ABSTRACT

NETWORK FORMATION OF SULPHUR CURED NATURAL RUBBER / BUTADIENE RUBBER BLENDS

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This dissertation presents the results of the research activities done on the curing behaviour of natural rubber / butadiene rubber blends. The main objective of the work was to predict and to determine more precisely the curing behaviour of unfilled NR / BR blends, and to find innovative ways to guide and to control the network formation and completion of the blend. However, it’s necessary to mention that the 2nd intention to adjust a defined and specific level of network density in every single elastomer phase, in a blend of distinct diene rubbers, mutually immiscible, remains still an unsolved objective and requires further research work.

Regarding the determination of the curing behaviour it was investigated the distribution and the homogeneity of the network-chain density, through theoretical and mathematical models explicative of the sulphur crosslinking growth in the homo/multi-polymer matrices, by physical and chemical analytical methods, such as rheological and mechanical analysis, equilibrium swelling, nuclear magnetic resonance (NMR) spectroscopy and morphological investigation (AFM) of the polymer blend, whole supported by theoretical inter-molecular interaction study through model compound vulcanization and approaches useful to obtain a deep analysis of the chemical structure of the intermedia compounds obtained during the vulcanization.

Hence, it succeeded to describe in detail the sulphur based networking behaviour of NR and BR as homo-polymers. The NR shows a very fast network formation speed and highly pronounced reversion, almost independent of the curative concentration or temperature. However, BR is slower in its reaction speed but achieves much higher network densities. Additionally it was found out that in case of di-phenyl guanidine the low solubility in the polymers, in particular in BR, creates a secondary, not desired, reaction in the vulcanization when the vulcanization is already in the plateau phase.

To allow a comparison of numerical calculations of the vulcanization behaviour of the blends with real measurements, it was defined a “cloud” - DoE based test program, varying the quantity of sulphur, TBBS and DPG in a broad range of concentrations and measuring in a temperature range from 150°C ÷ 180°C, allowing also a multi-correlation.Hence, it was possible to create a predictive tool, allowing the prevision of the vulcanization curve as a function of the temperature and the curative concentration.

To determine the potential curative concentration in the single polymer phases in the blend, it was necessary to run solubility and migration experiments.As expected and confirmed by former literature findings, even in case of BR and NR, so polymers with a similar polarity, the significantly higher affinity of TBBS towards BR creates a further source of unbalance in the network density in the blend. Additionally it was possible to show, that the phase morphology of the NR/BR – blend is majorly relevant for the mechanical properties of the resulting compound, but not for the vulcanization behaviour of the blends.

To suppress the negative effects of the migration an IR/BR co-(block)-polymer was synthetized by MCM metathesis and applied as «compatibilizer» in an IR/BR blend. As expected, it was possible to change the blend morphology, but the curing behaviour remained almost unchanged. Hence, there was still a contribution of the curative solubility.

Taking the same IR/BR co-(block)-polymer and vulcanizing it without additional dosage of IR and BR reveals a complete different reactivity. The vulcanization curve indicates a behaviour “just” based on the «monomer reactivity». The higher reactivity of the IR groups guide the reactivity of the co-polymer. Since the co-polymer is homogenous, there are no contributions of the morphology or migration any more.