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## Historical perspective

# A review of the fundamentals of polymer-modified asphalts: Asphalt/polymer interactions and principles of compatibility



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#### ABSTRACT

During the last decades, the number of vehicles per citizen as well as the traffic speed and load has dramatically increased. This sudden and somehow unplanned overloading has strongly shortened the life of pavements and increased its cost of maintenance and risks to users. In order to limit the deterioration of road networks, it is necessary to improve the quality and performance of pavements, which was achieved through the addition of a polymer to the bituminous binder. Since their introduction, polymer-modified asphalts have gained in importance during the second half of the twentieth century, and they now play a fundamental role in the field of road paving. With high-temperature and high-shear mixing with asphalt, the polymer incorporates asphalt molecules, thereby forming a swallowed network that involves the entire binder and results in a significant improvement of the viscoelastic properties in comparison with those of the unmodified binder. Such a process encounters the well-known difficulties related to the poor solubility of polymers, which limits the number of macromolecules able to not only form such a structure but also maintain it during high-temperature storage in static conditions, which may be necessary before laying the binder. Therefore, polymer-modified asphalts have been the subject of numerous studies aimed to understand and optimize their structure and storage stability, which gradually attracted polymer scientists into this field that was initially explored by civil engineers. The analytical techniques of polymer science have been applied to polymer-modified asphalts, which resulted in a good understanding of their internal structure. Nevertheless, the complexity and variability of asphalt composition rendered it nearly impossible to generalize the results and univocally predict the properties of a given polymer/asphalt pair.

The aim of this paper is to review these aspects of polymer-modified asphalts. Together with a brief description of the specification and techniques proposed to quantify the storage stability, state-of-the-art knowledge about the internal structure and morphology of polymer-modified asphalts is presented. Moreover, the chemical, physical, and processing solutions suggested in the scientific and patent literature to improve storage stability are extensively discussed, with particular attention to an emerging class of asphalt binders in which the technologies of polymer-modified asphalts and polymer nanocomposites are combined. These polymer-modified asphalt nanocomposites have been introduced less than ten years ago and still do not meet the requirements of industrial practice, but they may constitute a solution for both the performance and storage requirements.

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## 1. Introduction

Polymer-modified asphalts (PMA) derive their technological and conceptual origin from the need for enhancing the performance and durability of asphaltic materials as well as their adhesion to mineral aggregates. PMAs are produced by mixing asphalt and polymer (usually 3-7% by weight); they were developed because conventional flexible pavements had become inadequate in the last few decades because of a dramatic increase in traffic intensity and load, which shortened their in-service life, thereby increasing the frequency of road maintenance and re-paying required. Modification is normally achieved through simple mechanical dispersion of the polymer in molten asphalt under high shear. Approximately 75% of all modifiers are elastomeric, 15% are plastomeric, and the remaining 10% are either rubber or miscellaneous under these three categories [1]. The longer life and better quality of PMA-based pavements usually lead to both economical and safety requirements that overcome the initial investment, which is higher with respect to the use of conventional unmodified binders.

Since the introduction of PMA in the paving industry, researchers have attempted to use almost all available polymers as asphalt modifiers, including thermoplastics and thermosetting resins (the latter category represents a particular case of polymer modification and will not be discussed here in detail). However, the produced PMAs should satisfy a long list of requirements including appropriate mechanical properties, storage stability, high-temperature viscosity compatible with the traditional road-building processes and apparatus, and reasonable cost, which remains of primary importance. Given all these limitations, in contrast to the huge availability of different types of polymers, only a very small number of polymers are currently used in industrial applications. The preferred polymers have a common characteristic: ability to form a physical network, which usually originates from the simultaneous presence of both rigid (below glass transition temperature (T<sub>g</sub>) or crystalline) and flexible segments in their backbone. If the network is swelled by the asphalt molecules during the mixing phase without losing its main structure, it will become a determining factor for the binder properties. The polymers used in asphalt technology may be listed according to their importance in three main categories:

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