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STUDIES OF THERMAL STABILITY OF EPOXY COMPOUNDS FOR GLASS-FIBER PIPES

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Abstract. Thermal stability of different epoxy compounds designed for their use in certain temperature ranges has been studied. Effects of temperature are reported upon physico-mechanical properties of pipes, in particular, their failure stress under axial tension and their dependence on chemical nature of the solidifier.

Keywords: solidifier, failure stress, thermal stability, polymer compound, filler.

1. Introduction

Manufactured articles of different size and shape can be made of glass-fiber plastics: pipelines and reaction equipment, building mounds and roofings, casings and hulls of cars, ships, planes, rockets, *etc*. Glass-fiber plastics are especially appropriate for manufacturing articles that are shaped or covered with casing [1].

In municipal services, metal network pipelines are being largely replaced by glass-fiber plastics [2]. Of special interest are pipelines made of glass-fiber pipes produced by the method of cross-fibred longitudinal-circumferential winding (CFLCW). This is a specific method for manufacturing articles of glass-fiber plastics characterized by anisotropic or transversal-isotropic structure [3]. CFLCW is a "wet" method of winding, which consists in continuous winding of filler soaked in a bath with polymer compound onto a rotating substrate.

A peculiar feature of this method is limited mobility of the filler at the stage of combining it with the polymer compound, which makes soakage of the fibrous filler a crucial operation. Another feature of this process is formation of macrostructure of the fibrous filler in the article with the aim of achieving the required physicomechanical and performance characteristics. The orientation of the filler is determined by the ratio of

To obtain articles with specified properties, one should know the relationship between structural parameters of the composite and parameters of the technological process. Studies in the field of polymer mechanics have established, with higher or lower degree of accuracy, the relationship between structural parameters of the composite (*i.e.* content and orientation of the filler) and its physic-mechanical characteristics [5-7].

Thereby, pipes obtained by CFLCW can be used in pipelines of different properties: transportation of cool potable water or technical water or raising of mineral water from artesian wells. For these purposes, glass-fiber pipes have been successfully used for more than two decades. However, their use for transportation of hot water is limited. This is due to high temperatures involved, which can vary within 333–423 K.

By the present time, the role of glass-fiber fillers [9, 10] and epoxy polymer compounds [11, 12] has been studied in sufficient details with evaluation of physicomechanical properties of solidified composites. However, thermal stability of epoxy compounds in fabrication of glass-fiber plastic pipes is still not fully understood [13, 14]. There are no works where the effects of different components on thermal stability of epoxy compounds would be fully described [15].

It is known that epoxy oligomers in most cases acquire technically required characteristics as a result of their transformation into a cross-linked polymer. The chemical nature and molecular structure of solidifiers largely determines the cross-linked structure and affect not only the technological properties of the composites, but their performance characteristics as well [16].

Studies of solidification of epoxy compounds using anhydride and amine solidifiers were reported [17]. In these cases, fragments of the spatial network possessing chemical junctions will have different structure with the amine solidifier:

substrate rotation and stacker movement rates [4]. The content of the polymer compound is controlled by relative viscosity.

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O OH

$$HN_2 \sim NH_2 + CH_2 - CH \sim \rightarrow H_2N \sim NH - CH_2 - CH \sim$$
.
OH O OH
 $H_2N \sim N - CH_2 - CH \sim + H_2C - C \sim \rightarrow H_2N \sim N - CH_2 - CH \sim$.
 NH CH_2
 CH_2
 $CH - OH$

and with the anhydride solidifier:

$$\begin{array}{c} O \\ R \\ R-CH-C-N-R \\ R \\ R-CH-C-O-CH_2-CH-CH_2-R \\ O \\ O \\ \end{array} \rightarrow \text{and so on}$$

It is known that epoxy polymers formed using an amine agent for cross-linking is characterized by larger content of OH-groups per unit volume as compared with the initial oligomer, while solidification by anhydrides lowers somewhat the number of OH-groups.

Thus, the model fragments of spatial network as shown above will be distinguished, in the first case, by the presence of OH groups and tertiary nitrogen, and ester linkages in the second case, which will be reflected in properties of the respective compounds [18]. The content of OH-groups can be studied by means of IR-spectroscopy [19].

The present work was aimed at clearing up how the temperature changes in failure stress under axial tension would depend on the solidification method used, basing on thermal stability studies of glass-fiber plastics made of epoxy polymer compounds with different solidification systems.

2. Experimental

Our studies of thermal stability of epoxy compounds in different temperature ranges were carried out in collaboration with the company "Skloplastykovi truby" (Ukraine). The glass-fiber pipes were obtained by the continuous method of cross-fibred longitudinal-transverse winding [20]. This method has its technological requirements, so we used polymer compounds that met these requirements and had the following technical characteristics:

- viscosity at 298 K within 10–16 Pa's;

- time stability at 313 K more than 6 h;
- solidification temperature 353-423 K;
- solidification time not more than 5 min.

For our studies, we chose an imported analog of epoxy oligomer ED-22 (with respect to epoxy group content) – Epicote 828 (Netherlands) with solidification systems of different nature, namely:

- methyltetrahydrophtalic anhydride (MTHPA) as solidifier and tertiary amine 2,4,6-tris (dimethylaminomethyl)phenol as accelerant;
 - aliphatic amine BD H328;
- cycloaliphatic diamine 3-aminomethyl-3,5,5trimethylcyclohexylamine (IFDA);
- aromatic amine diethyltoluenediamin (DETDA);
 - aromatic amine BD H400.

We studied the effect of temperature on physico-mechanical properties of pipes with solidifiers of different chemical nature. As characteristics of physico-mechanical properties, we chose the values of failure stress under axial tension (σ_0) at 293, 333, 363, 393, and 423 K [21].

Before starting our studies, we analyzed certain factors that could affect the reliability of the obtained results. First, there are factors related to the technology used for sample preparation. Since the samples are obtained by mechanical treatment of glass-fiber pipes along the axis, radius-related effects could appear. Thus, the ultimate strength is decreased, because, alongside the failure stress under axial tension, the bending moment and stress concentrator should also be taken into account. The degree of the strength decrease depends upon the glass-fiber pipe diameter and wall thickness. Since these factors could not be avoided, we tried to make their contribution equal for all the samples. Thus, for all experiments glass-fiber pipes were made with the same geometrical dimensions, namely, diameter 130 mm and wall thickness 3 mm.

One more factor substantially affecting (σ_p) is the anisotropy, or transversal-isotropic structure, characterized by the anisotropy coefficient (the ratio of the fillers in the transversal and axial directions). We have chosen the transversal-isotropic system with anisotropy coefficient equal to 2.

Alongside with technological factors, the reliability of the results is also affected by the amount of polymer compound in the glass fiber and the degree of its solidification (degree of cross-linking). The content of polymer compound in the samples was determined by the burning-out method [21]. The solidification degree was determined using a Soxhlet extractor [22]. For testing, we took samples containing 28–29 % of polymeric compound with solidification degree of 96–97 %.

3. Results and Discussion

For each polymer compound, the failure stress under axial tension was determined as function of temperature. The obtained data are compared in Fig. 1.

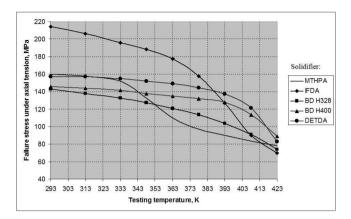


Fig. 1. Failure stress under axial tension as function of temperature and chemical nature of polymer compounds

Since all samples were of the same geometrical dimensions, the anisotropy coefficient (the ratio of the filler amounts introduced in transversal and axial directions) was also assumed to be equal, meaning equal amount of the filler in all samples.

It can be seen from Fig. 1 that lower failure stress at 293 K was shown by the samples with solidifiers MTHPA, BD H328, BD H400 and DEDTA. This suggests that at room temperature the solidification system nature does not significantly affect the failure stress of glass fibers, as under these conditions it is the filler that bears main responsibility for load resistance. Samples with solidifier IFDA have much higher failure stress indices (by 25–35 % higher as compared with other samples), which may be due to better compatibility of the compound and the filler oily substance.

The data on failure stress under axial tension at 423 K should be considered separately. Though samples with different polymer compounds show different dependences of σ_p on temperature, at 423 K all the obtained plots are close to the same value of the failure stress. This could be explained in the following way: when a polymer compound reaches a certain temperature, the load resistance is largely passed to the filler. Since the amount of filler is the same in all samples, at temperatures above the thermal stability level (e.g., at 423 K) the values of σ_p are nearly equal for all polymer compounds.

This is clearly shown by the plot obtained for samples with solidifier MTHPA. In this case, the failure stress under axial tension begins to decrease starting from 323–333 K. When the temperature of 373 K is reached,

this process slows down, and in the temperature range 393–423 K the values are the lowest among all the samples studied. This is an evidence that in the 333–373 K temperature range the polymer compound passes the limit of the thermal stability temperature due to the polymer compound, and the load resistance is determined by the filler. It should be noted that polymer compounds with anhydride solidifier have the lowest thermal stability among all the compounds studied.

All other compounds can be divided to two groups: polymer compounds with aliphatic amines as solidifiers (IFDA and BD H328) and polymer compounds with aromatic amines (BD H400 Ta DETDA). Each group is characterized by its own peculiar features of the temperature dependence of the failure stress under axial tension. Thus, with samples obtained in structuring using aliphatic amines, the σ_p vs. temperature plot is closer to linearity. When the temperature is increased, lowering of σ_p is more uniform, without a well-defined peak that would correspond to the thermal stability temperature. A slightly more intense decrease in σ_p for samples with solidifiers IFDA and BD H328 begins at 373 K. Comparing the compounds with solidifiers IFDA and BD H328, we see different decrease rates of σ_p with temperature. With IFDA, this decrease is the strongest among all samples. It should be noted that at 293 K the value σ_p of this compound is 25–35 % higher than with other cases, but at 393 K this advantage vanishes.

For glass-fiber samples structured by aromatic amines, the σ_p vs. temperature plots also show peaks corresponding to their thermal stability. When testing temperature was changed from 293 to 393 K, the σ_p values for glass fibers with solidifiers BD H400 and DETDA remained almost constant, though under further temperature increase those values were substantially lowered. This can be explained by higher thermal stability of pipes made of polymer compounds structured by aromatic amines as compared with anhydride and aliphatic solidifiers, which is due to the presence of benzene rings. These samples had also more stable physico-mechanical properties up to reaching the thermal stability temperature.

The obtained data on the effects of the polymer compound chemical nature upon σ_p should be accounted for in considering the working conditions. If glass-fiber pipes made of polymer compounds with aliphatic amine as solidifier are to be used at temperatures close to the thermal stability temperature, small unforeseeable temperature rises will not substantially affect the σ_p values, while with compounds structured by aliphatic amines minute temperature changes close to the thermal stability temperature can lead to a substantial decrease in σ_p , with imminent critical consequences.

In Fig. 2 the changes in σ_p vs. temperature for each polymer compound are presented in more detail. The temperature changes are divided into several temperature ranges (σ_p changes in per cent with respect to the initial value are given for each temperature step divided by 10 K).

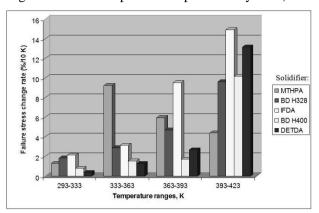


Fig. 2. Failure stress change rate (%/10 K) of polymer compounds structured by different solidifiers in differ ent temperature ranges

It can be seen from Fig. 2 that in the first temperature interval (293–333 K) changes in σ_p for glass-fiber pipes made of different polymer compounds do not exceed two per cent for each temperature rise by 10 K. The highest values are obtained for samples with aliphatic amine solidifiers while the lowest ones – for samples with aromatic amines.

If we consider samples with MTHPA solidifier, the strongest changes of the failure stress are noted in the temperature range of 333–363 K. With further temperature increase, the failure stress change rate is decreased. With glass fiber polymer compounds with aromatic amines, σ_p change rate in the 293–393 K range increases slightly, and substantial changes in the rate variation are observed only under further temperature rise.

For the samples structured by aliphatic amines, σ_p temperature challenges are more uniform as compared with aromatic amines, with maximum increase observed above 363 K.

4. Conclusions

As a result of our studies, we have obtained dependences of the failure stress σ_p on the solidification method used at different temperatures. It has been shown that, depending on the solidification system used, glassfiber pipes react to temperature increases in different ways. With glass-fiber plastics structured by aliphatic amines, σ_p decrease with temperature is continuous, while those structured by aromatic amines display the σ_p decrease only on reaching the temperature corresponding to the thermal stability. Samples structured by anhydrides have much lower thermal stability, resulting in substantial decrease in

 σ_p already at 333 K, with gradual lowering of the failure stress change rate in these compounds under further temperature rise. The obtained results should be accounted for in determination of suitable working conditions of fiber-plastic pipes.

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ДОСЛІДЖЕННЯ ТЕРМОСТАБІЛЬНОСТІ ЕПОКСИДНИХ СПОЛУК ДЛЯ СКЛОВОЛОКОННИХ ТРУБ

Анотація. Досліджено термічну стабільність різних епоксидних сполук, призначених для використання в певних температурних діапазонах. Визначено вплив температури на фізико-механічні властивості труб, зокрема, їх руйнівне напруження при осьовому розтягненні і залежність від хімічної природи затвердника.

Ключові слова: затвердник, руйнівне напруження, термостабільність, полімерна сполука, наповнювач.