Construction Sealants Based on EPDM Modified with Silane-Terminated Urethane Prepolymers

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Abstract. In connection with the use of new materials and structures in construction, the issue of developing sealing materials for construction purposes with an improved set of properties remains relevant. In particular, sealing materials based on ethylene propylene diene rubber (EPDM) are promising due to their resistance to UV radiation, ozone, and the absence of cold flow. The paper shows the possibility of obtaining reactive sealants based on EPDM and silane-terminated prepolymers - STP based on oligotetraoxymethylene glycol (polyfurite) and based on oligooxypropylene glycol (laprol). The use of prepolymers leads to an increase in the cohesive and adhesive strength of the sealing compositions, while maintaining the cohesive nature of the fracture. Also, the obtained sealants are more technological, since they have a lower viscosity under processing conditions. Extensive tests of reactive sealants based on EPDM have shown that after aging it has a higher level of properties compared to sealants without STP.

1. Introduction

In connection with the use of new materials and structures in construction, the issue of developing sealing materials for construction purposes with an improved set of properties remains relevant. In particular, sealing materials based on ethylene propylene diene rubber (EPDM) are promising due to their resistance to UV radiation, ozone, and the absence of cold fluidity [1]. Rolled roofing materials of membrane type based on EPDM have found widespread use around the world. Currently, for sealing the edge of the joint of glued panels based on EPDM is used the so-called one-component “edge sealant” (solvent concentration less than 50%) based on EPDM. Sealants for sealing the edge of the joint should have the same durability, resistance to water, ozone, ultraviolet rays, temperature extremes, the ability to completely isolate building structures from the environment, as well as roofing materials themselves. This is due to the fact that the joint edge is the most vulnerable part of the entire roofing waterproofing coating and if the joints are not properly sealed over the entire service life of the material, the adhesive joint can be destroyed and, as a consequence, the roof itself will be destroyed. In connection with the use of a solvent, formation of defects within the volume of the sealant and deterioration of the boundary tightness during operation are possible. To improve the quality of sealing, it is necessary to exclude the solvent from the composition of the sealant and increase the strength of the composition. This can be achieved by curing EPDM in the conditions of the construction site.
At present, the properties of non-curable, hot-melt, and reactive sealants based on butyl rubber and EPDM have been studied quite well [2–8]. In the case of butyl rubber (IIR), the use of reactive oligomers capable of curing in the presence of water from air in an amount of more than 20 parts by weight in the sealant composition and form a continuous matrix in the environment of the elastomer leads to the formation of compositions with high strength and adhesive properties. Given the insufficient resistance of the compositions based on IIR during operation in air to UV, it was decided to evaluate the possibility of obtaining reactive hot-melt sealants based on EPDM.

Also one of the possible directions of application of sealants based on EPDM is the sealing of interpanel joints. Such sealants are used in atmospheric conditions, therefore, the main requirement for such compositions is resistance to various adverse environmental influences, a certain strength and high adhesion to various building materials (steel, concrete).

Despite the high performance characteristics of sealants based on EPDM, it has one drawback - poor adhesion to most substrates. Currently, there are solutions that can improve the adhesion characteristics of sealants based on EPDM, in particular the use of silane-terminated oligomers in the composition of such sealants. At present, the use of silanes and silane-terminated oligomers is widely used to improve the properties of polymer composite materials for various purposes [9–12]. This paper presents a study of the effect of a silane-terminated prepolymer (STP) based on oligotetraoxymethylene glycol (polyfurite) and oligooxypropylene glycol (laprol) on the properties of a hot-melt sealant based on EPDM.

2. Experimental part

We studied the effect of STP based on oligotetraoxymethylene glycol (polyfurite) with MM 1000 with a content of isocyanate groups of 5.97 wt.% (STP-P) and based on oligooxypropylene glycol (laprol) with MM 3000 with a content of isocyanate groups of 3.5 wt.% (STP-L) modified according to terminal isocyanate groups of gamma-aminopropyltrimethoxysilane on the properties of sealants based on EPDM. The content of STP varied from 0 to 80 pts.wt.

Sealing compositions were prepared in 3 stages: EPDM was mixed in a rubber mixer with EVA at 125 °C for 3 minutes. In the second stage, reactive oligomers (STP-P or STP-L) were introduced at 80 °C, mixing for 5 min. The introduction of fillers, plasticizers, adhesive and technological additives (3 stage) was carried out at 80 °C for 5 minutes.

The rheological properties of the compositions were determined on a Getfert capillary viscometer. Strength and adhesive properties of sealants were evaluated after curing of the silane-terminated prepolymers in the environment of EPDM. The content and structure of prepolymers cured in the EPDM environment were determined by sol-gel analysis.

3. The discussion of the results

From Figure 1, it follows that the strength of the compositions with both STP-L and STP-P increases with increasing content of STP, and the breaking elongation decreases. In the case of STP-L, a gradual increase in strength and a decrease in elongation are observed. With the introduction of STP-P up to 40 pts.wt. while maintaining strength, there is a significant decrease in elongation. A further increase in the STP-P content leads to an increase in the strength of the sealant without changing the elongation.
A decrease in elongation indicates the formation of a semi-interpenetrating network of cured SPP in the environment of the uncured elastomeric phase (EPDM). As is known, as a result of the diffusion of water from ambient air into the sealant, hydroxymerization of the terminal hydroxymethyl groups of the silane-terminated oligomer with the appearance of reactive silanol groups with subsequent silanol condensation according to the following known scheme [13]:

![Chemical reaction diagram]

Figure 1. Influence of the STP content on deformation-strength properties: tensile strength (a), breaking elongation (b) of reactive hot-melt sealants based on EPDM.
Figure 2. The effect of the STP content on adhesion to duralumin, reactive hot-melt sealants based on EPDM.

From Figure 2 it follows that in the case of both STPs, the adhesion to duralumin increases significantly with an increase in the STP content, in the case of polyfurite by 1.7 times, in the case of laprol more than 2 times. All polyfurite-based STP compositions have cohesive character of discontinuity that is characteristic of all studied dosage intervals, i.e. adhesive strength to the substrate exceeds the strength of the composition itself. In the case of STP based on laprol, the character of discontinuity changes from cohesive to mixed at 40 pts.wt., and then changes on adhesive at 60 parts by weight, this is due to with a gradual increase in the strength of the composition.

Viscosity of uncured reactive hot-melt sealants based on EPDM with STP-P or STP-L was evaluated at 130 °C and 180 °C. The dependence of viscosity on shear rate and temperature indirectly indicates a good processability of the compositions.

Figure 3. The dependence of the viscosity of compositions based on EPDM with STP based on laprol and polyfurite on shear rate at 130 °C (a) and 180 °C (b), STP content is 40 pts. wt.
From the Figure 3 it follows that the viscosity of sealants containing STP is significantly lower compared to sealant without STP, which is apparently due to the effect of “temporary plasticization” appearing in the presence of uncured STP. As the shear rate increases, the viscosity of the composition decreases. According to the nature of the viscosity curves, it can be concluded that sealants behave as non-Newtonian fluids — the viscosity of the compositions also decreases with increasing temperature. The viscosity level of sealants with STP-P is somewhat lower in comparison with the compositions with STP-L, one of the reasons for this phenomenon may be the difference in the functionality of the reactive oligomer - laprol is three-functional, and polyfurite is two-functional.

Based on the results obtained, it can be concluded that, unlike conventional hot-melt sealants processed at 180-200 °C, reactive hot-mel sealants can be processed even at a temperature of 130 °C.

The structural characteristics of the silane-terminated prepolymer cured in the EPDM environment are shown in Table 1.

**Table 1.** The effect of the STP content on the gel content and the density of chemically cross-linked network chains.

| STP based on | Reactive oligomer content (pts.wt.) | Density of chemically crosslinked chains of network (νс)*10⁻⁴mol/cm³ | Gel content (%) |
|--------------|-------------------------------------|---------------------------------------------------------------|----------------|
| Laprol       | 20                                  | 0,3                                                           | 22             |
|              | 40                                  | 0,9                                                           | 32             |
|              | 60                                  | 1,2                                                           | 41             |
|              | 80                                  | 1,4                                                           | 43             |
| Polyfurite   | 20                                  | 0,2                                                           | 14             |
|              | 40                                  | 1,4                                                           | 21             |
|              | 60                                  | 1,8                                                           | 29             |
|              | 80                                  | 2,5                                                           | 34             |

An increase in the gel content and the density of the network chains with an increase in the STP content indicates the formation of a continuous matrix of a cured silane-terminated prepolymer in the EPDM environment. The somewhat lower gel content in the case of polyfurite is apparently due to the higher heterogeneity of the compositions, in view of the higher polarity of polyfurite compared to laprol.

The developed sealants naturally outperform conventional non-curable sealants in terms of their basic characteristics, and due to the curing of Reactive oligomers in the EPDM environment, they are able to be used at higher temperatures. The properties of the developed sealants are presented in Table 2.

From the results of extended tests (Table 2), it follows that, in general, the strength of the compositions during operation will increase slightly, the relative elongation will decrease, and the adhesion will practically not change. Developed sealants are able to be used not only in construction but also in mechanical engineering and other industries.
Table 2. Properties of developed reactive sealants.

| Characteristics | without STP | STP based on laprol<sup>a</sup> | STP based on polyfurite<sup>a</sup> |
|-----------------|-------------|-------------------------------|---------------------------------|
| Tensile strength, MPa | 0.5 | 0.85 | 0.6 |
| Adhesion to, MPa: | | | |
| duralumin<sup>b</sup> | 0.8 (mix) | 1.0 (coh) | 0.7 (coh) |
| steel<sup>b</sup> | 0.5 (mix) | 0.7 (coh) | 0.6 (coh) |
| glass<sup>b</sup> | 0.5 (mix) | 0.7 (coh) | 0.6 (coh) |
| Breaking elongation, % | 155 | 160 | 100 |
| Swelling in water, %: | | | |
| 25°C 7 days | 0.7 | 1.2 | 1.3 |
| 70°C 96 hours | 2.2 | 2.4 | 2.4 |
| Thermal-oxidative ageing (150°C, 48 hours): | | | |
| tensile strength, MPa | 0.4 | 1.0 | 1.1 |
| adhesion to duralumin<sup>b</sup>, MPa | 0.9 (coh) | 0.9 (coh) | 1.00 (coh) |
| breaking elongation, % | 120 | 110 | 60 |
| Ageing in water (70°C, 48 hours): | | | |
| tensile strength, MPa | 0.4 | 0.6 | 0.7 |
| adhesion to duralumin<sup>b</sup>, MPa | 0.8 (coh) | 0.7 (coh) | 1.0 (coh) |
| breaking elongation, % | 160 | 125 | 95 |
| Ageing in water (25°C, 14 days): | | | |
| tensile strength, MPa | 0.5 | 0.7 | 0.7 |
| adhesion to duralumin<sup>b</sup>, MPa | 0.8 (coh) | 0.9 (coh) | 1.0 (coh) |
| breaking elongation, % | 170 | 130 | 115 |

<sup>a</sup> Blends are content 40 pts.wt. of STP based on laprol and polyfurite
<sup>b</sup> mix – mixed character of discontinuity, coh – cohesive character of discontinuity

4. Conclusion

Thus, the possibility of obtaining reactive sealants based on EPDM and silane-terminated prepolymer has been shown. The use of prepolymer leads to an increase in the cohesive and adhesive strength of the sealing compositions, while maintaining the cohesive character of discontinuity. Also, the obtained sealants are more technological, since they have a lower viscosity under processing conditions. Extensive tests of reactive sealants based on EPDM have shown that after aging they have a higher level of properties compared to sealants without STP.

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