

Kurzfassung

Die vorliegende Arbeit beschäftigt sich mit der Herstellung von thermoplastischen Elastomeren (TPE) mit co-kontinuierlicher Phasenstruktur auf Basis von Polyester/Elastomer Blends. Die eingesetzten Elastomere wurden dazu gezielt chemisch funktionalisiert, um die Verträglichkeit mit den Polyestern zu verbessern.

Die Funktionalisierung der Elastomere wurde durch radikalisch initiierte Pfropfung von Glycidylmethacrylat (GMA) in der Schmelze erreicht. Anhand von Ergebnissen umfangreicher Untersuchungen an Ethylen/Propylen Copolymeren wurden die wesentlichen Einflussfaktoren auf die Produkteigenschaften, wie dem GMA-Pfropfungsgrad, dem Vernetzungsgrad und dem Anteil Nebenprodukte evaluiert und optimiert.

Zu diesem Zweck wurden entsprechende Analysewerkzeuge entwickelt und an das spezifische System angepasst. Durch Kombination von FTIR- und ¹H-NMR-Analysemethoden konnte eine normalisierte und allgemein auf Polymere mit Ethylenblocksequenzen anwendbare Kalibrierfunktion zur Bestimmung des GMA-Pfropfungsgrades entwickelt werden.

Weiterhin konnte das optimierte Funktionalisierungsverfahren erfolgreich auf andere Elastomere, wie Ethylen/Propylen/Dien Terpolymere (EPDM) und Nitrilkautschuke (NBR) übertragen werden.

Die funktionalisierten Elastomere wurden mit und ohne dynamische Vulkanisation mit Polyethylenterephthalat (PET) bzw. Polybutylenterephthalat (PBT) compoundingiert. Neben PET Neuware wurde auch PET Recyclat aus gebrauchtem Getränkeflaschenmaterial in die Untersuchungen mit einbezogen. Dabei konnten die mechanischen Eigenschaften der TPE nicht durch die dynamische Vulkanisation verbessert werden.

Die Blends wurden diskontinuierlich im Innenmischer und kontinuierlich im Doppelschneckenextruder reaktiv compoundingiert und anschließend mittels mechanischer, thermomechanischer, thermischer und morphologischer Untersuchungsmethoden charakterisiert.

Es zeigte sich, dass die GMA-funktionalisierten Elastomere deutlich verträglicher sind mit den Polyestern als nicht unfunktionalisierte Elastomere. Dies dokumentieren die feineren selbst-durchdringenden Phasenstrukturen, einhergehend mit höheren mechanischen Kennwerten.

Insbesondere GMA-gepfropfter Nitrilkautschuk mit hohem Acrylnitrilgehalt zeigte, auch verglichen mit kommerziellen Verträglichkeitsmachern, ein großes Potential in den hergestellten TPE.

Bei Verwendung von PET Recyclat konnten sehr gute mechanische Kennwerte erzielt werden. Damit stellen solche TPE eine interessante, wertschöpfende Recyclingoption für gebrauchtes PET Getränkeflaschenmaterial dar.

Abstract

This thesis aimed at developing thermoplastic elastomers (TPE) with co-continuous phase structures based on polyester/elastomer blends. The employed elastomers were chemically functionalized in order to improve the compatibility with the polyesters.

The elastomers were melt functionalized by free-radical initiated grafting of glycidyl methacrylate (GMA). Major parameters of the grafting reaction affecting the grafting degree, the degree of crosslinking and the amount of undesired by-products were studied and optimized for an ethylene/propylene rubber system.

Suitable analytical tools were developed and adapted to characterize the GMA grafting degree. By combining FTIR and $^1\text{H-NMR}$ techniques a normalized and universally applicable calibration function for the determination of the GMA grafting degree was established for polymers containing ethylene block sequences.

$^1\text{H-NMR}$ measurements evidenced that the epoxide rings of the grafted glycidyl methacrylate were not affected (i.e. ring opened) by the free-radical grafting reaction.

Increasing initiator concentration did not affect the total amount of polymerized GMA but shifted the ratio from grafted to homopolymerized GMA while increasing the crosslinking degree of the elastomer.

In order to achieve a high grafting degree the reaction temperature has to be adjusted as low as possible. Moreover the GMA loss due to evaporation is reduced, too. Even though GMA has a high melting point of 189°C it is highly volatile at lower temperatures.

The type of initiator proved to be a key parameter of the grafting reaction. All the investigated peroxides can be utilized for the grafting, but the grafted products differed significantly. For a certain type of peroxide no difference between liquid and solid types could be found.

The best grafting performance was reached by using 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane. This was the only initiator that combined high grafting degrees with an extremely low gel content. Grafting yields of $\sim 80\%$ were reached without using further coagents or comonomers. Surprisingly, this initiator is not customary used for grafting reactions.

Furthermore the optimized grafting method was successfully transferred to other elastomers, e.g. ethylene/propylene/diene terpolymers (EPDM) and nitrile rubbers (NBR).

NMR-analysis of the NBR-g-GMA revealed that the epoxide rings may react with the nitrile functions forming reactive oxazolines. A stereochemically controlled reaction pathway following Anti-Markoffnikoff rule was supposed for their formation.

The functionalized elastomers with and without dynamic curing were melt blended with poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). Beside typical virgin bottle grade PET material, discarded post-consumer softdrink bottle material was employed.

The reactive compounding of the blend was conducted both discontinuously using a batch mixer and continuously in a twin-screw extruder. The blends were characterized according to their mechanical, thermomechanical, thermal and morphological properties.

It was found that GMA functionalized rubber exhibits a much better compatibility towards polyesters than non-functionalized elastomers. This was evidenced by scanning electron microscopy (SEM) and the transmission electron microscopy (TEM) analysis. Improved compatibility was reflected in the formation of a finer dispersed co-continuous phase structure yielding a better mechanical performance.

By varying the blend composition ratio the region of co-continuous phase structures (IPN) was determined. Later, the blend composition was fixed at 50:50 wt.% polyester : elastomer. This composition yielded IPN structures in all examined blends and dynamic vulcanizates.

The technique of dynamic curing could not be adopted to the polyester/elastomer blends. The high melt temperatures for polyester processing were inappropriate for peroxidic curing systems. As a consequence a 2-step dynamic curing sequence was applied. In the first step a dynamic vulcanizate masterbatch using the functionalized elastomer along with a further elastomer was prepared. In the second step this masterbatch was blended with the polyesters. It turned out, that the mechanical performance of the TPE could not be improved by dynamic vulcanization.

All extruded and injection moulded TPE using the prior functionalized elastomers exhibited good mechanical performance. In particular GMA grafted nitrile rubbers with high acrylonitrile content performed very well and showed the capacity to compete with typical commercial ethylene/GMA copolymer grades.

Blends with recycled PET material showed outstanding mechanical performance. As a consequence the production of such TPE materials using discarded PET may be a value-added recycling option for post-consumer PET waste.