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FUTUR DES MATIERES PLASTIQUES
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NEUVES ET DANS LA MAINTENANCE,
LA REHABILITATION,
LA REPARATION ET LE
RENFORCEMENT DES STRUCTURES
EXISTANTES

FUTURE FOR PLASTICS IN
NEW CONSTRUCTIONS AND
IN MAINTENANCE, REHABILITATION
REPAIR AND REINFORCEMENT
OF EXISTING STRUCTURES



BELGIAN RESEARCH CENTRE FOR PLASTIC AND RUBBER MATERIALS

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PERFORMANCE CRITERIA FOR GRANULAR COMPOSITES SURFACING

LES CRITERES DE LA FIDELITE DES COMPOSITES PARTICULAIRES POUR LES COUCHES DE SURFACE

Polymer binders used for the surfacing of horizontal surfaces are supplied by the producers to the market without any detailed specification of their strain and rheological properties. The authors determined principal parameters which should be investigated and known for an optimum formulation of the binder system for surfacing applications, developed a methodology of ascertainment of internal stresses due to shrinkage and temperature changes and determined further procedures for ascertaining further strain properties. On the basis of these criteria and methodology 42 different epoxy and polyester resin systems produced in Czechoslovakia and in the FRG were assessed, none of which showed optimum properties. It is obvious that more attention must be afforded in the future to the investigation of the complex of properties of resins which are decisive for long term performance of their surfacing applications.

GENERAL ASPECTS

Resinous finishes /surfacing/ of horizontal surfaces in buildings and structures /whether in the form of resin concretes, screeds or cast floorings/ require effective and permanent softening of the binder, if they should show long life, particularly in extreme conditions /e.g. in exterior applications/. Although a number of new polymer systems /resins and hardeners/ has been developed all over the world in the past two or three decades, only few of them satisfy the requirements imposed on large area surface applications with reference to their deformation and rheological properties.

The producer, as a rule, investigates and gives in his prospectuses such properties as characterize the resinous system from the chemical viewpoint /e.g. molecular weight, density, viscosity, stability of shape, contents of non-volatile materials, in the case of epoxy resins the number of epoxy groups, contents of chlorine, etc./ or reaction kinetics /gelation time, maximum exothermic temperature, etc./. Only rarely do they state, without further specification, as a rule, /description of tests, age at test time, hardening régime/ some mechanical properties /tensile, flexural, impact and compressive strengths/. Sometimes the producer's description is supplemented with electrical properties, chemical properties, etc.

A number of these information items are useful or indispensable for the applicator. However, their majority does not tell him anything about those very properties which are essential for the forecasting of the long-term performance of the resinous system in the building structure /including the synergic effect of the individual

Les liants de polymère pour les couches de surface horizontales sont fournis par les producteurs /au marché/ sans spécifications détaillées des propriétés déformables et rhéologiques. Ils ont été sélectionnés les paramètres principaux qui devraient être examinés et poursuivis, pour un système optimum d'un liant destiné aux applications de surfaces pourrait être projeté. Une méthode de la détermination des contraintes internes par contraction et par changes de la température était formée et les méthodes de la détermination des autres propriétés résistives étaient choisies.

Selon des critères et méthodes citées 42 systèmes à la base des époxydes et des polyestères d'origine de la CSSR et de la RFA étaient évalués, pas d'eux ayant été présenté des propriétés optimales. Il est évident qu'il est nécessaire dans l'avenir de prêter plus d'attention au complexe entière des propriétés des résines, qui sont décisives pour la ténacité de longue durée des applications de surfaces.

factors/. Their number includes not only the deformation and rheological properties of epoxy resin /hardened and tested "en bloc"/, but primarily the properties of the whole composite system /with a minor representation of the resin in the form of microstrata in between filler particles/ and in interaction with adjoining materials /particularly the base/ and the environment.

THEORETICAL BACKGROUND

The binder /resin/ for a granular composite system must be evaluated, on the one hand, with reference to the kinetics of the origin of the solid polymer /as the characteristic of the material/, on the other hand with reference to the kinetics of the origin of the flooring system and long term cooperation of the binder with the base and the filler /as the characteristic of the system/.

In every exothermic polymerization of a monomer a volume reduction takes place called the polymerization shrinkage. This shrinkage produces in the resin, from the moment of limitation of its free motion /gelation/ unwelcome internal stress. Therefore, such resins are advantageous, in which the major part of this polymerization shrinkage takes place before the gelation time or in the beginning phase of hardening, e.g. because in the process of polymerization linear chains /which are flexible and enable mutual microdisplacements without much effort/ originate in the first phase and the transverse cross-linking takes place only in the last phase of hardening. Another condition is that the hardening should proceed within a realistically short period in normal environmental conditions /i.e. without any increase of temperature/ to the maximum degree of conversion.

Fig. 1 shows some possible histories of polymerization shrinkage and strength increase in time. The optimum composition is that for which $\frac{\partial \sigma_{lim}}{\partial t} > \frac{\partial \omega}{\partial t}$ /curves a/; in such a case the internal stress σ_{ω} is minimum. If

$\frac{\partial \sigma_{lim}}{\partial t} > \frac{\partial \omega}{\partial t}$ /curve b/, considerable internal stresses arise relatively quickly which can even exceed the momentary strength and cause the origin of microcracks. When both the strength and the shrinkage increase slowly /curve c/, the internal stresses are apparently small at the beginning, growing, however, over a long period, as a result of which the damage can occur even after the elapse of several years.

In a composite system the free shrinkage of the resin is prevented, apart from its structural skeleton, by the filler /particularly if aggregated, as it is the case of composites of the second and third types/ and the base on top of which the system has been placed /and the good bond with which creates the necessary prerequisite for a successful application/. The stresses σ_{ω} originating in the system as a result of polymerization shrinkage, are of long term character and necessarily depend on the rheological properties of the polymer. They comprize not only the stresses in the system itself, which depend on its modulus of relaxation E_r/t , but also on the stresses in the contact joint /particularly between the composite surfacing and the base/ which depend on its modulus of relaxation in shear G_r/t . However, since the

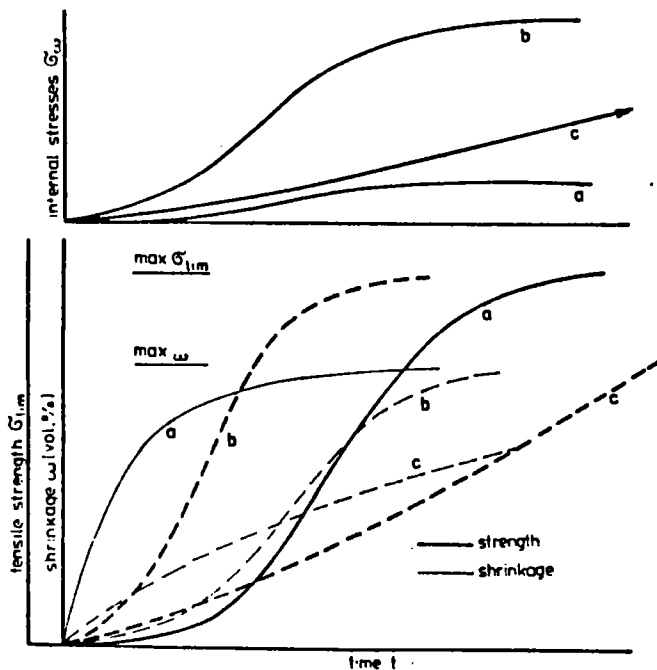


Fig 1 Increase of strength and polymerization shrinkage in time and history of internal stresses due to shrinkage

strengths grow in the course of time due to the proceeding polymerization, both moduli of relaxation are the functions of momentary strength σ_{lim}/t or τ_{lim}/t . Apart from the stress reduction in the system due to the relaxation it is necessary to take into account also the fact that the permanent strength of the resin /even if fully hardened/ σ_{lim}/t is reduced in the course of time

t in dependence on the magnitude of the stress σ . The prevention of shrinkage and the consideration of stress relaxation according to Fig. 2 gives rise in the system to the stress σ

$$\sigma_{\omega} = t/t \cdot \epsilon_{\omega} \cdot E_r/t /,$$

which must never attain the magnitude of the permanent strength for this stress, i.e.

$$\sigma_{\omega} < \sigma_{lim} = F/t, \sigma /;$$

the same applies also to the relation of τ_{ω} and τ_{lim} .

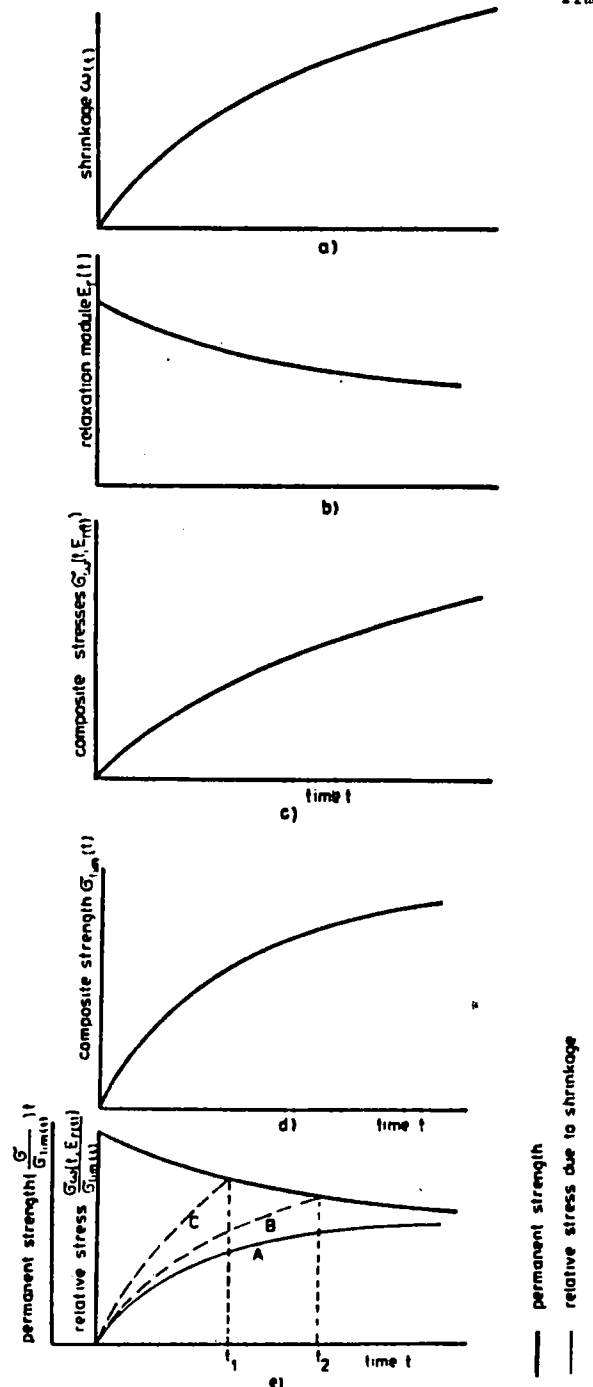


Fig.2 If shrinkage /a/ is prevented, internal stresses / originate in the system in accordance with the relaxation modulus /b/. As long as the relative stress /e/ due to shrinkage does not attain the permanent strength curve /which grows in time as a result of polymerization /d/a/

decreases in time as a result of permanent load ϵ , no damage occurs /Curve A/. If the relative stress ϵ due to shrinkage intersects the permanent strength curve, failure follows /Curve B in time t_2 , Curve C in time t_1 /.
of

Another circumstance, which is of decisive importance for the durability of the system, is its response to temperature changes. Unfavourable in this respect is particularly the temperature drop which produces stresses in the system due to the difference between the coefficients of thermal expansion $\Delta\alpha$ of the resin α_R and of the base /or filler/ α_B of the same sign as the polymerization shrinkage /tensile stresses in the composite/. Apart from that the rheological properties of the materials deteriorate with the sinking temperature, the modulus of relaxation E_{rel} increases, the toughness decreases together with ultimate strain, as a result of which the stresses due to polymerization shrinkage increase. Unsuitable combination of a high coefficient of thermal expansion of the resin, high generic temperature T_p /temperature at which the polymerization took place/ and excessive increase of the modulus of relaxation by a temperature drop may produce such stresses in the system that, together with the stresses due to shrinkage, they may result in exceeding the strength of the composite or the bond strength between the composite and the base /or the contact with the filler/. For internal stresses within the system it holds, therefore, that

$$\sigma_{in} = W/t, T, \epsilon_w, E_r/t, T, \Delta\alpha, T_0 / < \sigma_{lim} = C/t, \sigma, T /.$$

The general determination of the characteristics of the given system and the assessment, whether it satisfies the given criterion, is exceedingly difficult because of the complex /logarithmic or exponential, as a rule/ relations. For experimental verifications, therefore, suitable cumulative functions must be sought.

EXPERIMENTAL METHODS

One of the ways of experimental verification of the behaviour of the system is to follow, apart from the 'free' shrinkage /i.e. the shrinkage which is not confined by anything but the structure of the polymer/ and the 'free' temperature expansion /volume changes due to temperature changes proceeding without any external hindrances/ also the so-called "residual" shrinkage and "residual" temperature expansion or, preferably, /or simultaneously/ directly the stresses originating in the system as a result of the confinement of these dimensional changes. This method can be used, for example, with the apparatus /rheometer/ shown in Fig. 3. The resin /or the composite system/ is compacted in a special mould and is left to polymerize. The mobile front of the mould is connected to a strain indicator and a dynamometric stirrup /Fig.4/. As long as the length deformation equals zero, it is possible to read the originating stresses directly. With a loose stirrup, on the other hand, it is possible to read the shrinkage of length on the indicator. Both readings can be combined as well both for the effect of shrinkage and for that of temperature changes. If the stirrup is released at any time, it is possible to determine "residual" shrinkage, which incorporates the influence of both the strength change in time and the effect of stress relaxation. Analogously, after the zero strain has been maintained for some time, it is possible to determine directly the "residual" stress at any time. The tempering of the apparatus to the required temperature makes it possible to determine the "residual" stress or strain due to temperature changes at any time. Instead of long-term observation at normal room temperature it is possible to insert the whole apparatus into a high temperature environment and to accelerate the hardening /attaining the ultimate conversion of the polymer/ and determine not only the shrinkage increment /or stress increment/ due to complete hardening, but also its final value. The apparatus enables also the

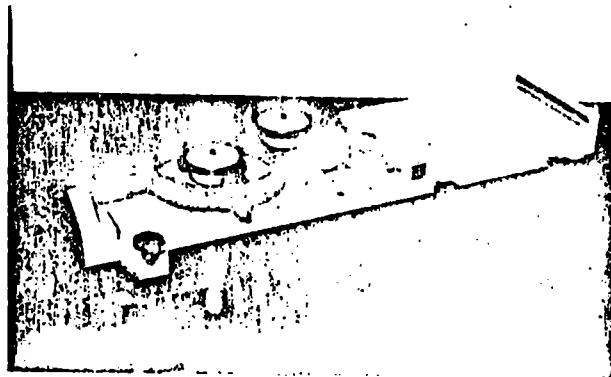


Fig. 3 Type RGM-03 Rheometer /Armabeton, Prague/ for the indication of linear residual shrinkage or linear residual shrinkage stresses or the indication of the indication of linear residual changes of length or linear residual stresses due to temperature changes

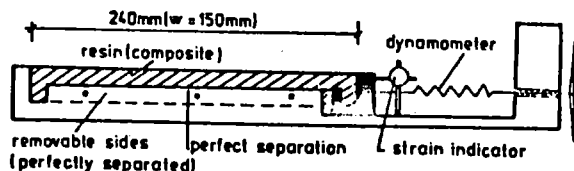


Fig. 4 Schematic drawing of type RGM-03 Rheometer

determination of the relaxation modulus of elasticity /by means of setting and maintaining certain strain, e.g. $1/100$ and reading the stress on a dynamometer/ or the creep compliance, either with the same sample at different temperatures or before and after the complete conversion of the polymer.

Apart from that it is advisable to determine the working diagrams /modulus of elasticity, strength, ultimate strain/ and creep and relaxation behaviour for suitable selected initial values by standard methods using tensile specimens.

EXPERIMENTAL RESULTS

For the purpose of relative assessment of a number of resins offered for the purpose of surfacing /flooring/ a number of experimental measurements was carried out, using the above mentioned methods.

The individual specimens were tested in a rheometer in accordance with the scheme shown in Fig. 5, first at a temperature of 20°C and different age /Test I/, then at a temperature of -20°C /Test II/. The whole experiment was always repeated after complete hardening by temperature increase to 85°C for 48 hours /at a temperature of 20°C - Test III, and at a temperature of -20°C - Test IV/. The data A and B afforded the values of residual stresses due to shrinkage, C the value of residual shrinkage, D indicating the relaxation modulus. The data E and G determine the inner stresses due to the sum of shrinkage and temperature drop of 40°C , F together with C enables the determination of the coefficient of thermal expansion of the flooring

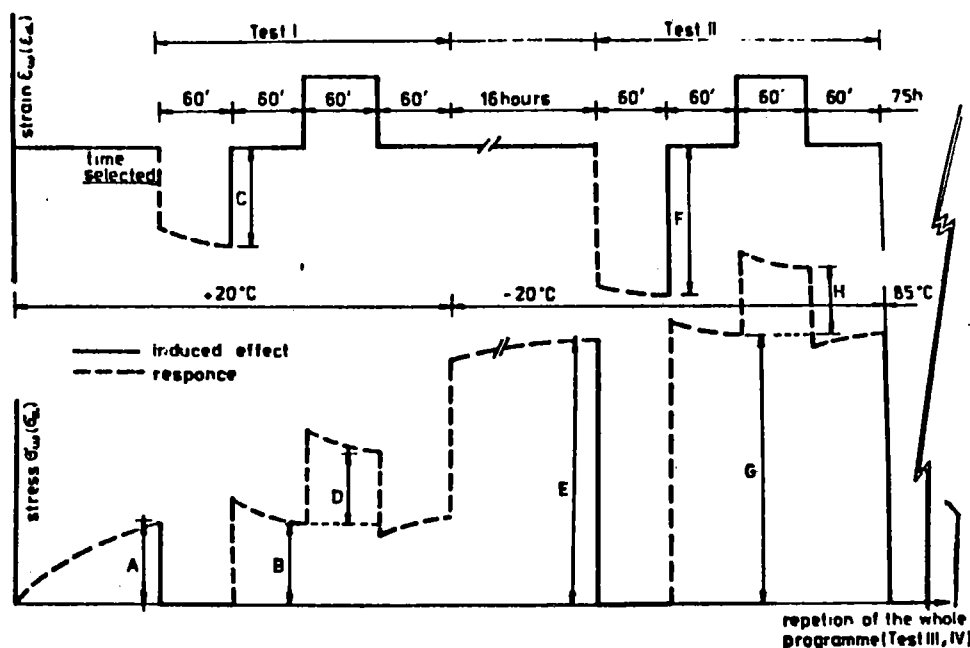


Fig. 5 Rheometer test process

material in the system /within the temperature range of 20°C, -20°C/, H affords the value of the relaxation modulus at a temperature of -20°C. The corresponding values measured after the completion of hardening can be considered as final, i.e. as the values which would be attained at normal temperature in infinite time. The differences of the corresponding values before and after the completion of hardening by high temperature also inform about the degree of conversion in the course of hardening at normal temperatures.

Apart from tensile strength, Young's modulus of elasticity and ultimate strain the working diagrams and the creep and relaxation moduli were ascertained on specimens with narrowed central part /cross section 10 x 20 mm, length 140 mm/ on the Testatron 10 t testing machine with the strain measurements by means of type Instron electric strain gauges and the recording of the readings by a BAK recorder. Tests were made, on the one hand, with the specimens hardened at normal temperature /20°C/, on the other hand, with the specimens hardened at a high temperature /85°C/.

DISCUSSION OF RESULTS AND CONCLUSIONS

So far the rheometer measurements have afforded the data about the inner stresses due to shrinkage and temperature changes /after the relaxation of 60 minutes/ for 42 different epoxy and polyester systems. The results are summarized in Table 1.

The stress-strain diagrams of the individual systems differed considerably /see Fig. 6/.

The systems with extremely low value of the modulus of elasticity and shrinkage stresses at a normal temperature attained the values of the modulus of elasticity which were slightly below the average after the improvement of polymerization conversion /hardening at a high temperature/, accompanied by a considerable increase of internal stresses, without equally significant increase of strength, the values of which remained on a very low level.

The system with low internal stresses due to shrinkage /and, consequently, advantageous in this respect/ have always a considerably higher coefficient of thermal expansion as a result of which also the stresses due to temperature changes attain higher values.

Table 1. Summarised Results of Experiments

Quantity	Hardening at 20°C /7-30 days/	Hardening at 85°C /48h/
Stress due to shrinkage /MPa/	0.010-0.891	0.130-3.1
Stress due to shrinkage together with the stress due to the temperature drop of 40°C /MPa/	1.968-6.180	2.738-8.1
Free shrinkage /%/	0.130-0.713	0.226-1.1
Short-term tensile strength /MPa/	2.6 - 59.0	3.4 - 100.0
Ultimate strain x 10 ³	3.4 - 630	5.9 - 1000
Young's modulus of elasticity /MPa/	50 - 3400	200 - 10000
Creep modulus /MPa/	5 - 3400	12 - 10000
Relaxation modulus /MPa/	5 - 3900	10 - 10000
Coefficient of linear thermal expansion x 10 ⁶ /K ⁻¹ /		56 - 124

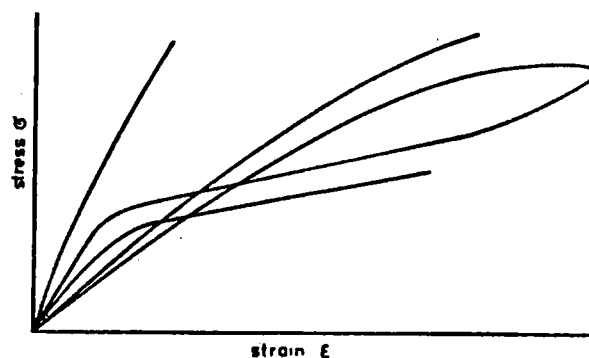


Fig. 6 Forms of working diagrams of various epoxy and polyester systems

From the 42 investigated systems /of Czechoslovak and West German producers/ none satisfies fully the strain and rheological requirements imposed on surfacing materials /in the form of self-levelling cast surfacings, screeds and resin concrete surfacings/, although they are intended for this purpose according to the producers' data. The stresses originating in the surfacing attain the values often approaching the tensile strength, and the bond stresses in the contact joint with these /which are three times as high as the stresses within the surfacing layer of the composite/ generally exceed the bond strength in extreme conditions. If any of the systems have proved satisfactory with reference to internal stresses, they have insufficient hardness and compressive strength, accompanied with very significant reduction of fracture energy with increasing loading speed.

The result of the described extensive experiment is alarming. It is obvious that so far very little attention of resin producers and macromolecular chemists has been afforded to the research of the complex of properties which are decisive for long-term performance of surfacing applications and that without the remedy of this shortcoming it will be impossible to eliminate a relatively considerable percentage of unsuccessful applications. It is only natural, that the properties of filled binders /Type I composites/ and particularly of Type II and Type III composites /such as resin concretes/ will be considerably different and that some unfavourable binder properties will be suppressed /e.g. low hardness and compressive strength/; on the other hand the significance of some properties /fracture energy, coefficient of thermal expansion, shrinkage/ will increase in the composite, since also its deformation and rheological properties are considerably different from those of the resin and are modified, moreover, by various internal stress concentrations resulting from the non-homogeneity of the system.