

Kurzfassung

Die Einmischung von Altgummipartikeln aus zerkleinerten Altreifen in Thermoplast-, Elastomer- und Duromer-Matrizes im Sinne einer stofflichen Wiederverwertung führt zu erheblichen Eigenschaftsverschlechterungen der altgummipartikelmodifizierten Polymerblends. Vor diesem Hintergrund gewinnt die Modifizierung der Altgummipartikel für eine Verbesserung der Verträglichkeit mit den Matrixmaterialien zunehmend an Bedeutung.

Zur Modifizierung der Altgummipartikel wurden photochemische Pfröpfungsreaktionen mit Glycidylmethacrylat (GMA) und Methacrylsäure (MAA) nach einem radikalischen Polymerisationsmechanismus durchgeführt.

Um Altgummipartikel erfolgreich chemisch modifizieren zu können, ist ein fundiertes Wissen über die entscheidenden Parameter des Pfröpfungsprozesses erforderlich. So haben beispielsweise die Art und Konzentration der Pfröpfungschemikalien wie Monomer und Photoinitiator, die Art des Spülgases, die Temperatur sowie die Bestrahlungszeit einen entscheidenden Einfluss auf das Pfröpfungsergebnis. Der Nachweis der Oberflächenmodifizierung erfolgte mit Hilfe chemischer Analytikmethoden sowie mittels Kontaktwinkelmessungen.

Ein weiterer Schwerpunkt dieser Arbeit lag auf der Herstellung von altgummipartikelmodifizierten Thermoplast-, Duromer- und Elastomer-Blends. Polyamid-6 (PA-6) und Polybutylenterephthalat (PBT) wurden als thermoplastische Matrixmaterialien ausgewählt. Als Vertreter der Duromere wurde beispielhaft ein Vinylester-Urethan-Hybridharz (VEUH) angewendet und als elastomeres Matrixmaterial kam ein Polyurethan-Gießelastomer (PUR) zur Anwendung.

Bei höheren Gummipartikel-Konzentrationen zeigte sich, dass durch die Pfröpfung die Verträglichkeit zwischen Gummipartikeln und den o. g. Matrixmaterialien verbessert wurde. Die Modifizierung von PA-6 und VEUH mit feinverteilten Gummipartikeln bewirkte bei geringfügigen Einbußen an Festigkeit und Steifigkeit deutliche Zähigkeitssteigerungen. Dieser Effekt war bei den GMA modifizierten Gummipartikeln stärker ausgeprägt.

Bei der Anwendung von 10 Gew.% MAA gepfröpften Gummipartikeln in PUR-Elastomeren konnten sehr gute mechanische Kennwerte erzielt werden. Damit stellen altgummipartikelmodifizierte PUR-Blends eine interessante Recyclingoption für Altreifen und Altgummiabfälle dar.

Abstract

Recycling of worn out tyres has obtained a great interest. Great efforts are therefore devoted to find new fields of application of ground tyre rubber (GTR).

A method that has the potential of utilising large numbers of discarded tyres involves grinding the rubber into small particles and then reusing it as a filler in thermoplastic, thermoset and rubber compounds. However, the incorporation of GTR particles into polymer matrices significantly impairs the properties of the resulting composites. This is because of the poor matrix-filler adhesion and the lack of reactive sites on the GTR particle surface.

There are several ways to „upcycle“ GTR. This thesis aimed at developing a suitable surface treatment for GTR particles by chemical modification in order to improve their compatibility with polar matrix materials.

Rubbers were treated by ultraviolet light (UV) initiated grafting of glycidyl methacrylate (GMA) and methacrylic acid (MAA). The viability of this grafting was first shown at unvulcanized and vulcanized styrene-butadiene rubber (SBR). Note that SBR is the major component in tyre mixtures. Major parameters of the grafting reaction affecting the grafting degree, the amount of undesired by-products and the crosslinking degree were studied and optimized for SBR.

Attenuated total reflectance Fourier-transform infrared spectroscopy (FTIR-ATR), X-ray photoelectron spectroscopy (XPS) and elemental analysis have been used for chemical characterization of the treated rubbers.

In order to achieve a high grafting degree and to avoid undesirable secondary reactions the reaction temperature and the irradiation time have to be adjusted as low as possible.

The best grafting performance was reached by using a photoinitiator mixture containing 80 % 2-Hydroxy-2-methyl-1-phenyl-propan-1-one and 20 % 1-Hydroxy-cyclohexyl-phenyl-ketone in nitrogen atmosphere. The increase of the photoinitiator concentration did not result in an enhanced grafting degree.

The rubber treatment is particularly efficient when the simultaneous grafting method is applied. Using the simultaneous grafting method, the grafting substrate is presoaked in the grafting solution and afterwards grafted in one step under the influence of UV radiation. A photo-initiator concentration of $0,2 \text{ mol/l}_{\text{solvent}}$ and a

monomer concentration of 6 mol/l_{solvent} were determined as optimal concentrations for the presoaking solution.

Carbon black content in SBR vulcanizates was found to be one of the major factors controlling the monomer grafting. The degree of monomer graft onto SBR decreased with increasing carbon black content. However, the degree of grafting of the filled SBR was slightly higher by replacing carbon black with silica in comparison with thus of the unfilled SBR.

According to these results, the presented grafting procedure can not be universally used for unvulcanized and vulcanized rubbers and GTR particles containing carbon black over 10 phr (parts per hundred rubber).

The optimized grafting procedure was transferred successfully to silica filled GTR particles and to GTR particles with low carbon black contents, i.e. less than 10 phr. XPS analysis of GMA treated GTR particles showed that epoxy and carbonyl groups have been introduced on GTR surface after grafting. In case of MAA treatment new carboxyl groups have been found.

By combining FTIR-ATR and elemental analysis a normalized calibration function could be deduced to determine the absolute grafting degree of unvulcanized SBR rubbers. The FTIR-ATR results of GTR sheets were calibrated by considering the XPS results.

A further task of this work was to apply the treated GTR particles in selected thermoplastics, thermosets and elastomers and thus to develop new compounds with improved performance, e. g. increased impact strength.

Untreated and treated GTR particles were melt blended with polyamide-6 (PA-6) and poly(butylene terephthalate) (PBT) in a twin-screw extruder. The blends were characterized according to their mechanical, viscoelastic and morphological properties.

It was found that the treated GTR particles exhibit at 20 wt.% much better compatibility with PA-6 and PBT than the untreated GTR ones. This was evidenced by scanning electron microscopy and dynamic mechanical thermal analysis (DMTA). Moreover, the modification of PA-6 with finely dispersed GTR particles resulted in clear improvement of the toughness with slight loss of the stiffness and strength. Irrespective of the surface treatment of the GTR particles, their incorporation in PBT

matrices did not result in any improvement of the mechanical performance of the blends. This is a clear indication that the effect of mean particle size in thermoplastics is more important than that of surface treatment. The effectiveness of treated GTR particles in a size range of 100 to 400 μm is limited for toughening of PA-6, while these particles are not suitable in PBT matrices.

The GTR particles could well be incorporated in vinyl ester-urethane hybrid resins (VEUH). Therefore, they were utilized for replacing the commercial expensive functionalized liquid rubbers by this cost-efficient recycling product. The addition of 5 and 10 wt.% of treated GTR particles to VEUH systems led to an improvement in toughness, while the stiffness was slightly reduced. It was also possible to use untreated GTR particles for toughening of VEUH. However, the toughness improvements were lower in this case. It is important to note that the material properties of the GTR modified VEUH resins are inferior to the commercial rubber-modified VEUH resins. Considering the cost of the commercial rubber modifiers, however, the application of waste rubber in fine fractions is economically beneficial.

A very promising application for surface treated GTR is given by its incorporation in hot cast polyurethane elastomers (PUR). PUR blends with GTR particles showed outstanding mechanical performance. The GTR particles could be mixed quite well with the polyol component of PUR up to 15 wt.%. The shore A-hardness as well as the modulus at 100 and 300 % elongation are increased by the incorporation of 10 and 15 wt.% MAA treated GTR particles into an unfilled PUR matrix in relation to that of unfilled PUR matrix. PUR compounds with 10 wt.% MAA treated GTR particles show the best mechanical performance. For example PUR with 10 wt.% MAA treated GTR particles has higher stiffness over the entire temperature range and an improved damping behavior in comparison to that of unfilled PUR matrix based on DMTA results.

As a consequence the production of such PUR materials using discarded GTR particles may be a valuable recycling option for post-consumer tyres.