethyl methacrylate and contact formation by putting premix on them were investigated.

Results of research of the samples presented showed truthfulness of the assumption that as raw materials at production of sheets secondary materials were used that led to defect in finished products in the form of stratification and crack.

Key words: layered material, thermoformation, contact formation, secondary material, raw material, sheet, defect, peeling, cracks.

Introduction. Nowadays products with polymers as a base are found in all fields of modern production. Materials based on polymers are a structural class characterized with high strength, large modulus of elasticity, fatigue endurance, viscoelastic and anti-frictional properties, combustibility, thermal and electrical conductivity. The distinctive characteristic of composite materials is the possibility to combine different production technologies determined by the purpose of products utilization and properties of the components.

Modern science makes it possible to develop composite reinforced plastics by changing their composition and structure to fully meet the demands claimed. The variety of composite materials is determined by the fact that they are complex heterophase systems characterized by having a wide choice of stress-strain properties of the composite material components [1] as well as manufacturing technology.

Lately the use of thermoformed articles from layered materials has been considered to be promising for the manufacture of products of different function, from parts of the automobile, tractor, and construction machines cabins to household bath tubs.

Thermoforming is a change in the shape of flat workpieces (sheets or films) from thermoplastic polymers into solid molded articles at elevated temperatures. The process of thermoforming is economic, since it requires no substantial investments in the equipment for producing small batches of articles. The problem is the specific requirements to strength, and impact load of the molded article. Operating conditions and aesthetic requirements to a product determine the use of ABS plastic coextruded with polymethyl methacrylate (PMMA). ABS-plastic possesses the necessary impact strength, and the layer of PMMA prevents aging caused by UV radiation and imparts high luster to the surface [3]. To provide additional strength and resistance to bending and impact loads, laminates based on ABS plastic are reinforced with fibrous fillers impregnated with a thermosetting binder which can be polyester resins, epoxy resins, etc. Thus, the sheet has glossy surface on the PMMA side and is strengthened with fibrous premix on the back side.

Main part. This work deals with the study of layered materials obtained by the method of contact molding.

Workpieces of two-layer sheet of PMMA-ABS plastic (from different manufacturers), obtained by extrusion were subjected to vacuum forming, after which they were covered with a premix consisting of unsaturated PEF resin and glass mat by using the method of contact forming.

Samples for testing were taken from household bath-tubs having the defects such as delamination and cracks. The figure shows photographs of the defects.

Two samples were taken for testing: No. 1 was produced in Russia, No. 2 being of Chinese production.

Tension being tested, the samples behaved in different ways. Sample No. 2 was delaminated when the tensile strength values were in the order of 13.6 MPa. Sheet No.1 was not delaminated and had tensile strength of 68.2 MPa. Thus, sheet No.1 shows high adhesion strength with the polyester premix used.

To check changes in the sheet characteristics during extrusion and at thermoformation heat

shrinkage of the sheets was measured in accordance with GOST 18616–80. Sheets of manufacturer No.1 turned out to have the shrinkage of 2.8%, those produced by No. 2 – possessing 3.4%. This shrinkage property, apparently, is determined by the speed of sheet extrusion and the composition of the material. Since shrinkage differs in the samples but only slightly, we have assumed that the bond strength between the layers is determined by the quality of ABS plastic.

At present in the manufacture of numerous products by extrusion secondary raw materials having operational compatibility with the original ones are used. Such materials can be secondary ABS, polystyrene and its copolymers. While possessing rather comprehensible physical-mechanical characteristics such materials may have deficient adhesive properties.

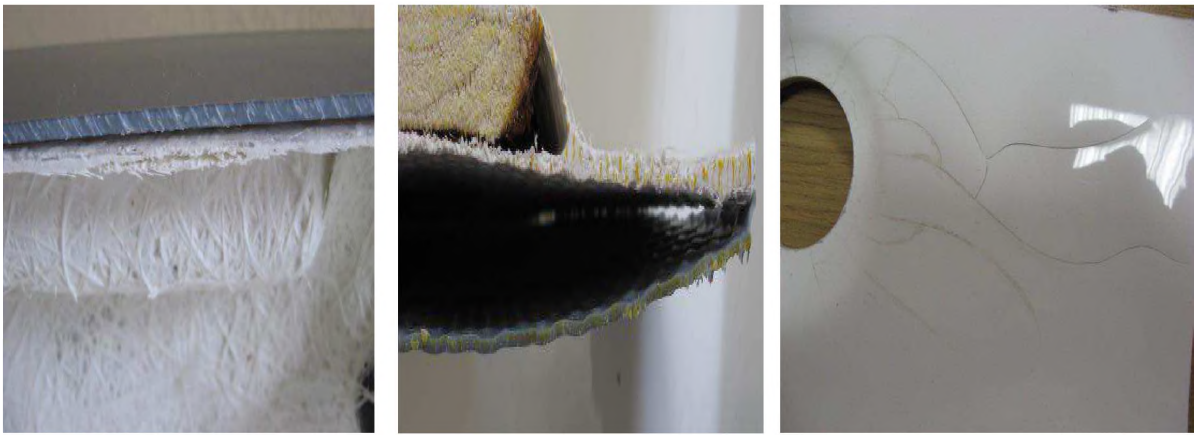
To estimate the adhesive characteristics of the sheet surface we determined the interfacial angle of the sheet wetting with polyester resin on the side of ABS plastic. For this purpose, from the height of 10 mm drops of polyester resin were applied with the glass rod onto the surface of the ABS. For sample No. 1 the angle of 32° was observed, while for sample No. 2 – it was 58°, which demonstrate poor wettability and adhesion of polyester binder to the surface of the ABS sheet.

The increase of the angle of wetting for sample No. 2 shows that on its surface there are components with low adhesion to polar substances. The assumption was confirmed by applying IR spectroscopy method. For the purpose samples were selected by using the microscalpel and dissecting needle in a field of view of the microscope, they being placed in the window of a diamond cell. Spectra were measured with BRUKER's VERTEX 70 spectrophotometer having attachment for a diamond cell of Pike's 6x beam condenser with a tolerance of 4 cm^{-1} after averaging the accumulated spectrogram, containing 32 scans. Spectra were recorded in the range of 4,000–400 cm^{-1} using RT-DLaTGS detector.

Spectral data on materials from different manufacturers show the non-identity of their composition. The spectra of samples No. 1 and No. 2 differed in that in the second specimen the appearance of absorption stripes was observed in the range of 2,238 and 2,361 cm^{-1}, indicating that sample No. 2 contained contaminants which had significant influence on its properties.

The presence of impurities in ABS plastic or the processing of mixtures based on ABS causes internal tension in the extrusion process and during vacuum forming. By exercising mechanical action on the product as, for instance, while forming drain holes of bathtubs and shower pallets, the manufacturer produces microdamages and cracks, characteristic of stressed polymeric materials.

The figure shows fragments of the products from ABS with cracks caused by mechanical impact: drilling of technological holes. It turned out that the cracks were formed throughout the entire thickness of the ABS plastic. Possible cause of internal tension and strength decrease is small sheet thickness, as well as the stresses due to stretch of the sheet since the sheet has different degree of stretch on perimeter and the thickness of the pallet varies from 2.5 mm to 1.05 mm around the drain hole. In addition, internal stresses in the extruded product are largely determined by "calender effect", which depends on technological process parameters and the material composition, branching and length of macromolecules. We tested samples in boiling water, which also showed their significant shrinkage. The shrinkage occurred throughout the layer of ABS plastic, which shows the tension of the sheet used that can be caused by deflections in the technology of sheet preparation, its thermoforming, and the lack of stage of heat treatment for the laminate in the process of its production.



Types of defects

Conclusion. Thus, on the basis of the research undertaken we can conclude that:

– the use of mixed compositions, as well as secondary raw materials for the manufacture of multilayer sheets leads to a significant loss of strength, namely, from 68.2 to 13.6 MPa due to the presence of impurities affecting the structure and morphology of the material;

– as a result of thermoforming and operation of such materials delamination of the sheet can occur, it being caused by low adhesive interaction of the sheet formed and polyester premix, as well as the tension of the sheet, which can be the result of deflections in the technology of sheet production, its thermoforming, and the lack of the stage of heat treatment for the laminate in the process of its manufacture;

– properties of the products from high-strength vacuum-formed polymeric materials depend on the mark of the material and its composition;

– strength of ABS plastic adhesion to polyester composite materials is determined by the quality of ABS plastic, the presence and nature of additives in the material;

– spectral data for the materials of different manufacturers show the non-identity of their compositions. The presence of impurities in ABS plastic or processing mixtures based on ABS causes internal stress during the process of extrusion and vacuum forming. Mechanical action of the manufacturer on the products results in microdamages bringing about the formation and growth of cracks, typical of polymeric materials.

References

1. Scheirs J. *Polymer Recycling: Science, technology and applications*. Chichester, John Willy@Sons, Inc., 2001. 610 p. (Russ. ed.: Shayers Dzh. *Retsikling plastmass: nauka, tekhnologii, praktika*. St. Petersburg, Nauchnye osnovy i tekhnologii Publ., 2012. 640 p.).

2. Schwarzmann P. *Termoforming. A Practical Guide*. Munich, Carl Hanser Verlag, 2001. 288 p. (Russ. ed.: Shvartsman P. *Termoformovaniye. Prakticheskoye rukovodstvo*. St. Petersburg, Professiya Publ., 2007. 288 p.).

3 Makarov V. G. *Promyshlennye termoplasty: Spravochnik* [Industrial thermolayers: Reference book]. Moscow, Khimiya Publ., 2003. 300 p.

4. Francesco La Mantia. *Handbook of Plastics Recyling*. Shawbury (United Kingdom), Rapra Technology Limited, 2002. 400 p. (Russ. ed.: F. La Mantia. *Vtorichnaya pererabotka plastmass*. St. Petersburg, Professiya Publ., 2006. 400 p.).

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