

# **THE MOST RECENT FRONTIERS OF PERFORMANCE IN APP MODIFIED BITUMEN WATERPROOFING MEMBRANES WITH THE USE OF NEW GENERATION POLYOLEFINS**

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## **KEYWORDS:**

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## **ABSTRACT:**

Following the “discovery” of bitumen, a new breakthrough in the field of water-proofing was achieved with the synthesis of polypropylene in the early 60's. The old generation Ziegler-Natta catalysis generated, as a by-product, considerable quantities of atactic polypropylene, which was used to advantage as a bitumen modifier in waterproofing applications: this was the birth of polymer-bitumen waterproofing membranes. SBS (styrene-butadiene-styrene), a new modifier for bitumen, was introduced in the early 70's. The mixtures obtained with these two types of modifiers were good, but their performance capabilities were limited in several respects.

A new frontier was opened up by the latest developments of macromolecular chemistry, which have made available a new generation of polyolefins. The water-proofing mixtures obtained with last generation polyolefins do away with the performance limits associated with the use of traditional APP and SBS and exalt the best features of these two “old” families of plastic materials.

## **WRITER**

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## **ZUSAMMENFASSUNG**

Nach der "Entdeckung" des Bitumens, hat die Synthese des Polypropylens in den ersten '60 Jahren eine wirklich revolutionäre Wendung für den Abdichtungsbereich bedingt.

Die alte Ziegler Natta Katalyse erzeugte eine grosse Menge von ataktischen Polypropylen als Nebenprodukt, das sich als nützliche Benützung für die Bitumen-Modifikation im Abdichtungsbereich bewies: die Polymer-Bitumen-Membranen entstanden.

Ungefähr am Anfang des '70 Jahren fing man an, die Bitumen auch mit der Benützung von SBS (Styrol Butadien Styrol) zu modifizieren.

Diese zwei verschiedenen Sorten von Modifikationsmitteln erzeugen gute Mischungen, die aber einige Leistungsgrenzen beweisen.

Die letzten Vorschritte der Makromolekular-Chemie haben neue Polyolefinen zur Verfügung gebracht. Die mit der Benützung des neuen Polyolefinen entstandenen Mischungen überschreiten die Leistungsgrenzen, die mit der Verwendung vom APP und vom traditionellem SBS gebunden sind, und überhöhen die besten Eigenschaften von diesen "alten" Kunststoffe-Sorten.

## **RESUME**

Après la "découverte" du bitume, on a eu un nouveaux développement effectivement révolutionnaire dans le secteur de l'étanchéité à la suite de la synthèse du PolyPropylène, vers les premières années '60.

La catalyse Ziegler Natta de vieille génération entraînait la production, comme sous-produit, d'une grande quantité de PolyPropylène atactique, qui était avantageusement utilisé pour la modification du bitume dans le domaine de la fabrication de les d'étanchéités: prenaient naissance les membranes d'étanchéités bitume-polymère.

Vers les premières années '70 on a commencé à modifier les bitumes aussi par l'emploi de SBS (Styrène-Butadiène-Styrène).

Ces deux types de modifiants ont donné origine à des bons mélanges, qui présentent de toute façon quelques limites de performance.

Une nouvelle frontière a été ouverte à la suite des plus récents progrès de la chimie macromoléculaire qui ont rendu disponible polyoléfines de nouvelle génération. Les mélanges d'étanchéités obtenus par l'emploi des polyoléfines de la dernière génération dépassent les limites de performance liés à l'emploi soit de l'APP soit du SBS traditionaux, et exaltent les caractéristiques meilleures de ces deux "vieilles" familles des matières plastiques.

## **SOMMARIO**

Dopo la "scoperta" del bitume, una nuova svolta effettivamente rivoluzionaria per il settore delle impermeabilizzazioni si è avuta in seguito alla sintesi del polipropilene, intorno ai primi anni '60. La catalisi Ziegler Natta di vecchia generazione produceva, come sottoprodotto, notevoli quantità di polipropilene atattico, che si trovò di vantaggioso impiego per la modifica del bitume nel settore delle impermeabilizzazioni: nacquero le membrane impermeabilizzanti bitume-polimero.

Più o meno all'inizio degli anni '70 i bitumi cominciarono ad essere modificati anche con l'impiego di SBS (stirene-butadiene-stirene).

Questi due tipi di modificanti danno origine a buone mescole, che però presentano in ogni caso alcuni limiti prestazionali.

Una nuova frontiera si è aperta in seguito ai più recenti progressi della chimica macromolecolare che hanno reso disponibili poliolefine di nuova generazione. Le mescole impermeabilizzanti ottenute con l'impiego delle poliolefine dell'ultima generazione superano i limiti prestazionali legati all'impiego sia dell'APP, sia dell'SBS tradizionali, ed esaltano le prerogative migliori di queste due "vecchie" famiglie di materie plastiche.

## INTRODUCTION

An extraordinary new breakthrough in the field of waterproofing was ushered in by the discovery that atactic polypropylene – APP (derived from the production of isotactic propylene – IPP) displayed a special compatibility with bitumen, and totally modified the rheological and thermal behaviour characteristics of bitumen: this gave rise to polymer-bitumen membranes, which could be prefabricated to considerable thickness values and possessed performance features that remained stable in a wide range of temperatures.

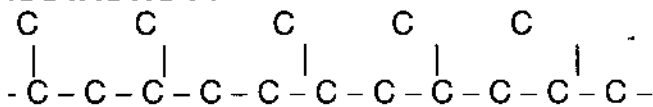
It can be stated without fear of exaggerating that after the German and British contributions (responsible for multi-layer and Bit-Ox membranes, respectively) polymer-bitumen membranes have been an all-Italian contribution to the technology of bitumen-based waterproofing products.

The synthesis of isotactic polypropylene has been one of the most important inventions of this century, mainly due to the endeavours of Prof. Natta who, together with Prof. Ziegler, was awarded the Nobel prize for chemistry in 1963.

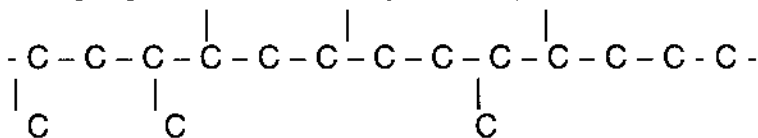
In its isotactic form, polypropylene displays good rigidity and impact resistance properties at ambient temperature, and it can be easily modified with amorphous polymers, such as EPR (Ethylene Propylene) rubber, or mineral charges. Moreover, it cannot be easily attacked by mineral oil, as borne out by its limited swelling upon being submerged in agents of this type.

The old generation Ziegler Natta catalysis produced as a by-product considerable quantities of atactic polypropylene, which then had to be removed through costly solution processes and had to be disposed of in some way (cave formation).

### ISOTACTIC PP



### ATACTIC PP



The only advantage of this fully amorphous polymer was that it dissolved easily in organic solvents (used for its removal); hence the idea of using it to increase the viscosity of bitumen. The addition of a small quantity of isotactic PP made it possible to obtain the desired degree of thermal resistance to solar heat in summer.

As a result, PP became an agent for the compatibilisation of bitumen with isotactic PP, as is necessary to obtain the mechanical properties of bitumen membranes for use in hot climates, such as those of the southern European countries.

The addition of atactic PP in bitumen membranes can be viewed as an excellent example of a market need satisfied by making use of a material which, at the time, was earmarked for recycling.

In the early 70's it turned out that another thermoplastic polymer, styrene-butadiene-styrene (SBS), of relatively recent discovery, could be mixed with bitumen to improve the elasticity and, above all, the resistance to low temperatures of this material. The production of the so-called elastomer modified bitumen membranes got underway.

For reasons to do with customary practice and the studies and developments initiated, the countries that first introduced the technology of bitumen modification with SBS (especially France and Germany) have continued to use mostly membranes of this type. Italy, instead, has always used primarily polypropylene based membranes.

Modified bitumen was born in Italy, with polypropylene, and the Italian industry immediately took advantage of this opportunity for growth with the manufacture of new products. As a result, Italian technology continues to play a leading role at world level in this specific sector. It is therefore not by chance that Italy is responsible for the latest developments in the macromolecular chemistry of plastic materials, that have made it possible to carry on the pioneering work begun with polypropylene in the waterproofing sector.

## **1. THE NEW FRONTIER: LAST GENERATION POLYOLEFINS**

The refinement of polymerisation processes has made it possible to incorporate special elastic type co-monomers into a polypropylene matrix so as to produce a new family of thermoplastic elastomeric polymers, which can be defined as polypropylene based elastomerised polyolefins.

Based on these capabilities of the chemical industry, collaboration with "roofing" specialists served as a stimulus for the fine-tuning of an innovative series of polymers that can be "made to measure" so as to obtain the desired chemical-physical and performance features, for specific use as bitumen based waterproofing mixtures. This has opened up a whole new horizon of great opportunities.

With old type polymers, whether APP or SBS, the quality of the final mixture is basically determined by several factors which can hardly be modified, such as, in particular, the degree of compatibility between a given polymer and a given bitumen type, and the rheological parameters of the polymers which affect the properties of the final mixture. Furthermore, as a rule, with a given type of old generation polymer it proves possible to improve some of the properties of a mixture (e.g. elasticity at low temperatures) but it is impossible to achieve simultaneously the optimisation of other features (e.g. resistance to high temperatures).

For these reasons, classical APP formulations are generally obtained through suitable blends, resulting in mixtures that possess good overall characteristics but are invariably penalised by the low specific "efficiency" of old generation modifiers. On the other hand, customary SBS formulations suffer from clear-cut limits stemming from the physiology of SBS itself (heat resistance, vulnerability to UV rays), which can hardly be used to advantage in conjunction with other types of polymer.

The new frontier defined by the newly developed elastomerised polyolefins has opened up the possibility of introducing bitumen modifiers with clearly defined properties, that can be selected as a function of the requirements. With these new polymers, the

modifications made to the bitumen can be so to speak “surgical”, resulting in well-optimised mixtures, reconciling technical characteristics which used to be rated as conflicting (e.g. rigidity at high temperatures/flexibility at low temperatures).

In actual fact, last generation polyolefins make it possible to overcome the limits associated with the use of classical APP and SBS modifiers, whilst the best performance features of these “old” families of plastic materials are enhanced.

## **2. SBS, APP, PNG (New Generation Polyolefins)**

An investigation was carried out to assess the efficacy of the new polyolefin modifiers, through the following steps:

- analysis of the characteristics of traditional (SBS and APP) polymers currently used in the market of modifiers for roofing applications;
- comparison between their characteristics and those of new generation polyolefins (PNG);
- production and analysis of sample mixtures, consisting of bitumen combined with each of the different modifiers being investigated;
- construction and analysis of mixtures according to current commercial formulations, using the different polymers being investigated.

The study of polymers and sample mixtures was conducted by analysing rheological parameters such as:  $G^*$  (complex shear modulus),  $\tan \delta$  ( $= G''/G'$ , loss tangent),  $G'$  (storage modulus), and  $G''$  (loss modulus), in keeping with the view of many authors who consider traditional tests, such as R&B or Penetration tests, as inadequate to describe the behaviour of a polymer-bitumen mixture. The following relationships were assumed to be true:

- $G^*$  modulus independent of temperature  
-> low thermal susceptibility
- $\tan \delta$  low at the highest temperatures  
-> better elastic response
- $G^*$  modulus high at the highest temperatures  
-> better resistance to permanent deformations

The mixtures produced with commercial preparations were analysed with the aid of the tests specified in the testing standards currently in force (e.g. UEAtc Directives).

### Type of bitumen used

A single type of bitumen was used in the tests to reduce the number of possible variables. This was a “medium” composition (as determined by Iatroscan) visbreaking bitumen, not specifically designed for optimised use in conjunction with either APP or SBS modifiers.

Bitumen characteristics are given in table 1.

R&B ASTM D36 (°C)	Pen ASTM D5	Asphaltenes  (dmm)	Saturated  (% wt)	Resins  (% wt)	Aromatic  (% wt)	Ic As + S/R + Ar  (% wt)
40.5	188	23.9	4.8	23.9	47.4	0.40

### Polymers used

Polymer characteristics are given in table 2.

Polymer	MI ASTM D1238  (dg/min)	$\eta$ ASTM D 2857  (dL/g)	ASTM 1505  (g/cm <sup>3</sup> )	Mw MA 15627	$\Delta H$ DSC - ASTM 3417 (J/g)
APP atactic propylene -ethylene copolymer	160 (230°C; 2.16kg)	0.83	0.88	103000	18
SBS-r Radial styrene-butadiene- styrene copolymer in blocks	≤1	1.37	0.94	350000	
PNG New generation polyolefins	4 (230°C; 2.16kg)	1.75	0.87	280000	38



### Preparation of "sample mixtures"

"Sample mixtures" were prepared to obtain initial indications on the behaviour of the new modifiers compared to that of traditional modifiers. The sample mixtures employed were produced by adding the polymer (5% by weight) to the bitumen (ca 300 g) at 160°C and then mixing the compound at ca 300 rpm, at a temperature of 210°C, for one hour.

### Preparation of everyday mixtures

Three different types of mixture were prepared by adding polymers to bitumen in the percentages specified below:

APP			SBS			New generation polyolefins PNG		
Polymer (wt %)	Filler (wt %)	Spec. Weight (kg/dm <sup>3</sup> )	Polymer (wt %)	Filler (wt %)	Spec. Weight (kg/dm <sup>3</sup> )	Polymer (wt %)	Filler (wt %)	Spec. Weight (kg/dm <sup>3</sup> )
25	0	1.00	12	25	1.18	25	0	0.96

## **Tests performed**

### *Tests on the bitumen*

The following properties were examined to compare the different types of mixture:

- Elastic return at 100% elongation (ASTM Guideline D 113)
- DSRT (Dynamic Shear Rheometer Test, 1 Hz – 2°C/min)

### *Tests on the polymers*

The polymers were subjected to the following tests:

- DMTA (Dynamic Mechanical Test Analyser, 1 Hz – 2°C/min)
- Load / elongation (ASTM D 412)
- Residual strain (ASTM 412 – ASTM D 1329)

- Oil absorption (ASTM D 471), measured to simulate “swelling” in the bitumen mixture, and determined through the following formula:

$$\Delta\%wt = (w_f - w_i/w_i) \times 100$$

where  $w_f$  and  $w_i$  stand for the final and initial weight of the test piece, respectively.

#### *Tests on the “sample mixtures”*

- DSRT (Dynamic Shear Rheometer Test, 1 Hz – 2°C/min)
- Softening point (R&B, ASTM D 36)
- Penetration at 25°C (ASTM D5)
- Elastic return at 100% elongation ( ASTM Guideline D 113)

#### *Tests on mixtures in everyday use*

- Softening point when new (UEAtc Directives)
- Softening point when aged (6 months at 70°C - UEA to Directives)
- Low temp. flexibility when new (UEAtc Directives)
- Low temp. flexibility when aged (6 months at 70°C - UEA to Directives)
- Penetration at 60°C (UEAtc Directives)
- Fatigue on cracked specimen (-20°C; 2 mm thick test pieces; F.I.T. Guidelines)

### **Results and discussion of the tests performed on the polymers**

#### *DMTA test*

During the tests, the test pieces were subjected to small oscillatory strains (< 1%) so as to maintain the visco-elastic response within the linear region, without inducing irreversible structural changes. Figure 1 shows the value of  $\tan \delta$  ( $\tan \delta = G''/G'$ , where  $G'$ , the storage modulus, and  $G''$ , the loss

modulus, represent the energy preserved and the energy dissipated in the deformation, respectively), in a temperature range of between -100 and + 100°C.

The peaks observed in the curves correspond to the temperature of vitreous transition ( $T_g$ ). In the SBS curves we observe two peaks that represent the points of transition of butadiene (ca -80°C) and styrene (ca +95°C). This characteristic curve accounts for the great ductility of SBS at low temperatures, and it also explains the low structural resistance of SBS at high temperatures, even below 100°C.

Traditional APP displays a peak between -15 and -20°C, confirming its elasticity limit at low temperatures; this limit is improved to ca -30°C by the new generation polyolefins.

#### *Load / elongation*

This test supplies interesting indications on the ability of the polymers employed to improve the mechanical strength of the bitumen layer.

As can be seen from figure 2, in this respect, new generation polyolefins ensure better performance capabilities than either traditional APP or SBS.

#### *Residual deformation*

This test can be correlated with the elastic response of the bitumen mixtures examined when exposed to high temperatures.

SBS polymers display a low degree of residual strain in the temperature range from ca -15 to ca +80°C. Beyond such values, as the high temperature resistance limit of the polymer is about to be reached, the test pieces fail.

New generation polyolefins display a higher residual deformation level compared to SBS; however, they will not tear upon being subjected to tensile loads at typical working temperatures.

### *Residual deformation after ageing*

This test was performed on SBS and PNG test pieces, aged in an oven at 115°C and then tested at ambient temperature (+/- 23°C). The results were checked after an initial ageing period of one hour, and were then tested again following longer ageing periods, in 1 h increments.

In these tests, SBS displayed an ageing capacity of 4 hours: after this time period, the test pieces were unable to withstand the tensile load and failed right away. On the contrary, new generation polyolefins retained the same residual strain values after an ageing period 10 times as long (after 48 hours of ageing the test was stopped).

The appreciable difference between the results obtained in accelerated ageing tests on SBS as opposed to PNG test pieces is probably due to the fact that the chemical structure of SBS contains double links which will break easily, even just by direct exposure to the light of the sun.

### *Oil absorption*

The oil absorption test was performed to simulate the "swelling" of the polymer in the bitumen mixture and was carried on for 7 days at 40°C.

As can be seen from figure 5, SBS displayed a better absorption capacity than either traditional APP or PNG. However, when the same test was repeated at a temperature of 90°C (bitumen mixtures are prepared at 180-200°C), new generation polyolefins were seen to improve their absorption capacity fast, approximating the values previously recorded for SBS.

## **Results and discussion of the tests performed on the sample mixtures**

### *DSRT*

The value of  $\text{Tan } \delta$  is one of the key parameters to obtain information on the performance capabilities of the mixtures at high temperatures. Figure 6 shows the evolution of the value of  $\text{Tan } \delta$  in the different mixtures examined compared to pure

bitumen, in the temperature range from -30°C to + 100°C.

The mixture obtained with the addition of new generation polyolefins displays the lowest values of  $\tan \delta$ , which correspond to a better elastic response.

Figure 7 shows the evolution of  $G^*$  (the complex shear modulus), which is appreciably higher for PNG mixtures, compared to APP and SBS mixtures: higher values of  $G^*$  correspond to a lower susceptibility to heat.

#### *R&B, penetration and elastic recovery*

Figure 8 shows the results of the R&B, penetration and elastic recovery tests conducted on the sample mixtures and compares them with the results obtained on pure bitumen.

To enhance the performance capabilities of a mixture, the contribution of the polymer should tend to improve the R&B and elastic recovery capabilities of the bitumen without having excessive repercussions on penetration values.

SBS polymers display the best elastic recovery but, as can be seen, the new generation polyolefins strike the best compromise between these three characteristics.

### **Results and discussion of the tests performed on the mixtures in everyday use**

#### *R&B, cold bending*

The values determined on the mixtures when new (not aged) are important, but special significance must be attached to the downgrading of their characteristics after ageing, which should be as limited as possible.

	APP	SBS	PNG
Cold bending: deterioration after ageing	$\Delta cb = 10^\circ C$	$\Delta cb = 15^\circ C$	$\Delta cb < 5^\circ C$

As confirmed by figure 9, the value of R&B decreases by a few degrees in SBS mixtures, but in PNG mixtures it actually improves, as it does in APP mixtures. These results confirm the

greater durability and hence greater ageing resistance of the new compounds compared to traditional APP and SBS based mixtures.

#### *Penetration at 60°C*

This value is smaller in PNG mixtures, which therefore feature superior consistency as walking surfaces, combined with a better “management” of the material during the scorching and installation stages.

#### *Fatigue test on a crack specimen at -20°C*

The test was not performed on the APP mixture (flexibility at low temp. -15°C). PNG mixtures achieved an excellent result at -20°C (when new and after ageing), thereby “invading” a test area which was once viewed as an exclusive prerogative of SBS.

#### *Specific weight*

Like traditional APP based mixtures, the mixtures obtained with the addition of new generation polyolefins have a specific weight which is 20% lower than that of SBS. This offers obvious advantages in terms of ease of transport and on-site handling.

### **CONCLUSIONS**

Though they were the first to appear on the market, traditional APP mixtures, produced with modifiers not too optimised in terms of chemical-physical properties, failed to meet with the favour of ever more demanding users, working in the most diversified climatic conditions.

On the other hand, though they feature greater elasticity at low temperatures, classical SBS based formulations suffer from greater thermal susceptibility and undergo excessive softening at the top temperatures of their normal utilisation range, and are vulnerable in terms of direct exposure to sunlight. These features depend on the chemical structure of SBS and cannot be improved to any significant extent, even though new “special” (SBS) polymers are proposed every now and then,

which are virtually able to overcome such “physiological” limits. As confirmed in actual practice over many years of use, an SBS type polymer can hardly combine (at least at an affordable cost) optimised performance at low temperatures with adequate heat resistance and, above all, cannot ensure the durability required of a waterproofing material in the case of (even sporadic) sight installation.

Nowadays, new generation polyolefins are the ideal bitumen modifiers for roofing applications. These “pure” compounds, possessing constitutive properties that can be selected as a function of specific requirements, ensure optimised performance capabilities over the entire operating temperature range. Of traditional APP they maintain and enhance the excellent properties in terms of heat resistance and resistance to ageing. Of SBS they approximate the best performance features at low temperatures. The final outcome is a material that can be relied on in all circumstances to retain its performance capabilities unaltered in every respect.