THE POLYMER BITUMINOUS MEMBRANES : THE NEW GENERATION

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Abstract

The qualitative evaluation of waterproofing membranes must also be based on the capacity of the product to maintain its characteristics over the years.

Being necessary to know the performances of waterproofing membranes before introducing them into the market and not having many years to evaluate the ageing action, various tests have developed with the precise function of accelerating this process.

In the following survey we take into consideration how different tests and thermal treatment act on chemical bitumen composition, on polymers employed as modifying agents and on polymer bitumen blends.

Thus, this survey intends to show how, by using the test just mentioned, the use of particular polymers and additives can influence the ageing process as well as modify substantially the duration of the characteristics over the years.

LE MEMBRANE BITUME POLIMERO DELL'ULTIMA GENERAZIONE

Presentazione

La valutazione qualitativa delle membrane impermeabilizzanti deve anche essere fondata sulla capacità del prodotto a preservare le proprie caratteristiche nel tempo.

Data la necessità di conoscere le prestazioni delle membrane impermeabilizzanti prima d'immetterle nel mercato e dato che non si hanno a disposizione anni per valutare l'azione dell'invecchiamento si sono sviluppate prove in grado di accelerare tale processo.

Nel seguente rapporto si considera come le varie prove ed il trattamento termico agiscono sulla composizione chimica del bitume, sui polimeri usati come modificanti e sulle mescole bitume polimero, e come l'azione degli additivi possa influenzare il processo d'invecchiamento e come l'uso di particolari polimeri possa incrementare la longevità del prodotto.

DIE NEUE GENERATION DER POLYMERBITUMENABDICHTUNGSBAHNEN

Zusammenfassung

Die Qualität polymermodifizierter Bitumenbahnen wird zunächst bestimmt durch die thermischen und physikalischen werte zum Herstellungszeitpunkt. Wesentlicher für die Bewertung des Qualitätsstandards einer Dachbahn ist jedoch das Langzeitverhalten, das heisst die Beständigkeit gegenüber UV-Strahlung sowie die thermo-oxydative Alterungsbeständigkeit.

Um diese Werte des Alterunsprozesses schneller zu erhalten wurden verschiedene Untersuchungspraktiken etwickelt.

Wie durch die Benutzung von besonderen Polymeren und Additiven der Alterungsprozess beeinflusst werden kann, möchten wir ihnen in dieser Studie erklären.

LA NOUVELLE GENERATION DES MEMBRANES EN BITUME MODIFIE.

Résumé

L'évaluation qualitative des membranes d'étanchéité doit tenir compte aussi de leur capacité de preserver leur caracteristiques dans le temps.

Compte tenu de la nécéssité de connaître les performances des membranes d'étanchéité avant de les distribuer sur le marché, et compte tenu aussi du fait qu'on ne peut pas disposer d'années pour évaluer les conséquences du vieillissement plusieurs essais ont été developées pour accélerer ce phénomène.

Cet étude a pour but d'illustrer comment, à l'aide des essais ici rapplés, l'emploi de polymers et additifs spéciaux puisse modifier le phénomène du vieillissement en prolongeant la durée de vie des caracteristiques des membranes dans le temps.

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INTRODUCTION

Generally speaking, protection from water and humidity has always been the heart of our living needs. The evolution of building material technology gives us today the opportunity to use long lasting and effecting materials.

This notwithstanding, it is fundamental to look to the future in particular to the duration of materials, in fact we do not only have to solve the problem of building waterproofing but we also have to grant the duration of our intervention over the years.
The duration of waterproofing products changes a lot according to the work conditions of the product, to the external environment, to the physical and mechanical characteristics of the waterproofed work and in the end, but not less important, to the quality of employed products.

Bitumen membrane tends to loose over the years its original characteristics of elasticity and malleability not withstanding the mechanical stress of the building. Expansion joints, vertical turnings and water drains are only some critical points where the membrane can fail, creating in this way a leak and therefore the need to remake the waterproofing covering.

A waterproofing product such as the bitumen membrane does not have, on the other side, such an aesthetic component which lets us foresee its substitution for architectural reasons before its end (as it happens on the contrary for sanitary components of a bathroom or ceramic tiles); it is therefore substituted just when it is ineffectual, but when and why?

We do not have a general answer, it can last for 10 years under standard conditions but it can last longer if the membrane is not directly exposed to the action of atmospheric agents which are the main cause of its ageing.

The solution can be the research of products which do not show traces of the degrading effects caused by atmospheric agents (sun, rain, thermic shock, etc.) or by other environmental diseases (smog, chemical aggressions etc.).

The duration over the years of its original characteristics which grant therefore a longer living comfort level and a higher economic value of the manufactured article spurs us to the search and the development of technologies which let us realise some long lasting products.

These are in short the reasons which brought us to deeply study the ageing causes of polymer bitumen membranes with the aim to get near the solution.

2. AIM OF THE WORK

The aim of the following work is to evaluate how and how much the constitutive components of bitumen membranes change during their ageing processes. On this purpose we use ultraviolet light together with QUV condensate cycles and forced air bath as ageing methodologies. We moreover evaluated the effects of EPR synthetic polymers, recently introduced, on the ageing processes.

3. THE DEGRADATION REACTIONS OF THE BITUMEN MATRIX

The bitumen, composed by a hydrocarbon blend soluble in carbon disulphide, is obtained through oil refining processes. It contains a very high number of chemical species including linear hydrocarbons, naphthenes, aromatic hydrocarbons, saturated and unsatured, with or without heteroatoms or functional groups. Such chemical species co-exist thanks to mutual interactions together with the formation of a compatible and firm system equipped with viscous elastic properties.

The theoretical model concerning the bitumen micelle structure is commonly accepted, and it is characterised by the dispersion of asphaltene micelles peptizated by molecules with intermediate complexity (asphaltic resins) towards an oily phase which is formed by both aromatic and saturated molecules having a lighter molecular weight.

Many studies have been made on bitumen ageing and on the way its constituents vary during such process. Generally speaking one can state that during the ageing process there is a displacement of the different constituents towards aromatic fractions having a heavier molecular weight. This leads to an augmentation of the asphaltenic fraction to the prejudice of aromatic compounds, while the saturated fraction stays nearly unchanged. Such an augmentation modifies mutual molecular interactions with subsequent hardening of the mass and related structural fragility.

4. POLYMER DEGRADING REACTION

Speaking about polymers, with the term degradation we refer to those processes which lead to some changes of their chemical and physical properties.

Polymer degradation can happen both through the action of physical agents such as heat, sun light, high energy radiations, mechanical strains, and through the action of chemical agents such as oxygen, ozone, water, acids, bases, etc. The behaviour of polymers during their degradation depends on their chemical structure but, in general, it is not deductible from the behaviour of model compounds which have a light molecular weight. This happens because polymers contain a small percentage of structural irregularities which create some unstabilities whence the degradating reaction starts.

The different reactions are :

a) Depolymerization reaction : its mechanism is of chain radical kind and starts by the homolitic fission of a link within the polymer chain or a link of a terminal structural unit. Such process goes on through following propagation reactions with the elimination of monomeric units or through transfer reactions among molecules with the formation of polymer chain fragments.

   The course of the depolymerization reaction depends from the speed connected to the propagation and transfer processes. Polypropylene shows transfer reactions which distinctly prevail over propagation ones with a subsequent fission of polymer chains into fragments which during the reaction process become shorter and shorter.

b) Oxidative degradation reaction : its mechanism is started and controlled by a thermic or photochemical way. Such distinction is mostly formal since the processes usually start in parallel and sometimes with synergical effects. In both processes one can see the formation of peroxide intermediates which later go through a homolitic fission of thermic or photophysical kind. The speed of polyhydrocarbon thermal oxydation depends on the reactivity of formed peroxide radicals and on the homolitic fission energy of the C-H links available in the polymer matrix. The deterioration of the synthetic polymers exposed to the action of sun radiations and atmospheric agents mostly happens through oxidative processes created by the ultraviolet sun radiation component (290-250 nm). The speed of photoxidation varies according to the radiation dose and therefore according to the latitude, the seasons, the chemical structure, the thickness of the material and depends above all on the intrinsic extent and kind of the irregularities or structure lacks of the polymer, and all these mostly act as sensors of the oxidative process itself.

c) Mechanic-chemical degradation: The work processes which cause big cutting efforts are able to accumulate in macromolecule segments such a quantity of energy as to produce homolitic link fissions with the subsequent formation of radical fragments. These latters can lead to a new arrangement or a dismutation, but if there is some oxygen, they can start the autoxidative degradation process.

d) Biophysical degradation. With this definition we refer to all those processes due to micro-organisms' attack and digestion of polymer materials.

After analysing the composition and the structure of bitumen and polymers and how single compounds take part to the degradation process, we start our study with the aim to find which means can slow down ageing processes by finding out, first of all, a system to replicate them in laboratory.

5. EXPERIMENTAL PART

In this part of the work we compare the blends obtained with traditional polymers (a combination of amorphous and isotactic polymers) to the blends obtained mostly with the use of the following :

- ➢ APAO polymer (APAO= amorphous polialphaolephine).
- ➢ EPR polymer (EPR= ethylene propylene rubber).
- ➢ Newly introduced TPO polymer (TPO= EPR-IPP polymer alloy).

Such polymers are chemically stabilized and obtained with highly efficient and performing catalysts, therefore they are able to reduce the presence of structural irregularities.

5.1 PREPARATION OF SAMPLES

Two different types of blends are prepared. The first one is prepared with a standard formula (bitumen + different fresh polymers). The second one prepared using the same standard formula but polymers aged through several ageing cycles.
The composition followed for the study is : 80 parts of bitumen and 20 of polymer blend.
The blending process happens through polymer heat-resisting dispersion with a mixer at a varying speed up to 2000 rpm. The

blending temperature is between 180 and 190°C while the preparation lasts 3 hours.

5.2 CHARACTERIZATION OF OBTAINED BLENDS

The characteristics of the blends are evaluated with the following analytical methods:

- Ring and Ball temperature (ASTM D 36 method)
- Penetration at 25°C and 60°C (ASTM D 5 method)
- Brookfield viscosity at 180°C (Brookfield DVII, S27 rotor)
- Cold flexibility (according to EN 1109)
- Blend dispersion determined with an epifluorecent microscope at 250 enlargements (Microscope Olympus BX 60)

The tests are made both on fresh and artificially aged material.

5.3 AGEING PROCESSES

Accelerated ageing is realised by using the following methods:

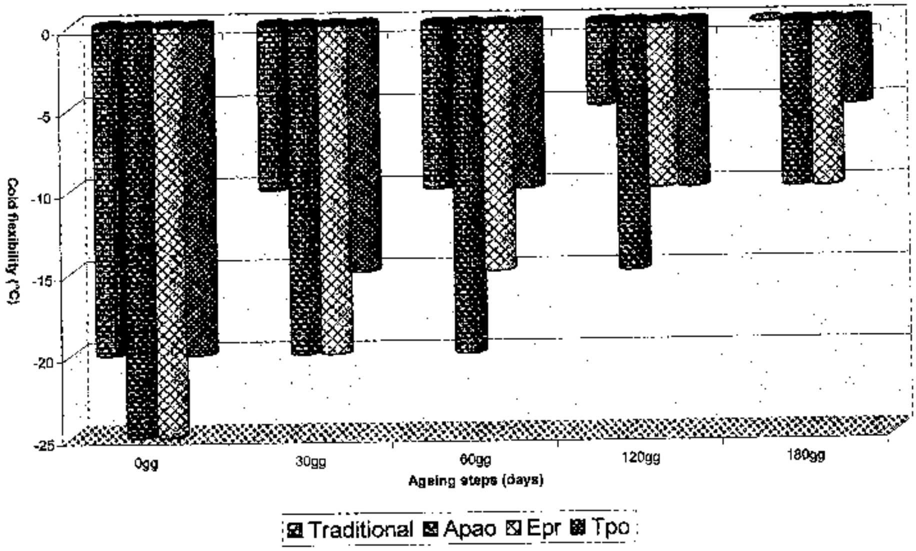
- Ageing in a forced air bath at a temperature of 70°C for 6 months (according to UEAtc).
- Ageing through the QUV Accelerated Weathering Tester (Q-Panel Lab Products, Cleveland, Ohio) by using a UVB-313 fluorescent lamp and alternating 4-hour light cycles at the temperature of 60°C with 4-hour condensate at the temperature of 50°C. The test is made for about 3,000 hours.

All different blends were object of the ageing stove test with intermediate passages every 30/60/120/180 days. Polymers only after 180 days.
The QUV test for the blends was made every 500/1,000/1,500/2,000/2,500/3,000 hours and for polymers only after 3,000 hours.

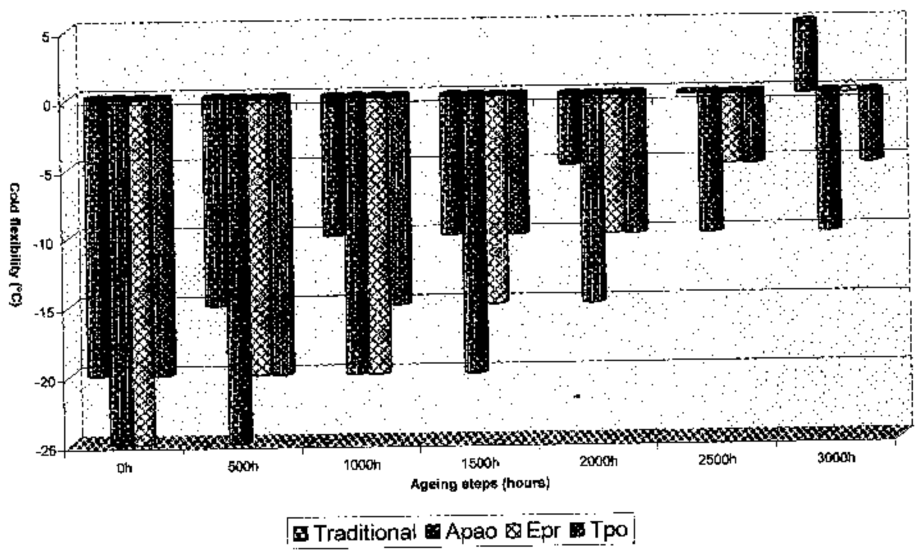
5.4 KIND OF SAMPLES

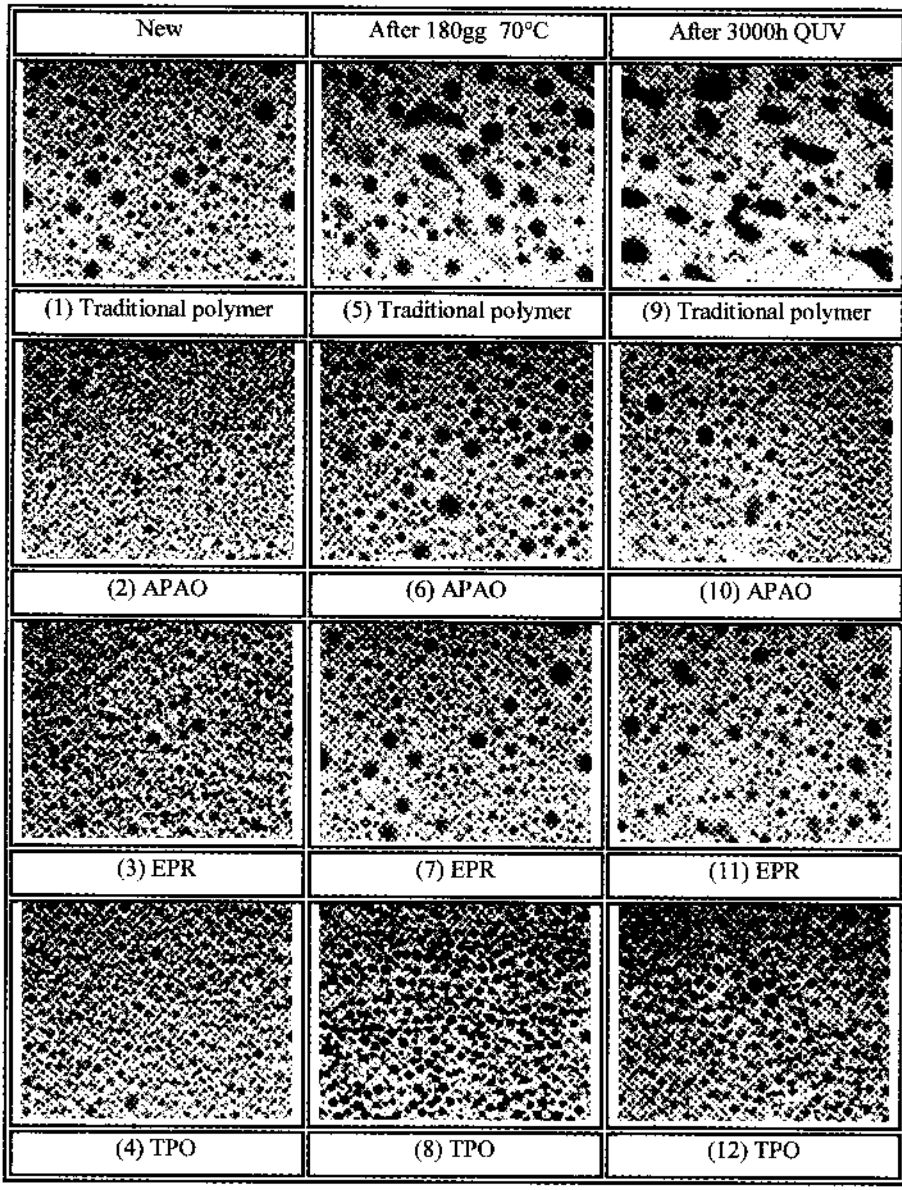
The samples employed for the ageing are made of compound pieces 2 mm thick.

Thermal ageing in air (70 °C)



Q.U.V. ageing




New
After 180gg 70°C
After 3000h QUV
(1) Traditional polymer
(5) Traditional polymer
(9) Traditional polymer
(2) APAO
(6) APAO
(10) APAO
(3) EPR
(7) EPR
(11) EPR
(4) TPO
(8) TPO
(12) TPO

6. RESULT ANALYSIS

The theory according which one can consider the bitumen compound of polymer kind is confirmed, since the polymers influence its chemical and physical characteristics.
Therefore if polymers are stabilized, also the compound can be considered much more stable during degradating processes.
Such behaviour is clear both during the ageing process with the QUV test and during the ageing process in stove.

In the graphics 1 and 2 concerning the blends we point out the variation of cold flexibility values over the years. In the pictures 1 :4 we examine the dispersions of the bitumen and polymers blend which was not previously aged. In the pictures 5:12 we point out the dispersions with polymers on which different artificial ageing cycles were made, before they were again blended with bitumen.

CONCLUSIONS

The use of stabilized polymer compounds substituting traditional polymers clearly points out an important slow down in the various degenerating processes granting in the meantime an important augmentation of the product's duration.

Our recent industrial productions, where stabilized polymer compounds have been employed, let us obtain bitumen membranes with an impressive improvement of ageing resistence in comparison with the traditional methods of membrane modifying. This limited ageing means the duration of the polymer bitumen compound characteristics and, more precisely, the duration of cold flexibility values and product penetration.

The results obtained, according to the definition of the research, cannot and must not be considered definitive. Big development areas are in the search of a balance among the different components of the compound in order to grant the repeating of industrial productions.

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