

Recycling of Ground Tyre Rubber and Polyolefin Wastes by Producing Thermoplastic Elastomers

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Abstract

This thesis deals with the development of thermoplastic polyolefin elastomers using recycled polyolefins and ground tyre rubber (GTR).

The disposal of worn tyres and their economic recycling mean a great challenge nowadays. Material recycling is a preferred way in Europa owing to legislative actions and ecological arguments. This first step with worn tyres is already done in this direction as GTR is available in different fractions in guaranteed quality. As the traditional applications of GTR are saturated, there is a great demand for new, value-added products containing GTR. So, the objective of this work was to convert GTR by reactive blending with polyolefins into thermoplastic elastomers (TPE) of suitable mechanical and rheological properties.

It has been established that bituminous reclamation of GTR prior to extrusion melt compounding with polyolefins is a promising way of TPE production. By this way the sol-content (acetone soluble fraction) of the GTR increases and the GTR particles can be better incorporated in the corresponding polyolefin matrix. The adhesion between GTR and matrix is given by molecular intermingling in the resulting interphase.

GTR particles of various production and mean particle size were involved in this study. As polyolefins recycled low-density polyethylene (LDPE), recycled high-density polyethylene (HDPE) and polypropylene (PP) were selected. First, the optimum conditions for the GTR reclamation in bitumen were established ($160\text{ °C} < T < 180\text{ °C}$; time ca. 4 hours). Polyolefin based TPEs were produced after GTR reclamation in extrusion compounding. Their mechanical (tensile behaviour, set properties), thermal (dynamic-mechanical thermal analysis, differential scanning calorimetry) and rheological properties (both in low- and high-shear rates) were determined.

The PE-based blends contained an ethylene/propylene/diene (EPDM) rubber as compatibilizer and their composition was as follows:

$$PE/EPDM/GTR:bitumen = 50/25/25:25$$

The selected TPEs met the most important criterion, i.e. elongation at break $> 100\%$; compression set $< 50\%$. The LDPE-based TPE (TPE(LDPE)) showed better mechanical performance compared to the TPE(HDPE). This was assigned to the higher crystallinity of the HDPE.

The PP-based blends of the compositions PP/(GTR-bitumen) 50/50 and 25/75, whereby the ratio of GTR/bitumen was 60/40, outperformed those containing non-reclaimed GTR. The related blends showed also a better compatibility with a PP-based commercial thermoplastic dynamic vulcanizate (TDV).

Surprisingly, the mean particle size of the GTR, varied between < 0.2 and 0.4-0.7 mm, had a small effect on the mechanical properties, however somewhat larger for the rheological behaviour of the TPEs produced.

Kurzfassung

Die vorliegende Dissertation ist der Entwicklung von thermoplastischen Polyolefin-Elastomeren gewidmet, die rezyklierbare Polyolefine und Gummipulver aus Altreifen (ground tyre rubber, GTR) beinhalten.

Es ist eine große Herausforderung die Probleme bei der ökonomischen Verwertung von Altreifen zu lösen. Eine werkstoffliche Wiederverwertung wird heutzutage in Europa politisch präferiert und wird auch mit ökologischen Argumenten unterstützt. Der erste Schritt in die Richtung des werkstofflichen Recyclings ist zweifelsohne die Zerkleinerung von Altreifen. Die Technologien sind entwickelt und haben dazu geführt, dass Altgummipulver (GTR) in verschiedenen Fraktionen und in garantierter Qualität auf dem Markt verfügbar ist. Die traditionellen Anwendungsbereiche von Altgummipulver sind gesättigt. Daher ist es von großer technisch/wissenschaftlicher Relevanz GTR-haltige Werkstoffe zu entwickeln mit denen neue Anwendungen realisiert werden können. Das Hauptziel dieser Arbeit war GTR-haltige thermoplastische Elastomere (TPE) zu entwickeln und sie bezüglich ihrer Eigenschaften (und damit ihrer potenziellen Marktfähigkeit) zu charakterisieren.

Es wurde festgestellt, dass sich GTR in Bitumen regenerieren lässt. Regenerierung bedeutet einen partiellen Abbau der vernetzten Struktur der Altgummipartikel. Dadurch ist die wichtigste Voraussetzung für ein gutes „Einbinden“ dieser Partikel in verschiedene Polyolefine erfüllt da dieser Abbau die molekulare Interdiffusion und Verhakung fördert.

Altgummipartikel aus verschiedenen Herstellungsverfahren und mit unterschiedlicher Partikelgröße dienten als Ausgangsmaterial. Als Matrix wurden Polyolefine wie Polyethylen niedriger und hoher Dichte (LDPE bzw. HDPE) und Polypropylen (Neuware oder Rezyklate) untersucht. Zunächst wurden die optimalen Regenerierbedingungen für die jeweilige GTR-Fraktionen geklärt ($T=160-180\text{ °C}$, 4 Stunden). Danach wurden TPE-Verschnitte durch Extrusionskompoundierung hergestellt. Die TPE-Variationen wurden mechanisch (Zugeigenschaften, Verformungsrest), thermisch (mittels dynamisch-mechanische Thermoanalyse und Differenzial Enthalpiekalorimetrie) und rheologisch (sowohl bei niedrigen als auch bei

hoher Scherraten) charakterisiert. In den PE-basierten TPE kam ein ein Ethylen/Propylen/Dien Elastomer (EPDM) als Verträglichkeitsmacher zum Einsatz, welches sowohl mit PE als auch mit dem regenerierten GTR kompatibel war. Die Zusammensetzung der jeweiligen TPE/PE Mischungen besteht aus jeweils 25 Gewichtsteilen EPDM/GTR/Bitumen mit 50 Gewichtsteilen PE. Diese Blends erfüllten die wichtigsten Kriterien eines TPE, d.h. Zugdehnung >100 % und Druckverformungsrest < 50 %. TPE(LDPE) hat aufgrund seiner Eigenschaften besser abgeschnitten als TPE(HDPE). Dies wurde dem großen Unterschied in der Kristallinität des LDPE gegenüber dem HDPE zugeschrieben.

Die PP-basierten TPEs wurden ohne EPDM und mit deutlich höherem GTR-Gehalt als im Falle des TPE(PE) hergestellt. Die Zusammensetzung der jeweiligen PP-Blends besteht aus PP/(GTR+Bitumen)= 50/50 bzw. 25/75 Gewichtsteile, wobei das GTR/Bitumen Verhältnis bei 60/40 lag. Diese PP basierten TPE's zeigten deutlich bessere mechanische Eigenschaften wenn das GTR in Bitumen regeneriert wurde. Desweiteren wurde eine deutlich verbesserte Verträglichkeit von TPE(PP) gegenüber TPE(PE) mit einem thermoplastischen dynamischen Vulkanisat (TDV) auf PP-Basis festgestellt. Der Einfluss der GTR Partikelgröße (0,4-0,7 mm bzw. < 0,2 mm) in diesen Blends blieb unerwartet klein bezüglich der mechanischen und nur wenig ausgeprägter in Anbetracht der rheologischen Eigenschaften.

List of Abbreviations and Symbols

Abbreviations

ABS	Acrylonitrile-Butadiene-Styrene
BR	Polybutadiene Rubber
CPE	Chlorinated PE
DCP	Dicumyl Peroxide
DMTA	Dynamic Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
d	Day
EAA	Ethylene/Acrylic acid copolymer
E-GMA	Ethylene/Glycidyl-methacrylate copolymer
ENR	Epoxidized Natural Rubber
EPDM	Ethylene/propylene/diene rubber
EVA	Ethylene/Vinyl-acetate copolymer
Eb	Elongation at break
GTR	Ground Tyre Rubber
GTR ^D	GTR thermochemically devulcanized in an open mill
GTR ^{TD}	GTR thermomechanically degraded on an open mill
HDPE	High-Density Polyethylene
h	Hour
IR	Polyisoprene Rubber
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density PE
MA	Maleic Anhydride

MBTS	Dibenzothiazole Disulfide
MFI	Melt Flow Index
NR	Natural Rubber
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinylchloride
Phr	Parts per hundred parts rubber
RT	Room Temperature
RTR	Reclaimed Tyre Rubber
SBR	Styrene Butadiene Rubber
SEBS	Styrene-Ethylene-Butylene-Styrene
SEBS-g-MA	Maleic Anhydride-grafted-SEBS
SEM	Scanning Electron Microscopy
TBBS	N-tert-butyl-benzothiazole Sulfenamide
TGA	Thermogravimetric Analysis
TMTS	Tetramethyl Thiuram Disulfide
TPE	Thermoplastic Elastomer
TPE(HDPE)	TPE based on LDPE
TPE(LDPE)	TPE based on HDPE
TPE(PP)	TPE based on PP
UMSICHT	Fraunhofer Institut für Umwelt -, Sicherheits - und Energietechnik
VTMS	Vinyltrimethoxy Silane

Symbols

A	[mm ²]	Area
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b	[mm]	Width
E'	[MPa]	Young's modulus
E^*	[MPa]	Complex modulus
E	[MPa]	Storage modulus
F	[N]	Load
$\tan\delta$	[1]	Mechanical loss factor
$\tan\delta_{max}$	[1]	Maximum of the mechanical loss factor
T	[°]	Temperature
T_g	[°]	Glass transition temperature
wt	[%]	Weight fraction
t	[s]	Time
ε_y	[%]	Strain at yielding
ε_b	[%]	Elongation at break
η^*	[Pa.s]	Complex viscosity
ρ	[g/cm ³]	Density
σ	[MPa]	Tensile strength
σ_b	[MPa]	Tensile strength at break

Introduction

From the 15 member states of the European Union (EU), 2659 kt post/consumer tyres were accumulated during 2003. The ranking of states according to tyre arisings is as follows:

Germany (640 kt), UK (435 kt), Italy (434.5 kt), France (401 kt), Spain (280 kt), Belgium (70 kt), Holland (67.5 kt), Sweden (62 kt), Greece (58.5 kt), Portugal (52 kt), Austria (51 kt), Denmark (41.2 kt), Finland (32.3 kt), Ireland (32 kt) and Luxemburg (3.1 kt). The related report of the European Recycling Associations (ETRA) estimates the historic “stockpile of tyres” within the EU in 2003 for an additional 1000 kt. [1]

Tyres have a four phase life-cycle: new, part-worn (road-worthy tyres), retreadable (casing suitable for retreading) and recyclable.

The composition of tyres for passenger cars (7.5-9 kg) and trucks/buses (50-80 kg each) is summarized in Table 1.1.

Table 1.1: Composition of Tyres in the EU [1]

The Composition of Tyres in the European Union		
Material	Passenger Cars	Trucks/Buses
Rubber/elastomers	48	43
Carbon black	22	21
Metal	15	27
Textile	5	-
Zinc oxide	1	2
Sulfur	1	1
Additives	8	6

The major disposal routes for post-consumer tyres in the EU are depicted in Figure 1.1.

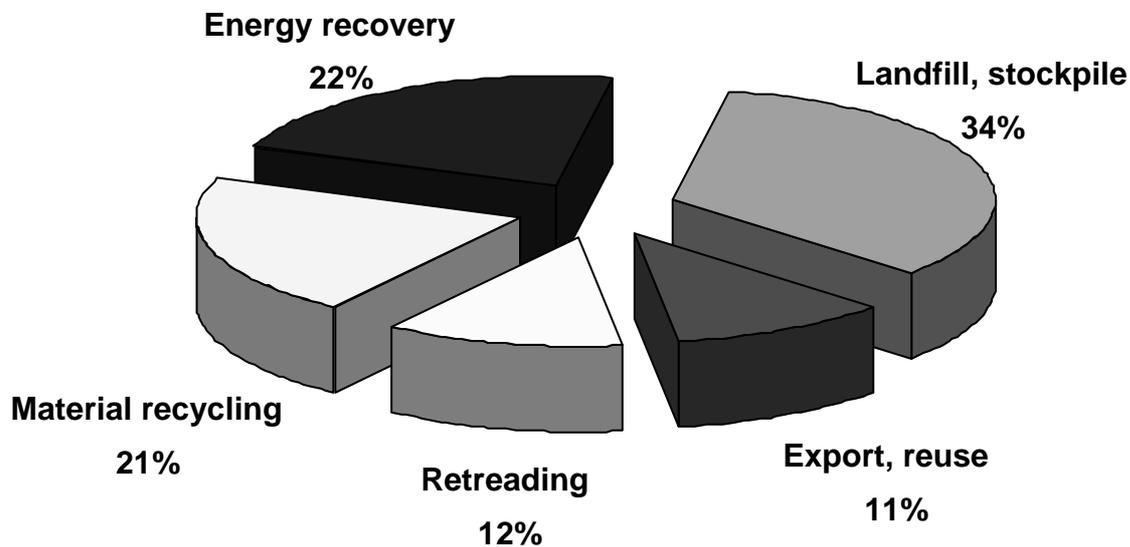


Figure 1.1. Average breakdown in postconsumer tyre disposal in the EU [1]

The export of part-worn tyres is directed towards less developed countries. Retreaded tyres meet the same standards as new ones. Note that during retreading 2-3 kg fresh rubber is applied to rebuild a tyre, the rubber content of which is 48% for a passenger and 43% for a truck tyre. Energy recovery covers apart the use of tyres as non-fossil fuel (in cement kilns, paper mills, electricity generation plants) also energy recovery/material recycling (pyrolysis, production of synthesis gas etc.). [1-3]. In the latter case, the products (oils, aromatics, gaseous products, steel, ZnO and carbon black) are marketable. Landfilling is no more a viable option in the EU as the Landfill Directive (1999/31/EC) forbids the disposal of entire tyres from 2003 and shredded ones (size between 50 and 300 mm) from 2006.

Material recycling is strongly favored due to several reasons:

- Legislative actions: 2000/53/EC End of Life Directive - requires that from 2006 80% and from 2015 85% of all cars should be recyclable (werkstoffliches

Recycling). This has a strong impact on rubber products built in passenger cars. Note that a compact car contains ca. 60 kg rubber; the major part (ca. 70%) is given by tyres. [2]. A further EU directive, viz. Incineration of Waste 2000/76/EC - also supports the material recycling via lowering the emission standards of cement kilns and the like

- Energy balance

The energy equivalent of 1 kg of tyre is ca. 128 MJ. Its recovery by energy generation yields, however, only 30 MJ. On the other hand, ca. 6.8 MJ of additional energy is required to produce 1-1.5 kg ground tyre rubber (GTR). [4]

This is likely the major driving force to develop advanced grinding techniques for worn tyres.

Material recycling of post-consumer tyres goes in two directions:

- Civil engineering is using greater quantity and larger pieces, such as whole tyres, shred and chips (particle size between size between 10 and 50 mm) in various applications (sound deadening, insulation, artificial reefs, soil stabilization, dam/road constructions, etc.)
- Product/material manufactures are using smaller quantity (at the present) and smaller pieces (granulates laying in the range of 0.5-15 mm and powders with a particle size less than 0.5 mm).

The related products comprise outdoor sport surfaces, interior floor covering, playground facilities, footwear, whereas the materials may be revulcanizable rubber compounds, inks and paints (from the pyrolytic char), and even thermoplastic elastomer (TPE) compositions.

Granulates and powders have been used to produce noise absorbing sheets, floor tiles, paving blocks and the like. These applications are often termed "Downcycling" as the recycled product has a different application than the initial (i.e. tyre) one [2]. Nowadays under "Downcycling" low-tec, inexpensive applications are meant the

costs of which are controlled by the rubber granule or powder themselves. Further, the related applications have been saturated with the major exception of road paving. Accordingly, there is a considerable demand to find new, value-added use for GTR fractions.

Numerous efforts were made and are in progress to modify thermoplastics, thermosets and rubbers by GTR incorporation in order to improve their selected properties. This work is devoted to an “Upcycling” strategy with GTR: to develop thermoplastic elastomers containing GTR and recycled polyolefins.

The term “Upcycling” is related to the final TPE which is a value-added material based on its unique properties (elasticity properties combined with thermoplastic processability). In addition, the corresponding TPE should be competitive in price.

In the following chapter the state-of-art with GTR recycling will be surveyed. Emphasis will be put to derive the adequate conclusions from past works in order to develop a suitable strategy for the development of TPEs containing GTR.

2 Background and State of Art

The use of recycled rubber was more prominent in the 60ies than now. The drop is due to the favourable price of synthetic rubbers, product liability concerns and the market penetration of steel-belted radial tyres of long duration [3]. As pointed out before the “revitalization” of recycling strategies nowadays is triggered by legislative actions.

2.1 Rubber reclamation and devulcanization

Reclaiming and devulcanization are related but quite different processes. The outcome is practically the same: a rubber compound that can be compounded and revulcanized similar to fresh rubber stocks. The difference between reclamation and devulcanization is given by the chemical attack. Devulcanization targets the crosslinks in the vulcanized rubber and thus C-S and S-S bonds are selectively cleaved. Note that devulcanization requires high energy to break the $-C-S-C-$ (285 kJ/mol), $-C-S-S-C-$ (268 kJ/mol) or $-C-S_x-C-$ (251kJ/mol) bonds [5]. Needless to say that this energy should be selectively directed towards the sulfuric crosslinks without scissioning the main chain. On the other hand, reclaiming is usually accompanied with considerable scission along the polymeric chains resulting in lower molecular mass fractions. Irrespective to the above clear distinction between reclamation and devulcanization [3] the related processes can hardly be grouped accordingly. So, in the brief survey below the processes will be classified as follows: thermomechanical, thermochemical, ultrasonic, microwave and other processes. Note that the reclamation/devulcanization strategies could also be summarized whether physical or chemical processes are mostly exploited [6]. In physical processes the 3D network of the crosslinked rubber breaks down via additional energy introduced by different ways. In chemical processes usually the di- and polysulfide bonds should be cleaved.

2.1.1 Thermomechanical processes

In those process variants crumb rubber is subjected to shear and/or elongational stresses on suitable equipments such as open mills, twin-screw extruders etc. .

Milling and extrusion are usually carried out at high temperatures. This results in a prominent decrease in the molecular mass. The characteristics of the products strongly depend on the processing equipment, its characteristics (e.g. local shear rate) and processing parameters (e.g. residence time). Earlier for that purpose discontinuously operating open mills were used ([5] and references therein). Nowadays there is a clear tendency to prefer continuous operations (e.g. [7]). It is worth of noting that such thermomechanical processes are often performed in the presence of reclaiming agents (e.g. [8] and references therein). As a consequence they belong to the category of thermochemical decomposition processes.

2.1.2 Thermochemical processes

To manufacture reclaim rubbers usually chemical reclaiming agents are used. They are generally organic disulfides and mercaptans as reviewed by Adhikari and Maiti [6]. Those chemical agents work exclusively at elevated temperatures and the related processes involve mechanical mixing/working.

The “pan process” is one of the oldest method according to which the ground rubber is heated in saturated steam at a high temperature (150-180 °C) in the presence of disulfides (termed “catalysts” or peptizer) and reclaim oil. First, the mixture is allowed to swell for at least 12 hours (h). Note that GTR is retaining its “free powder flow” characteristics when containing up to 35 parts per hundred resin (phr) parafinic oil [8]. The material is then in 2-3 mm thickness in pans to allow oxygen to penetrate. The trays are autoclaved in air/steam atmosphere (ca. 9 bar) at ca. 190 °C for ca. 5 h. After that the material should be strained/refined in order to get a homogeneous mixture from the more degraded skin (outer layer) and less degraded bulk (inner layer) [3,6]. The digester processes, reclaim the rubber crumb in a steam vessels equipped with agitators, which continually stir the crumb rubber while steam applied.

The generalized structures in sulfur-vulcanized natural rubber (NR) are depicted in Figure 2.1 [9]. The vulcanizable properties and thus the related crosslinks strongly depend in what kind of vulcanization system was used. The latter is grouped according to the sulfur and accelerator contents (and thus accelerator/sulfur ratio). One distinguishes between conventional (C), semi-efficient (semi-EV) and efficient vulcanization (EV) systems-cf. Table 2.1.[9]

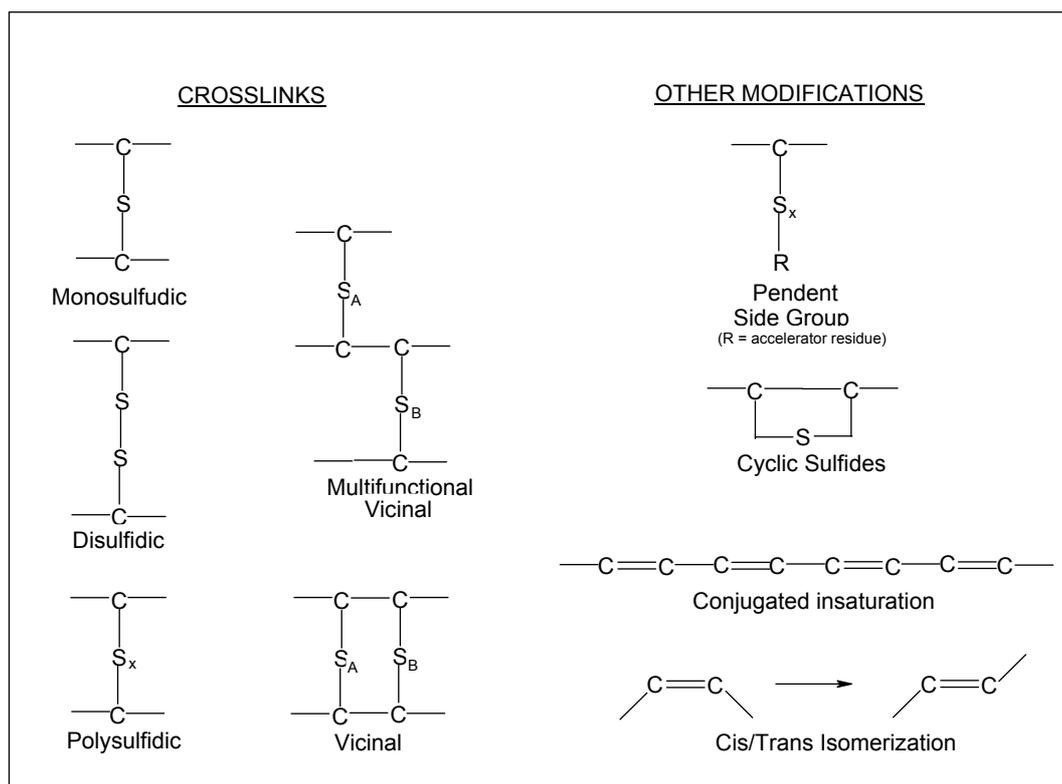


Fig 2.1 Generalized structures in sulfur-vulcanized natural rubber

Table 2.1 Sulfur vulcanization systems and the resulting crosslinked structure

Type	Sulfur phr	Accelerator phr	A/S ratio	Poly-and disulfidic crosslinks %	Monosulfidic crosslinks %
Conventional	2.0-3.5	1.2-0.4	0.1-0.6	90	5
Semi-EV	1.0-1.7	2.5-1.2	0.7-2.5	50	50
EV	0.4-0.8	5.0-2.0	2.5-12	20	80

The attacking positions of the chemical agents are different. Some of them attack the polysulfide linkages, others the disulfide ones, further variants cleave the monosulfide linkages. However, most of these agents have a combined action (e.g. on polysulfide/disulfide crosslinks). Based on the knowledge deducible from Figure 2.1 and Table 2.1 the reclaiming strategy should consider the vulcanization system used (viz. C, semi-EV, EV). Albeit considerable body of work was devoted to clarify the mechanisms of breaking the sulfide linkages (cf. [6] and references therein), the

related knowledge is not yet final. The proprietary compounds of the De-Link[®] and De-Vulc[®] processes [3,6] which are marketed now under Regen[™] Agents [10] cleave the polysulfide linkages under shear (milling) below $T=160$ °C. The resulting compound can be revulcanized without addition of vulcanization agents ($T= 140-150$ °C, time = 10-20 min). [3, 6]

Attempts were also made devulcanize rubber scraps and waste in swollen state by inorganic compounds. As swelling agents toluene, naphta, cyclohexane etc. served, whereas inorganic compounds alkali metals, H_2O_2 , O_3 were used. Swelling the GTR in suitable solvents at high temperatures followed by “mechanical” disintegration of the GTR in an extruder proved to be also very promising (cf. [6] and references therein). It is worth of noting that researchers try to replace the problematic solvents by oils from renewable resources (e.g. [11]).

2.1.3 Ultrasonic, microwaves

A viable alternative to decompose crosslinked rubber is the use of powerful ultrasound (low frequency range of the ultrasound defined by the interval 20 kHz to 500 MHz). The chemical and mechanical effects of the ultrasound are caused by cavitation of bubbles during the negative pressure period of the ultrasound. Two competing theories exist to explain the cavitation-induced chemical changes: the “hot spot” and “electrical theory”. The former postulates that the localized bubbles may have a temperature of 5000 K and a pressure of 500 bar. The electrical theory assumes that on the surface of the bubble locally generated electrical field gradient is enough to break chemical bonds [12]. Ultrasonic devulcanization of rubber was attempted with success by several research groups ([3,6,13] and references therein). Isayev and coworkers studied the continuous devulcanization of various rubbers using an extruder coupled to an ultrasonic generator (e.g. [14,15]). In that case the plasticized rubber was pumped trough a narrow gap between the stationary die and the vibrating horn.

In the microwave technique the waste rubber must be polar in order to generate the heat (> 250 °C) necessary for devulcanization. Microwaving is often coupled with extrusion and mixing. The transformation to refined, devulcanized stock is rapid and cost efficient. In addition, the outcoming compound may serve as raw material for the same product it has been produced from ([6] and references therein)

2.1.4 Others

There are many other methods of reclamation/devulcanization, which however, represent some combination of the above listed ones. The microbiological devulcanization deserves a separate entry. Encouraged by the fact that NR-latex is target of microbiological attack in the nature, researchers looked for bacteria able to scission the polysulfide linkages (e.g. [16]). It has been reported that several bacteria are able to “digest” (break) the sulfide linkages and the extent of reaction can be regulated, via the temperature, pH, etc ([3,6,16-18]). The result is a “surface modified” GTR, the surface layer of which is no more crosslinked. Microbiological devulcanization processes may become important issues in the future.

2.1.5 Quality of the reclaim/devulcanizate

Recall that the major task of the rubber (material) recycling is to produce from the initial infusible, insoluble, 3D crosslinked structure (100% gel content) a melt processable one. This means that the 3D crosslinked structure should be destroyed, at least partially. As a consequence the material becomes partially soluble (sol content > 0%) and will show a lower crosslink density than initially. It is worth of noting that the sol content of most rubbers is higher than 0 due to different low molecular mass additives, processing aids which can be removed by extraction. The (sol) gel content is exclusively determined by extraction (in Soxhlet apparatus). To determine the crosslink density usually the Flory-Rehner equation is used [19].

The melt processability can be characterized by the Mooney viscosity (ISO 289, ASTM D1646), torque (apparent viscosity)-values or torque (apparent viscosity)-time curves assessed by various torque rheometers, plasticity values (Wallace, Defo plasticity) change in hardness etc. The Vredestin Co. for example uses the Mooney viscosity for quality assurance of the rubber (NR) reclaim-cf. Figure 2.2. [20].

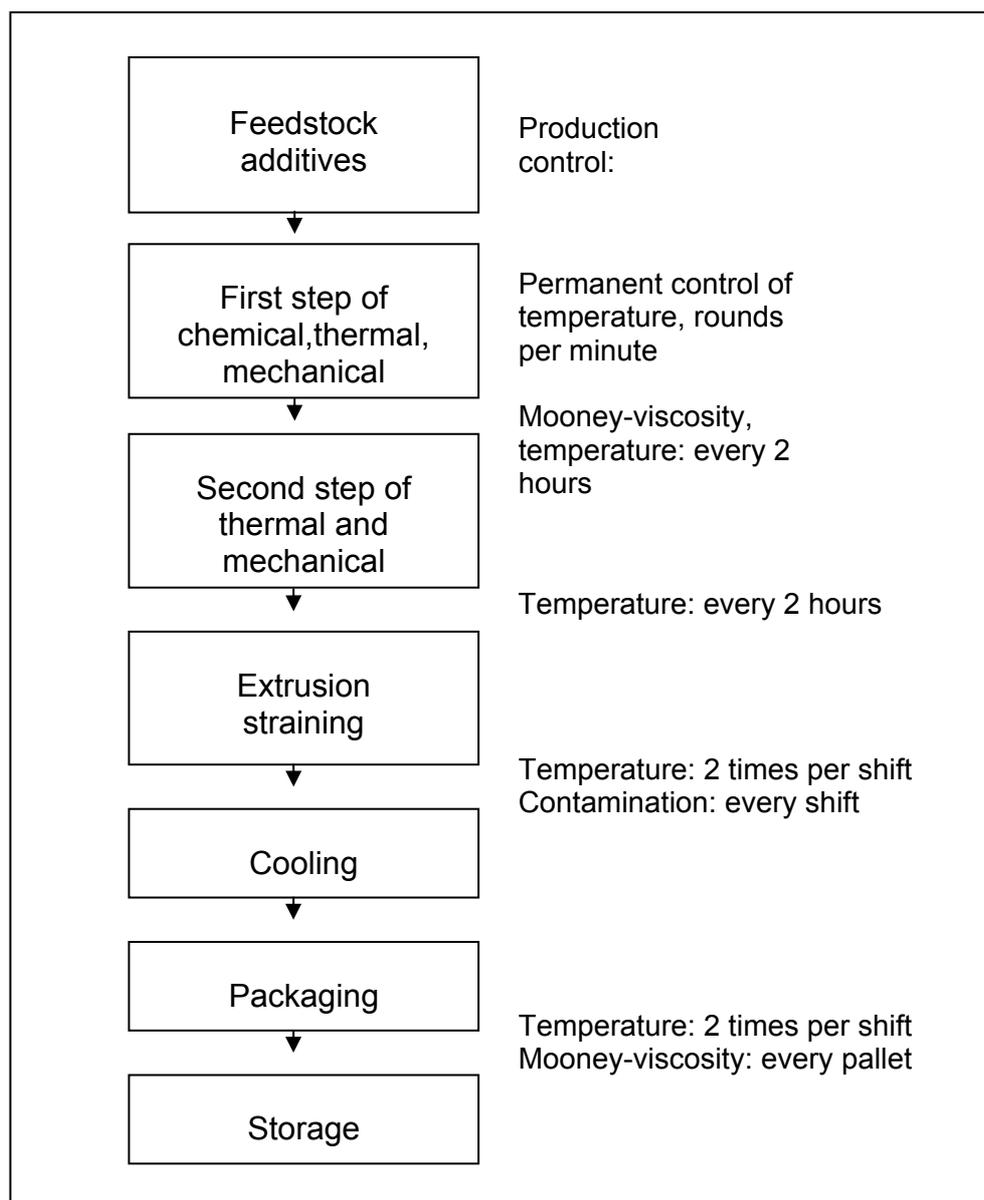


Figure 2.2. Production of natural rubber reclaim at the Vredestein Co

If the target material was a revulcanizable one, the usual tests for fresh rubber stocks may be used (curemeter, stress-strain behaviour).

2.2 Tyre size reduction

2.2.1 Shredding and grinding

As mentioned in Chapter 1, the size reduction of tyres is a must from the viewpoint of both economy and ecology. The outstanding mechanical performance of automotive

tyres owing to the fiber reinforcement along with the inherent resilience of rubber makes the shredding of whole tyres and the production of rubber granules and crumb (GTR) very demanding processes. Shredders use rotating elements with knives and the like. In order to avoid the high transport cost several mobile tyre shredders have been developed [3]. To convert the whole tyre into GTR the related technology comprises the following steps: shredding, separation (steel, textile), granulation and classification. Granulation/grinding may be performed at ambient temperature (warm), in wet condition (wet) and at cryogenic temperatures (cryogenic grinding), e.g. ([21-24]). Warm grinding results in granules of 1-6 mm. This limitation is given by the viscoelastic nature of rubber along with its low heat conductivity. In order to reduce the temperature loading of the rubber during grinding water may be added. This wet process may produce GTR of less than 100 μm mean particle size. Disadvantage of this process is that the GTR should be dried afterwards. Cooling the rubber below its glass transition temperature (which is type dependent and lies between -30 and -80 °C) the energy needed for grinding can be substantially reduced. Further, no thermooxidative degradation of the rubber takes place when grinding occurs. On the other hand, the cooling via liquid nitrogen is very costly. Nevertheless, the finest fraction of GTR can be achieved by this way. Needless to say that the surface structure of the GTR depends on its methods of production. Warm grinded GTR particles are markedly more rough than cold/cryogenic produced ones (showing clear cut, smooth surfaces).

2.2.2 Quality of GTR

It was early recognized that the quality of GTR has to be determined and guaranteed accordingly. The major quality properties of GTR are the particle size range (particle size distribution) and level of contamination (steel, textile).

The standard released on how to characterize “particulate rubber” is the ASTM D 5603 (1996). According to this prescription rubber powders are classified in respect to feed stock and sieve analysis. So, the rubber powder should meet a range of chemical and physical properties including the maximum allowable concentration of fibers and metal. Manuel [25] pointed out that the ASTM D 5603 cannot be used in its current form in Europe as the raw materials and their composition in the tyres in the USA differ from those in Europe.

The specifications of commercial rubber powders offered by Vredestein Rubber Resources contain the following characteristics: rubber origin, grinding technology, chemical composition, particle distribution, physical properties and impurities. Note that the ASTM D 5603 does not inform about the grinding technology, physical properties and impurity leaching to the environment. Among the chemical composition the acetone extract (ASTM D 297), ash content (ASTM D 297), carbon black content (ASTM E 1131), rubber content (ASTM E 1131), NR/synthetic rubber composition (ASTM D 3452) and heat loss (ASTM D 1278) are listed. The particle size fraction is usually determined according to the ASTM D 5644 and the particle size distribution is given in mm (or mesh). Among the physical properties the Vredestein specification reports about the surface appearance (rough/edgy) determined by microscopy, and various densities of the rubber (specific density – ASTM D 297; pour density –ISO 1306 and compacted density –ISO 787). Among the impurities the maximum allowable values of the steel, textile and others (all of them according to ASTM D 5603) are indicated [25]. Earlier, researchers were interested in other properties, such as surface to volume ratio, nitrogen absorption, surface area, surface activity (by absorption of cetyl-trimethyl-amonium bromide) e.g. [26].

The determination of the above parameters is either labour intensive and/or hardly reproducible. The latter note holds especially for specific surface values influenced by outgassing phenomena [26-27]. As mentioned before, the appearance of the rubber powder strongly depends on the type of grinding. For this the distinction between rough and edgy from visual (microscopic) inspection is used. Researchers tried to describe the uniformity of the powder [28] along with its surface roughness also by other means, e.g. fractal dimensions [29]. Nevertheless, it has to be emphasized here that the mean particle size and particle size distribution are of great practical relevance as the properties of compounds with GTR are governed by them ([29] and references therein).

2.2.3 Use of GTR

Manyfold trials have been made to find economic applications for GTR fractions. They have been incorporated in rubbers, thermoplastic and thermoset polymers, asphalts, bitumen, concrete etc. Due to the great variety of applications only a brief

survey will be given here. Further, emphasis will be put on those applications that are relevant to this work from a given aspect.

There has been always considerable interest to recycle GTR in rubber stocks (e.g. [2-3, 30-40]). From the earlier studies the following rule of thumb was deduced: incorporation of 1 wt% of GTR result in 1% deterioration in the mechanical properties. Accordingly, the GTR content of vulcanizable rubbers generally did not surpass the 10 wt% threshold [41]. Further learning from these studies was that the property degradation is the smaller, the finer the used GTR fraction is. The reports are mostly in harmony about the reason of the property (ultimate tensile and tear properties) drop. They locate it in the missing interfacial bonding between the GTR and the rubber matrix. This argument is supported by the fact that the mechanical properties of GTR containing rubbers are the less affected the smaller the GTR particles are. Klüppel et al [32] consider the GTR containing rubber as a rubber with locally varying network density and filler (carbon black) content. This may be beneficial in respect of some properties (oil-resistance, compression set, acoustic damping) whereas detrimental for others (fatigue, tensile and tear characteristics). Albeit efforts are in progress to use 100 % GTR to make new rubber products (e.g. [40]), majority of the works tackles the GTR use as filler furtheron. Recognizing the problem with interfacial bonding/adhesion numerous approaches were introduced for the surface modification of GTR. The “common denominator” of these approaches is to enhance the polarity of the GTR surface. This should yield a drastic change in the surface energies favouring the wetting by the matrix. Attempts made so far differ, however, in the nature of the surface treatments (physical and chemical methods).

a) Physical methods

GTR may be coated with fresh rubber. In the “SURCRUM” (surface activated rubber) process of Vredestein Co. GTR is coated with a sulfur vulcanizable latex [3, 6, 41], the Tyrecycle[®] process uses liquid unsaturated polymers for coating [42]. Transpolyoctenamer (TOR), a synthetic rubber of low crystalline melting temperature [43] is also a suitable coating agent.

For surface modification of crumb rubber reactive gas (a mixture of oxygen and chlorine [3,44]) plasma, corona and electron beam irradiation treatments (e.g. [27]) were also explored.

b) The chemical methods

These methods focused on various grafting procedures. Grafting of unsaturated monomers and oligomers on the GTR surface which may participate in the subsequent crosslinking with the fresh rubber is a very promising approach. This has been followed by several research groups making use of redox grafting [29], ultraviolet light [45] and electron beam induced grafting. The monomers preferred were: styrene, glycidyl methacrylate, acrylic and methacrylic acids and the like.

Surface modified GTR was added also to thermoset resins aiming at enhancing their toughness. The related results [46-50] showed that the surface modification of the GTR is indispensable. On the other hand, the toughness improvement achieved was marginal. This was traced to the coarse particle size of the GTR. Note that in order to achieve high toughness the size of the rubber inclusions in the thermoset matrix should be in the range of a few micrometers [51-52]. However the combined use of surface modified GTR and functionalized liquid nitrile rubber (state of art modifier) yielded toughness improvement. This was traced to a bimodal distribution of the additives (GTR-coarse, liquid rubber-fine) [46-47].

The overwhelming majority of works dealt with the incorporation of GTR in thermoplastics. This strategy has been fuelled by the possibility of melt reprocessing. GTR was incorporated in different thermoplastics via various melt processing procedures. Among the thermoplastic matrices polyolefins and polyvinylchloride (PVC) were always preferred as they belong to the category of "high volume" thermoplastics of low price.

Already in the late 70s, early 80s great effort was made to use GTR as toughener in various thermoplastics. The driving force behind this strategy was the great success achieved in respect with toughness enhancement via rubber/thermoplastic blending. Pittolo and Burford [53] concluded that GTR may work as a toughening agent in brittle polystyrene (PS). The toughness of the blends increased with increasing GTR/matrix adhesion and decreasing GTR particle size. The adhesion of GTR improved by free radical-induced grafting of styrene onto the GTR.

Tuchman and Rosen [54] investigated the incorporation of cryogenically ground tyre with and without grafting in a series of thermoplastics. Major conclusions of the authors were the following: incorporation of such fine GTR fraction up to 60 wt% does not cause any processing difficulties. The impact strength of polypropylene (PP) could be doubled at 20 wt% of GTR content. On the other hand, GTR was a

worthless filler for acrylonitrile-butadiene-styrene (ABS) thermoplastics. The GTR is, in best case, an extender in low density polyethylene (LDPE) formulations, and has a better action in high-density polyethylene (HDPE). It was also claimed that GTR could not be grafted to LDPE by the usual crosslinking procedure [54]. According to Deanin and Hashemiolya [55] in respect with ultimate tensile properties the most promising polyolefins are linear low density PE (LLDPE) and PP. Mayadunne et al [56] showed that a GTR filled (up to 60 wt%) LDPE composition exhibits a pronounced melt shear thinning behaviour which is of great importance for injection moulding applications. McKirahan et al [57] investigated the mechanical properties of HDPE/GTR compositions. The authors found that GTR incorporation reduced the ultimate tensile properties and even the hardness of HDPE. Reduced GTR particle size had no effect on the strength and hardness in contrast to the ductility (the elongation was slightly improved). Tantayanon and Juikham [58] studied the impact behaviour of PP/GTR and PP/reclaimed tyre rubber (RTR) blends. As expected, the PP/RTR blends outperformed the PP/GTR ones. Further, dynamic vulcanization (will be explained later) in the presence of sulfur curatives enhanced further the toughness of PP/RTR blends opposed to PP/GTR where this procedure had no effect.

As mentioned already in relation with GTR/fresh rubber blends, the missing adhesion between the GTR surface and thermoplastic component was concluded as a major problem for the property reduction. Depending on the grinding process the GTR surface may have some reactive groups. The latter are formed by oxidation and by free radicals generated during grinding [3]. So, it is a straightforward strategy to use low or high molecular mass functionalized polymers to get a better adhesion between the GTR and matrix. Such materials are usually termed compatibilizers (sometimes coupling agents) in the literature. In order to force the interaction between the functional groups of the compatibilizer and GTR, the latter was treated accordingly. Like reported for GTR/rubber mixes, the same physical and chemical methods were applied for GTR functionalization. Duhaime and Baker [59] produced LLDPE blends with 10-60 wt% GTR. The LLDPE was modified with ethylene/acrylic acid copolymer (E/AA), whereas for the GTR amine-terminated liquid nitrile rubber was added with or without peroxide initiator. All blends, whether reactive or non-reactive, exhibited reduced properties at all portions of GTR. However, in the reactive blends the relative property improvement compared to the non-reactive ones reached ca. 50 %. This

property recovery was attributed to the coupling reaction between the carboxylic and amine groups. Rajalingam et al [27] used poly(ethylene-glycidyl-methacrylate) copolymer as compatibilizer in LLDPE/GTR blends. The GTR was surface modified by plasma, corona or electron beam treatments. In addition, GTRs produced in different grinding methods were involved in the related study. The highest toughness improvement was noticed for the composition containing wet ambient ground tyre (high surface oxygen concentration) treated by electron beam irradiation.

In a companion paper Rajalingam and Baker [60] found that LDPE is more suitable than HDPE as matrix and precoating the GTR particles by E/AA is very beneficial. This precoating technique was explored further and found that LLDPE blends with 40-50 wt% GTR may attain the impact properties of the neat LLDPE [61]. The authors concluded that the properties of very ductile matrices containing coarse GTR particles with moderate adhesion to the bulk are still acceptable. On the contrary, in semi-brittle matrices (like HDPE) coarse particles and their moderate adhesion result in a drastic property reduction. Pramanik and Baker [62] tried different compatibilizers (epoxidized natural rubber, ENR, and E/AA) and in-situ reactive modification (maleic anhydride, MA and peroxide). The improvement in the impact performance was either due to interaction of the compatibilizer at the GTR/polymer interface or due to the matrix crosslinking generated. Pramanik and Dickson [63] reported that compatibilizers (elastomeric and thermoplastic matrix, unfortunately undisclosed) had marginal influence on the tensile and flexural properties of the blends composed of polyolefins (LDPE, HDPE and PE+PP) and GTR. However, the Izod impact strength increased for some compounds. Choudhury and Bhattacharya [64] have chosen chlorinated PE (CPE) being elastomeric and showing some symmetry in the chain build up with LDPE. All CPE compatibilized blends possessed better mechanical properties over the control blend (LDPE/GTR=70/30 parts) without compatibilizer. This finding was attributed to the CPE which forms a strong interphase between the GTR and LDPE via molecular intermingling. It is worth of noting that adding CPE reduced the melt flow of the blends. Surface chlorinated GTR proved to be a suitable filler (added in 40 phr) for plasticized PVC formulations [65-67]. The acceptable properties of the outcoming "melt processable rubber" were traced to dipole-dipole interaction between the components. A further rubber compatibilizers, via styrene-ethylene-butylene-styrene block copolymer (SEBS) and its maleated version (SEBS-g-MA), were tried by Phinyocheep et al [68] for PP/scrap rubber dust blends.

Note that these SEBS-type thermoplastic rubbers are good compatibilizers for many other binary and ternary blends. On the other hand, their high price prevents their use in most cases. Li et al [69] compatibilized HDPE and GTR by mixing with ethylene-propylene-diene rubber (EPDM), peroxide and silicone oil. After this modification the impact strength and elongation increased by ca. 150% for the HDPE blends with 40 wt% GTR compared to the unmodified reference composition. Reactive blending in the presence of peroxide was followed by Jain et al [70] to produce waste ground EPDM/PP (composition range: 10/90-60/40 parts) compounds. When researchers noticed that the GTR, even after surface modification, acts further on as filler/extender in thermoplastics ([45,71] and references therein), their interest was directed towards elastomeric compositions. Because of the relevance of the related works to this Thesis the learning from these works is summarized under a separated heading.

2.2.4 GTR containing thermoplastic elastomers

Thermoplastic elastomers (TPE) are thermoplastic polymers which can be melt processed at elevated temperatures while possessing elastomeric behaviour at their service temperature. TPEs thus contain a thermoreversible network (also called physical network) structure. This is formed by phase separation in all cases. In segmented (multi)block copolymers the “knots” of the physical network are given either by glassy or crystalline domains. They are referred as “hard phase” dispersed in a “soft” rubbery one. The latter is the matrix that is given by the flexible segments of the block copolymers –cf. Figure 2.3. The highest structural diversity shows the thermoplastic polyolefin elastomers. They can be directly synthesized or produced by various melt-blending procedures [72-76]. The appearance of elastomeric polyolefins of different chain build-up is an advent of the metallocene catalysis ([75]).

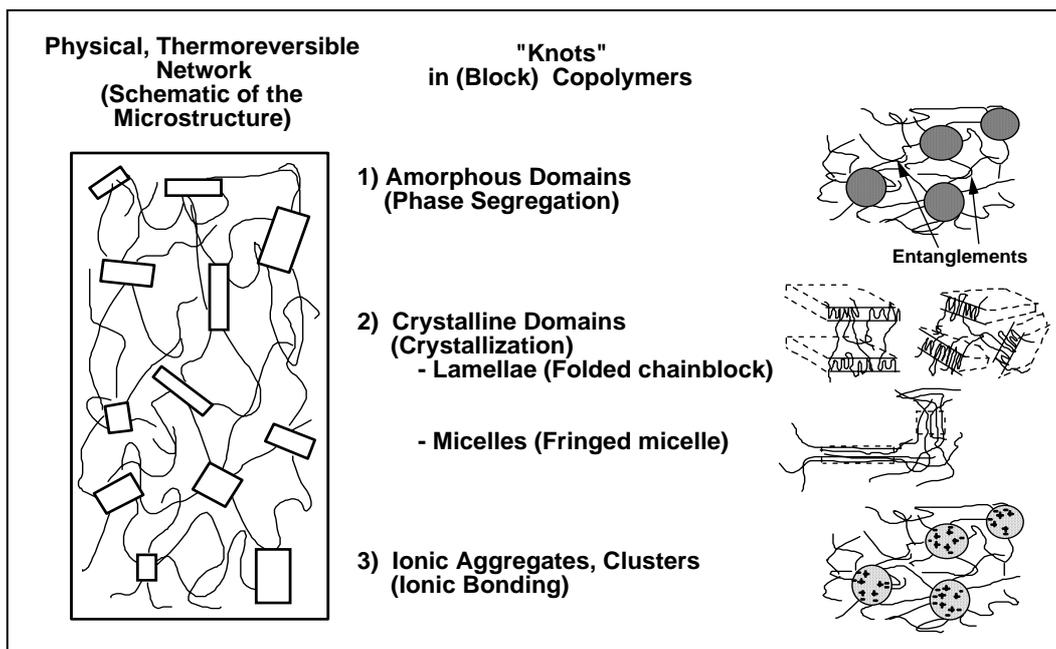


Figure 2.3. Alternative physical network structures in thermoplastic elastomers of (block) copolymer type

Blending of polyolefins with rubbers (NR, EPDM etc) to produce thermoplastic elastomers has a long history (e.g. [73]). A further impetus to the related R&D activities was given by the invention of dynamic vulcanization ([72, 74, 77] and references therein).

Thermoplastic dynamic vulcanizates (TDV) are new members of the family of TPEs. TDVs are produced by dynamic curing of blends composed of thermoplastics and crosslinkable rubbers. The term “dynamic curing” means the selective curing of the rubber and its fine dispersion in the molten thermoplastic via intensive mixing/kneading [74-77]. The microstructure of TDV fundamentally differs from the physical networks formed by phase segregation and shown in Figure 2.3. Note that matrix phase here is given by the “hard” thermoplast which accounts per se the melt processability. The rubbery properties (recovery) are guaranteed by the non-yielded matrix ligaments (between the crosslinked rubber particles) and their inhomogeneous deformation ([72,78] and references therein). It is important to emphasize how fine the rubber particle dispersion in the thermoplastic matrix of the TDV is – cf. Figure 2.4.

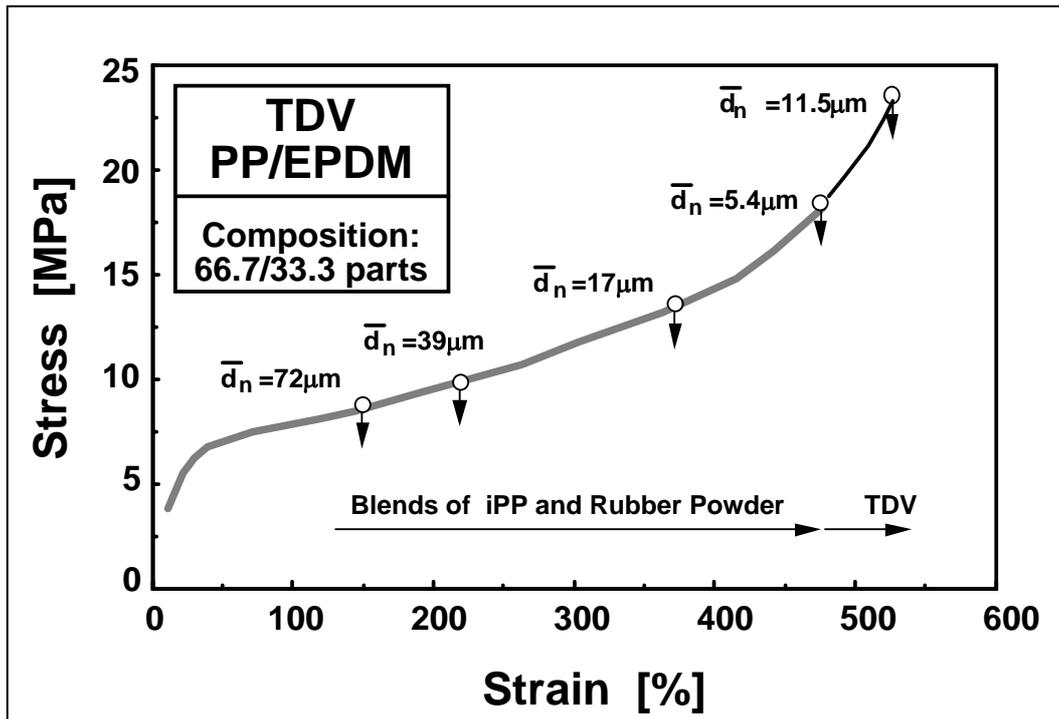


Figure 2.4. Stress-strain behavior of vulcanized rubber particle filled PP and PP-based TDV at the same composition (PP/EPDM = 2:1). Note: original reference in Ref. [72]

The success with melt blending including the TDV technology forced the researchers to develop TPEs with GTR content. Fig 2.4 already shows that this is not easy task at all as the GTR size (from economic reasons between 100 and 1000 μm) never meets the required one (i.e. $< 1 \mu\text{m}$). In addition, the good bonding between the in-situ formed rubber particles and matrix, achieved by chain partitioning (involving co-crystallization phenomena) between the thermoplastic and rubber phases, can also hardly reach with GTR without activation.

One of the first report on TPEs composed of RTR and PP or PP/LDPE blends appeared in 1989 [79]. Al-Malaika and Amir found that the reclaimed tyre rubber should be used together with fresh rubber (NR) in order to enhance the mechanical properties of PP-based blends. Dynamic vulcanization by dicumyl peroxide (DCP) resulted in a further property improvement. The group of Mennig developed a method to produce, “elastomeric alloys” from PP and GTR (particle size ca. 250 μm) e.g. [80-81]). According to the assumption of these researchers a strong boundary layer (interphase) was created between the GTR and PP matrix via covulcanization. Under dynamic vulcanization conditions the results achieved were still far from commercial

TDV of the same hardness range but considerably better than those of simple melt blended versions –cf. Figure 2.5.

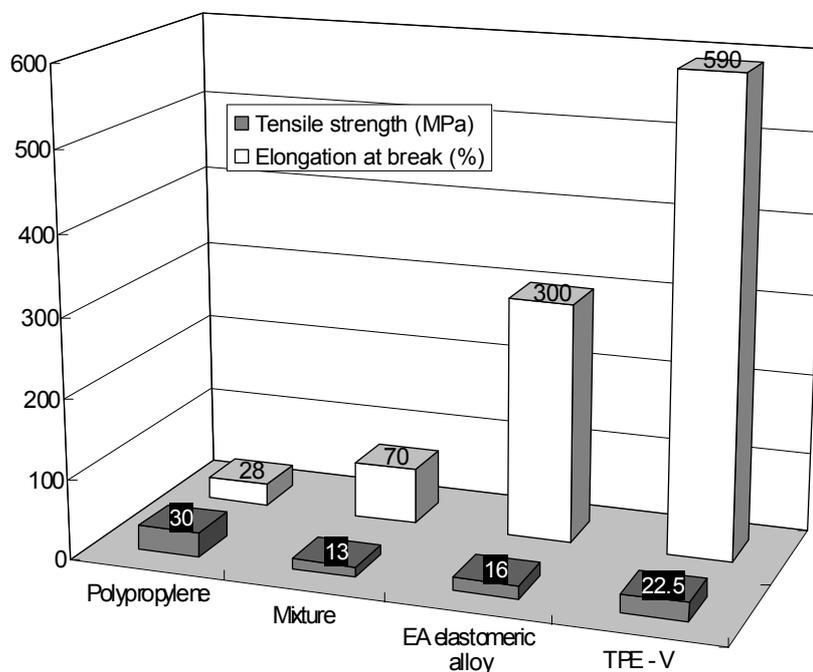


Figure 2.5. Properties of the elastomeric alloys and a mixture in comparison to PP and commercial TDV (TPE-V)

A similar method was developed by Liu et al [82] using “peroxide compatibilization” for PP/ground waste EPDM. The authors selected a long half-life peroxide, viz. t-butyl hydroperoxide, to graft PP onto the EPDM particle surface. This strategy made use of the reactivity of the available double bonds in EPDM even after its vulcanization. The in-situ peroxide-induced grafting/covulcanization strategy was followed by other authors, [83-84]. Recall that all these processes are special variants of the dynamic vulcanization. It should be underlined that Naskar et al [84] used fresh EPDM in their formulations set at an overall rubber/plastic ratio of 60/40. In a follow-up work Naskar et al [85] incorporated maleated GTR in a maleated HDPE/fresh EPDM mix by keeping the rubber/plastic ratio at 60/40. For dynamic curing DCP was added. Compared to non-functionalized GTR a strong improvement in some mechanical properties (strength, moduli, work of rupture) was found, whereas other properties remained practically unchanged (tear strength, tension set,

hardness). The effect of GTR maleation on TPEs was further under spot interest of the Bhowmick group [86], however with different compatibilizer (E/AA). Thermoplastic elastomers produced from reclaimed rubber and LDPE waste with and without dynamic curing (peroxide, sulfuric) and compatibilizer (SEBS, ethylene-co-vinylacetate, EVA) exhibited the best performance (processing, ultimate elongation and set properties) at 50/50 rubber/plastic ratio [87]. Nevatia et al found that the sulfur-accelerator systems worked better than the peroxide one under dynamic curing conditions [87]. The group of Karger-Kocsis [88-89] used coarse GTR fraction (0.4-0.7 mm) for TPE production. The recipe of the TPE was kept constant: LDPE/fresh rubber/GTR = 50/25/25. These works addressed the following issues: effects of the type of fresh rubber, effects of dynamic curing with various curing systems, influence of thermomechanical and thermochemical reclaiming of the GTR. Major results of these studies were: EPDM is the best compatibilizing fresh rubber, thermochemical reclaiming is far more efficient than thermomechanical one and sulfur curatives are most efficient under dynamic vulcanization. Kim et al [90] reported about a strong influence of the screw configuration and processing parameters on the mechanical performance of blends composed of waste EPDM powder (5-20 μm) and PP (EPDM/PP ratio $\approx 75/25$). Continuous production of the same TPE on an “ultrasonic extrusion reactor” (i.e. treating the blend by ultrasonic vibrations) yielded further property improvements [91]. Fukumori et al [92] developed a continuous TPE process. In this technology the following steps are involved: devulcanization of the EPDM waste, blending of the devulcanized EPDM with PP, dynamic vulcanization of the rubber component- cf. Figure 2.6.

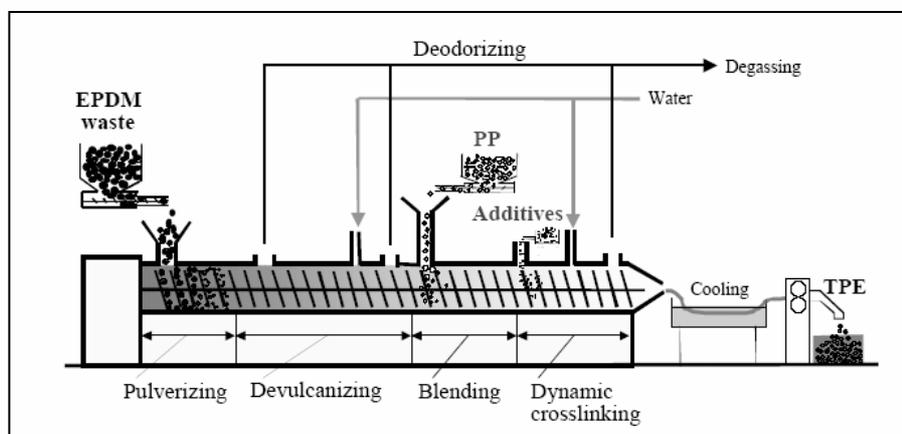


Figure 2.6. Outline of the processing to produce TPE containing waste EPDM in “shear flow reactor” (twin-screw extruder)

The devulcanization step is based on the fact that the -S-S- linkages of the sulfur cured EPDM can be broken selectively. In the blending zone of the extruder the devulcanized rubber is blended with PP (being introduced by side feeding). Dynamic vulcanization is achieved by incorporating curatives. The process involves a “deodorizing treatment” achieved by water injection (cf. Figure 2.6). The mechanical properties of the resulting TPV were comparable with those of commercial products having the same hardness. Recently the group of Mennig [93] showed that the properties of advanced TPEs based on PP and GTR (particle size < 400 μm) could reach those of commercial products. In addition, the related TPEs can be reprocessed without property penalty even 10 times. In the framework of the “Recuprot” project (in which this Thesis has been worked out [94]) Chepel’ et al [95] produced TDVs of useful characteristics. As thermoplastic resin post-consumer LDPE and as a fresh rubber polyisoprene (IR) polybutadiene (BR), butadiene-methylstyrene rubber and EPDM were used with and without dynamic sulfur curing. The LDPE/rubber ratio was set at 1/1. In a recent work Guo et al [96] blended scrap rubber powder with LLDPE in the presence of a dual compatibilizer. The latter consisted of grafted LLDPE (monomers: MA, methyl methacrylate and butyl acrylate) and ENR. The LLDPE/rubber ratio was 30/70. The most encouraging result was that the mechanical properties of the blends did not change with particle size of the scrap rubber powder, at least below a threshold value ($\sim 400 \mu\text{m}$). Last but not least TPEs containing GTR up to 60 wt% are on the market according to recent news. NRI Industries market a Symar-T[®] thermoplastic vulcanizate. In this case the GTR was subjected to a proprietary “surface devulcanization process” [97].

3 Strategy and Aims of this Work

Summarizing the state of wisdom surveyed in chapter 2 the following conclusions can be drawn:

- It is viable to produce TPEs containing (even coarse) GTR fractions
- In order to guarantee a strong bonding between GTR particles and matrix the GTR must be devulcanized/reclaimed at least on the surface
- The thermoplastic matrix should be polyolefinic nature. Further, the lower the crystallinity of the polyolefin, the higher ultimate properties can be expected
- Surface modification, functionalization of GTR by various techniques is less straightforward compared to some kind of “encapsulation” (coating etc.) by fresh, vulcanizable rubber. This fresh rubber has to show dual compatibility toward both GTR and polyolefin matrix
- Covulcanization, coreactions of the GTR with the matrix or even additional crosslinking of the matrix itself may be beneficial
- Dynamic vulcanization, especially by sulfur curatives, is likely advantageous
- As GTR is a product of post-consumer tyres, it is reasonable to blend it with post-consumer polyolefins (waste, recycle)

Based on this information this work was aimed at the development and characterization of TPEs containing GTR. The final TPE grades should possess a property profile rendering them competitive with marketed TPE grades. A further aim was to explore the possibility of a continuous, high-output process for the TPE production

The literature survey in Chapter 2 led us to two promising strategies:

- a) (co)crosslinking: through grafting of silane compounds followed by moisture induced-crosslinking

- b) thermochemical activation: treatment of the GTR with bitumen prior to its incorporation in the polyolefin matrix

The silane-grafted moisture crosslinking approach is well established for PEs and ethylene/propylene copolymers, including related rubbers [98-105]. Figure 3.1 displays the related reaction path.

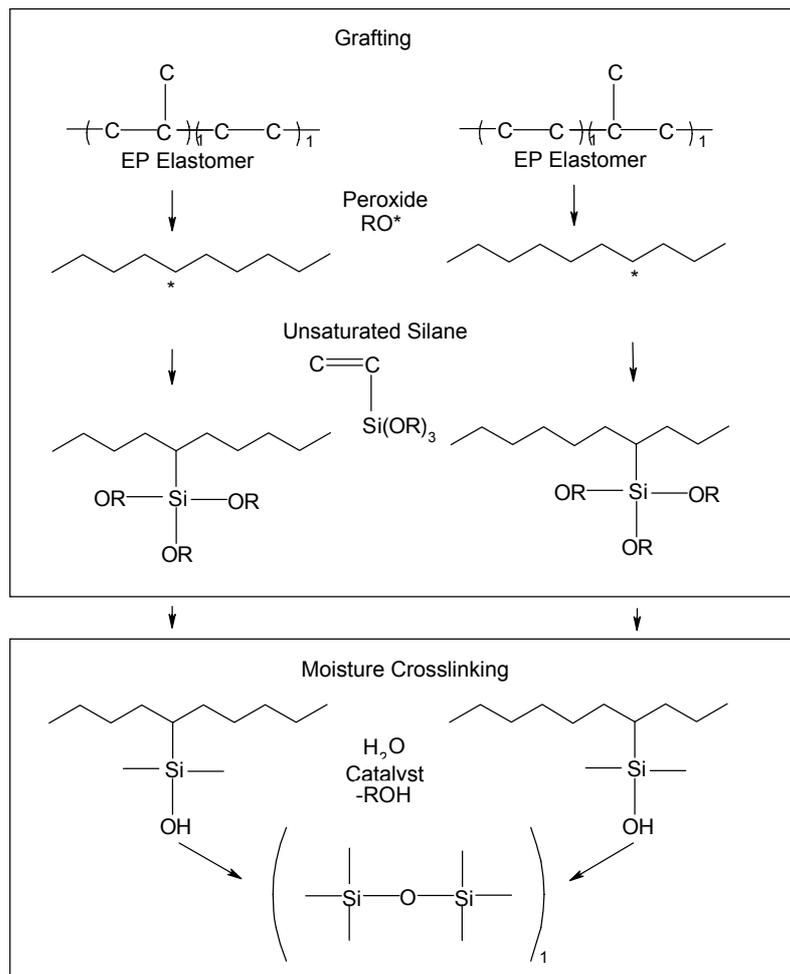


Figure 3.1. Chemistry of the silane-grafting/moisture-cure process on the example of ethylene/propylene copolymer-based elastomers

The basic problem with this approach is that the melt processed/shaped product is crosslinked and thus no more reprocessable. On the other hand, the product should have outstanding rubber characteristics, including recovery.

The alternative approach is based in the success story with “rubberized asphalt”. GTR is often added to asphalt (loading up to 20 wt%) in road construction. The benefits are, improved service life, noise/vibration reduction, resistance to thermal cracking etc. [3, 6,106-108]. In hot bitumen the GTR can be decomposed (activated) resulting in better compatibility between GTR and bitumen (e.g. [109]). Further, bitumen contains sulfuric compounds that may contribute to the devulcanization of GTR. This happens by sulfur partitioning between GTR and bitumen. Note that the related effect it is similar to that of adding fresh rubber. Albeit not explicitly mentioned, and never studied in detail, the action of fresh rubber is nothing else than the “uptake” of some sulfur after breakage of the sulfide crosslinks in the GTR. As a consequence, the crosslinking degree of the GTR decreases via various mechanisms. A further beauty of this approach is that bitumen is quite compatible with polyolefins ([110-111] and references therein).

4 Experimental

4.1 Material used

4.1.1 Polymers

4.1.1.1 Polyolefins (LDPE, HDPE, PP)

As LDPE a recycled grade, produced from used greenhouse films, was mostly used. Used greenhouse films (ca. 1 year old) were collected in the province Ragusa (Sicily, Italy). The composition of this LDPE was as follows: LDPE 65-70%, LLDPE: 12-17%, EVA-copolymer: 12-15%, fillers: ~500 ppm, UV-stabilizer: 2500 ppm. The melt flow index (MFI) of this LDPE grade was 0.18g/10 min measured at 190 °C and 2.16 kg load (ISO 1133:1966, ASTM D 1238-95). The tensile strength and elongation at break values of injection molded specimens showed 16 MPa and \approx 500% (ISO 37, ASTM D 412) [94].

Recycled HDPE was produced from post-consumer bottle transportation crates. The selected crates were collected in Kyiv (Ukraine) washed, cut and granulated after homogenization in the melt. The MFI values of this HDPE were 2.13g/10 min at 190 °C and 2.16 kg load. Its tensile strength and elongation at break values were 17.7 MPa and ca.10%, respectively [94].

PP-based TPEs were also produced. For that purpose a non-recycled PP homopolymer (Novolen[®] 1100 N produced by Targor, Mainz, Germany) with the following characteristics were selected. The MFI of this PP (injection molding grade) was 16 g/10 min measured at 230 °C and 2.16 kg load. The mechanical properties (tensile strength and elongation at break) values were 35 MPa and 50%, respectively.

4.1.1.2 Ground Tyre Rubber (GTR)

Various GTR fractions were involved in this work. The GTR fraction with a particle size between 0.4 and 0.7 mm was preferentially used. This is denoted, however as coarse fraction, when a finer one, with a nominal particle size between 0.2 and 0.4 mm, was involved in the test series (designated as “fine”).

The above GTR fractions were delivered by Scanrub AS (Viborg, Denmark). They were produced by a proprietary technology (Genan [8]) from outsourced tyres (both passenger cars and trucks). According to this Genan technology [8], grinding to fine fractions occurs at ambient temperature, however in an air-gab at supersonic speeds. As GTR is made from very different tyres, only guiding values can be given on the elastomer composition of the powders. Accordingly, the rubber components are: NR - ca. 30%, styrene/butadiene rubber (SBR) – ca. 40%, butadiene rubber (BR) – ca. 20%, butyl and halogenated butyl rubbers – ca. 10%. Major characteristics of the GTR fractions of Scanrub are summarized in Table 4.1.

Table 4.1. Characteristics of GTR produced by Scanrub

Properties	Test Methods		Unit	Specification values after ASTM D 5603	Typical values
	ASTM	ISO			
Specific gravity		2781	[g/cm ³]	NA	1.1-1.2
Ash	E 1131		[%]	< 8	< 5
Acetone extract	D 297	1407	[%]	8-22	11-17
Carbon black content	E 1131		[%]	26-38	32-36
Rubber hydrocarbon	D 297		[%]	>42	> 42
NR content	D 5603		[%]	13-35	ca. 30
Free metal content	D 5603		[%]	< 0.1	< 0.05
Free textile/fiber content			[%]	< 0.5	0.3

The particle sizes distribution of the coarse and fine GTR fractions are depicted in Figure 4.1, whereas scanning electron microscopic (SEM) pictures taken on the related powders are seen in Figure 4.2.

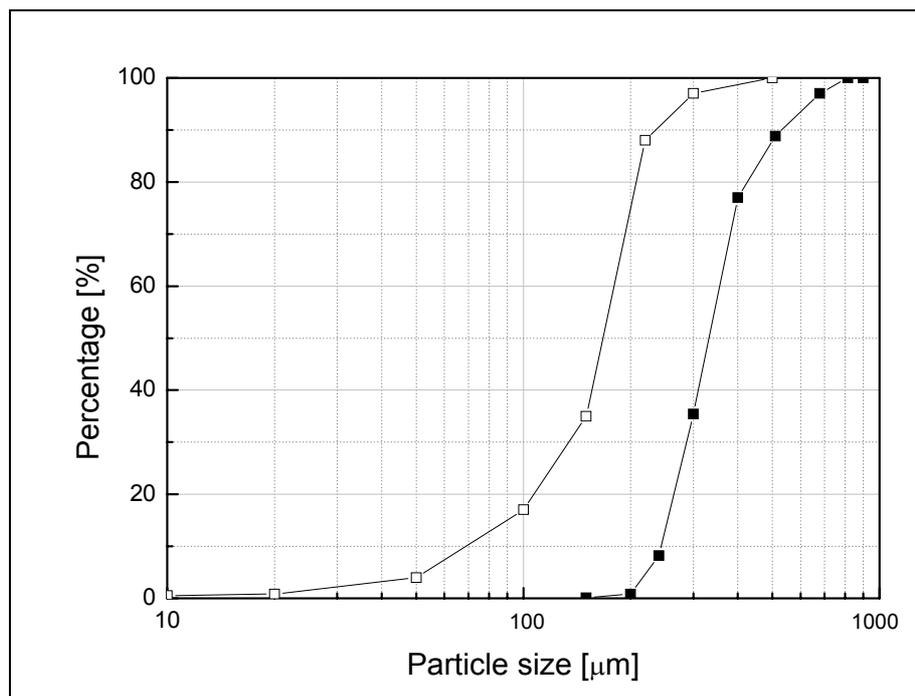


Figure 4.1. Particle size distributions of the Scanrub GTR powders according to sieve analysis. ■ GTR fraction 0.4-0.7 mm; □ GTR fraction 0-0.4 mm

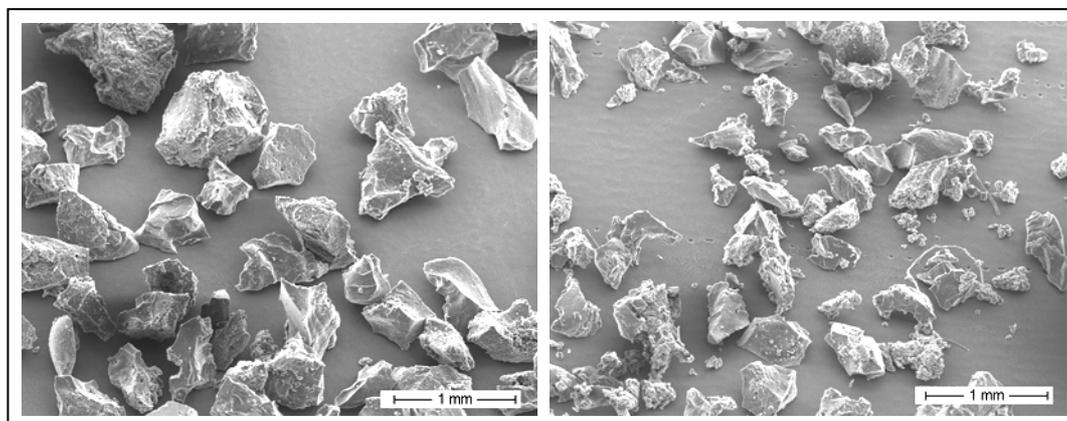


Figure 4.2. SEM pictures taken in the GTR fractions with particle size ranges 0.4-0.7 mm (left) and less than 0.4 mm (right) produced by the Genan technology

Albeit in the majority of the work done, the above Scanrub GTR fractions were used, two further rubber powders were also involved in this study. A GTR fraction with a nominal particle size of less than 0.2 mm and an EPDM powder with particles less than 0.1 mm. The particle size distributions of the latter powders are indicated in Figure 4.3, while SEM pictures are given in Figure 4.4. These powders were produced

by cryogenic grinding at the Fraunhofer Institut für Umwelt -, Sicherheits – und Energietechnik (UMSICHT) Oberhausen, Germany. For this GTR production truck tyres whereas for the EPDM powder used window seals served. Note that the grinding technology applied was a cryogenic one. SEM pictures taken from these ultrafine GTR and EPDM powders are displayed in Figure 4.4.

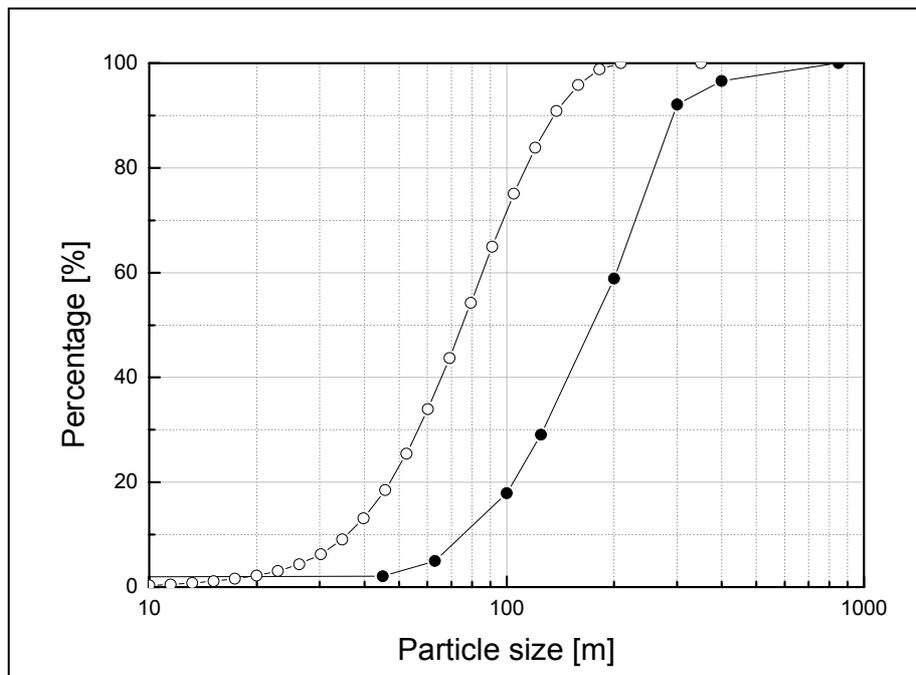


Figure 4.3. Particle size distributions of the ultrafine powders according to sieve analysis. • Ultrafine GTR ; ° EPDM powder

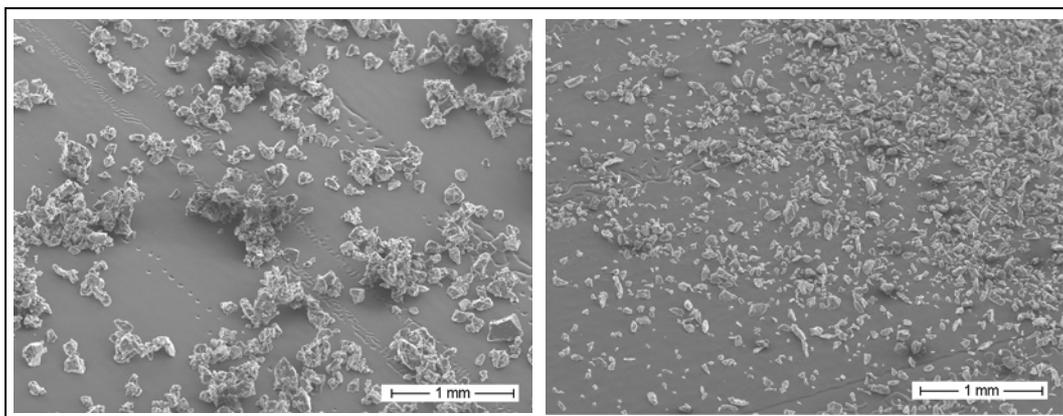


Figure 4.4. SEM pictures taken from the ultrafine GTR (left) and EPDM powder (right) produced by “UMSICHT”

4.1.1.3 Fresh Rubbers (EPDM, NR, SBR)

As fresh rubbers styrene-butadiene (SBR), natural (NR) and EPDM were selected. This selection was determined by the fact that the major rubber ingredients of tyre compositions are SBR and NR (cf. Table 4.1). On the other hand, EPDM is fairly compatible with both PE and PP. The SBR (Buna[®] VSL 2525-0 of Bayer AG, Leverkusen, Germany) contained 25 wt.% vinyl and 25 wt.% styrene. Its Mooney viscosity, ML(1+4) 100°C, was 50±5. Note that this SBR is vinyl-styrene butadiene rubber. The NR was a standard Malaysian rubber – SMR-L with a Mooney viscosity ML(1+4) 100° C = 78. The EPDM rubber (Buna[®] EP G 6470 of Bayer) with 71 wt.% ethylene and 4.5 wt.% ethylidene norbornene contents, respectively, had a Mooney viscosity of ML(1+4) 125°C= 59. Note that this EPDM rubber is available in flake form making it suitable for feeding in an extruder. Unlike EPDM, SBR and NR were bale products.

4.1.1.4 Thermoplastic Dynamic Vulcanizate (Santoprene)

For purpose of comparison and in order to check the compatibility with our TPEs, a commercial PP-based thermoplastic dynamic vulcanizate (TDV), viz. Santoprene 201-80 of Advanced Elastomer Systems (www.santoprene.com), was also involved in this study. This Santoprene grade exhibited the characteristics summarized in Table 4.2.

Table 4.2. Basic properties of Santoprene 201-80 TDV

Properties	Test method ASTM	Unit	Typical values
Density	D 792	g/cm ³	0.97
Hardness, Shore A	D 2240		80
Tensile Strength, Ultimate	D 412	MPa	11.3
Elongation at Break	D 412	%	520
100 % Modulus	D 412	MPa	4.6
Tear Strength	D 624	kN/m	34
Compression Set	D 412	%	29

4.1.2 Ground Tyre Rubber Reclaiming Agents

4.1.2.1 Regent™ –S

The proprietary devulcanization compound Regen™ Agent- S of Sin Rubtech Consultancy (Penang, Malaysia) cleaves the sulfuric bonds in the rubber allowing the resulting compound to be revulcanized without addition of vulcanizing agent. The related process was called earlier De- Link™ and the recycled material De –Vulc™ [3,112-113]. The rubbery Regen™ Agent-S had a density of 1.3 g/cm³ and a Mooney viscosity of ML(1+4) 100°C = 50.

4.1.2.2 Bitumen

The bitumen used was a road construction grade (70/100) according to the standard EN 12591. Its chemical composition (determined by elemental analysis) and other characteristics are listed in Table 4.3.

Table 4.3. Properties of the bitumen used

Elemental analysis

Elements	Content, wt. %
C (carbon)	84.6 – 84.8
H (hydrogen)	9.69 – 9.6
S (sulfur)	3.6 – 3.4
N (nitrogen)	1.5 – 1.4
Other elements	1.0 – 0.4

Other properties

Characteristics	Experimental data
Penetration, dmm (at 25°C, 0.1mm)	45
Content of asphaltenes, %	18 – 20
Softening temperature, °C (Ring & Ball technique)	50 – 50.5
Solubility:	

CCl ₄	Completely
CS ₂	Completely
Alkanes n-C ₆₋₇	Partially
Molecular-mass distribution:	
M _w	9324
M _n	5516
M _z	17719
M _w /M _n	1.69
M _z /M _w	1.90

4.1.3 Crosslinking Agents

4.1.3.1 Rubber Curatives

For dynamic vulcanization of the fresh rubbers in the blends sulfuric and peroxidic curatives were adopted. The related recipes are summarized in Table 4.4.

Table 4.4. Vulcanization recipes. Designations: MBTS = dibenzothiazole disulfide; TBBS = *tert*-butyl-2-benzothiazole sulfenamide; TMTD = tetramethyl thiuram disulfide

Curing	Additive	Amount, phr		
		SBR	NR	EPDM
Sulfuric	ZnO	3	5	5
	Stearic Acid	1	2	1
	Sulfur	1.75	2.25	2
	MBTS	1	-	0.5
	TBBS	-	0.7	-
	TMTD	-	-	1
Peroxide	DCP	3	3	3

All the required additives were donated by Bayer AG (Leverkusen, Germany). DCP with 40 wt% peroxide content was a product of Akzo Nobel Chemicals (Düren, Germany).

4.1.3.2 PE Crosslinking Agents

To check the possibility of co-crosslinking between the GTR and PE phase, the concept of moisture-induced silane crosslinking was followed. For that purpose vinyltrimethoxysilane (VTMS) was used as grafting agent which was also available in masterbatch form. The XL PEarl[®] 31 silane masterbatch was developed for moisture crosslinkable PE cable jackets by Brugg Cables (Brugg, Switzerland – www.brugg.com). For its active silane content 40 wt% was indicated. This PEarl compound was added in 5 phr to the blends produced. In order to get a clearer picture about the grafting, VTMS was melt grafted via the following recipe: VTMS (3 phr), DCP (0.15 phr) and dibutyltin dilaurate (activator) 0.05 phr, (Sigma-Aldrich, Munich, Germany). Note that if VTMS can be grafted on either PE or GTR or both, then the follow-up curing in the presence of moisture results in a rubbery material that afterwards cannot be processed in the melt. The related elastomer can thus be considered as an “on-way” TPE.

4.2 Production of Thermoplastic Elastomers (TPE)

4.2.1 GTR Reclamation

4.2.1.1 Thermomechanical

GTR was thermomechanically degraded in the tight nip of a heated laboratory-mixing mill (model XK-160 of Labtech Eng. Co. Ltd, Bangkok, Thailand). In order to support the sheeting of GTR in a test series parafinic oil was used as processing aid. After 10 min mastication at 60 °C the selected fresh rubber was introduced and rolling followed for additional 10 min. The friction of the laboratory mill was kept constant, viz. 1.2.

Masterbatches composed of GTR/NR, GTR/SBR and GTR/EPDM, all at 1/1 ratio, were produced by this way. Recall that the goal with this masterbatch technique was to partition the sulfur (and thus the sulfuric crosslinks) between the reclaimed GTR

and fresh rubber. This is of great importance in order to avoid “recrosslinking” within the GTR.

4.2.1.2 Thermochemical

The thermochemical treatment of GTR occurred either in the presence of Regent™ Agent –S (denoted as DL furtheron) or bitumen. DL was added in 6 phr to the GTR based on the recommendation of previous studies [111-112]. The GTR/bitumen ratio was varied, however, mostly the composition ratio 1:1 was kept.

a) with DL

Devulcanization of GTR in presence of DL occurred in the open mill as described in section 4.2.1.1.

b) with bitumen

For the GTR reclamation with bitumen both batchwise and continuous operations were tried.

Kneader/open mill (batchwise): GTR was incorporated in molten bitumen and reclamation performed under various conditions:

- at $T = 120\text{ °C}$ for 4 h
- kept at $T = 120\text{ °C}$ for 4 h followed by rolling on the open mill at $T = 40\text{ °C}$ for 40 min
- stored at $T = 170\text{ °C}$ for 4 h followed by rolling on the open mill at $T = 40\text{ °C}$ for 40 min
- stored at $T = 170\text{ °C}$ for 4 h followed by mastication in the kneader chamber (type of Brabender) of a Brabender Pasticorder PL 2000 (Brabender OHG, Duisburg, Germany). Kneading took place at $T = 160\text{ °C}$ for 5 min at 60 rpm. Owing to the very low viscosity of the GTR/bitumen blend under the above mixing conditions, the required amount of fresh rubber was introduced.

Twin-screw extruder (continuous): GTR and bitumen were fed in a corotating laboratory twin-screw extruder type DSE 25 of Brabender (Duisburg, Germany). The

length to diameter ratio was ($L/D = 22$). The screw configuration is indicated in Figure 4.5.

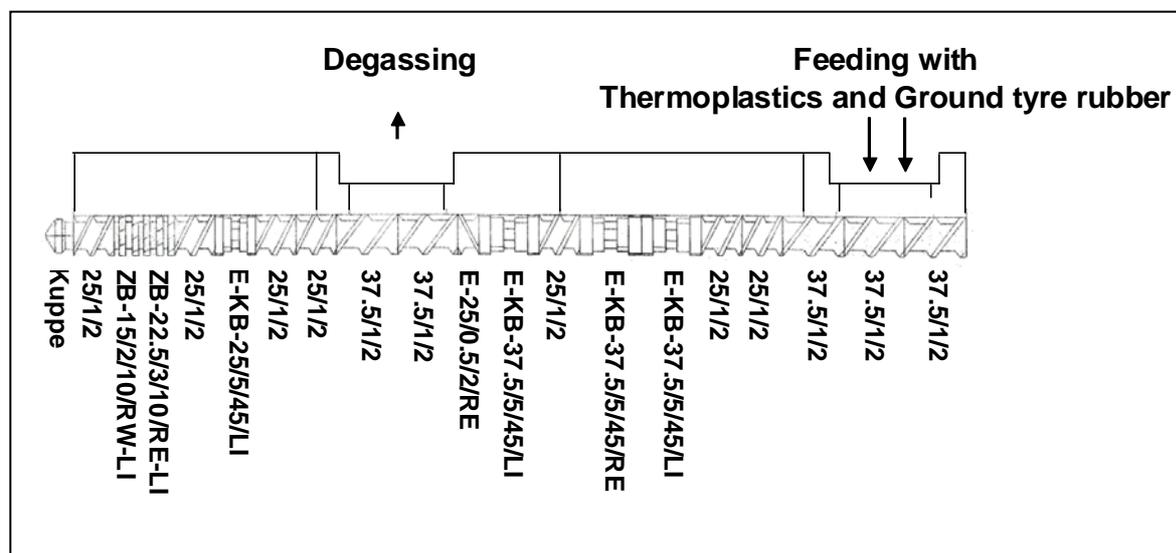


Figure 4.5. Screw configuration of the Brabender corotating twin-screw extruder

The GTR/bitumen (1/1) mix was passed through the extruder under the following conditions: $T = 80/90/100/110$ °C, 40 rpm, residence time: ca. 60 s. In another test series the temperature intervals were: 125/135/145/155 °C.

4.2.1.3 Characterization

Acetone extraction

Reclamation/devulcanization of GTR was followed by measuring the gel content of the resulting compounds, masterbatches. This occurred via Soxhlet extraction in acetone as solvent. Duration of the extraction was 22 h, followed by drying in an oven at 50 °C for 7 h. Note that the acetone extractable is usually considered as a suitable measure of “decrosslinking”. When determining the acetone solubility of the reclaimed GTR (“net” acetone extract) the solubility of the other components (i.e. bitumen, fresh rubber) and their relative amount have been considered, accordingly. The acetone extractable of the initial GTR fractions of Scanrub was ca. 12.1% see Table 5.2, whereas 14.9% and 4.5% were found for the cryogenically produced GTR and EPDM of UMSICHT Fraunhofer Institut (Oberhausen, Germany), respectively.

4.2.2 Compounding of Thermoplastic Elastomers

Reclaimed GTR was melt compounded with polyolefins either in batch (Brabender kneader) or continuous processes (Brabender twin-screw extruder).

4.2.2.1 Batchwise

The mixing conditions in the Brabender kneader varied as a function of the thermoplastic polyolefin (cf. Table 4.5).

Table 4.5. Processing conditions set for batchwise (kneader) and continuous (extruder) TPE production.

Processing parameters	Batch			Continuous	
	LDPE	HDPE	PP	LDPE	PP
Operating Temperature [°C]	170	170	230	~ 170	~230
Rotation speed [rpm]	60	60	60	40	40
Mixing, residence time [min]	10	10	10	1-2	1-2
Output [kg/h]	-	-	-	20-30	20-30

4.2.2.2 Continuous

The notes in 4.2.2.1 holds also for continuous melt blending (cf. Table 4.5). Further, the production of some TPEs involved two or three extrusion steps. Attention will be put on this aspect in the following chapters.

When studying the effects of reprocessing on the residual properties of the TPE, usually the same conditions, as used for their initial compounding and listed in Table 4.5, were set.

4.2.3 Specimen preparation

Specimens for investigations were produced either by compression or injection molding.

4.2.3.1 Compression Moulding

The TPEs produced were compression molded on laboratory manually-closing presses with heating platens from Paul Otto Weber EP-Stanzteile, (Remshalden, Germany), using a metal frame of ca. 2 mm thickness. Weighted amount of TPE was placed in the frame sandwiched between two thin Al films. The heated mold was closed and after 2 min and after 5 min pressure (1.25 MPa) applied. The temperature of the press molding plates was $T = 180$ and 230 °C for the PE- and PP- based TPEs, respectively. After 4 min holding the press plates were cooled to room temperature (RT) and the sheets demolded and deflashed. Specimens were punched or cut from the sheets.

4.2.3.2 Injection Moulding

The injection molding conditions for PE- and PP-based compounds are given in Table 4.6.

Table 4.6. Injection molding conditions used for PE- and PP-based TPEs, respectively

	Material	
	PP-based	PE-based
Rear Zone (°C) ±5	175	180
Center Zone (°C) ±5	180	185
Front Zone (°C) ±5	190	195
Nozzle (°C) ±5	195-235	200-220
Mold	RT in all the cases	
Injection Pressure (bar)	700	500
Injection Volume (cm/s)	20	20
Holding Pressure (bar)	500	400
Injection Time (s)	1 to 15	1 to 15
Cooling Time (s)	5 to 30	5 to 30
Overall Cycle Time (s)	6 to 45	6 to 45

Dumbbell specimens (type 1A according to ISO 527-2) with and without weld line in their center part were injection molded on an Allrounder 270 C machine of Arburg Co., (Lossburg, Germany).

The molds to produce single- and double- gated specimens, i.e. without and with weld line, are shown in Figure 4.6.

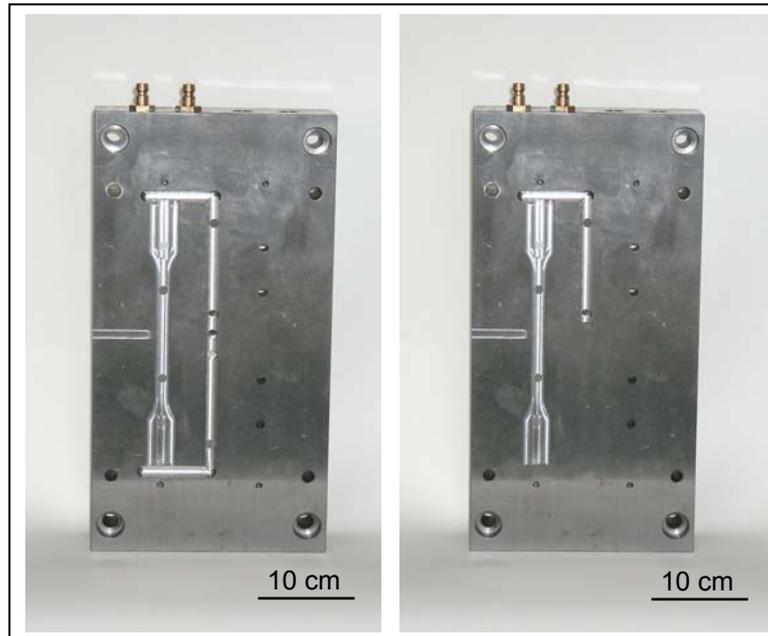


Figure 4.6. Molds to produce dumbbells with (left) and without (right) weld (knit) line. Note that the other plate of the molds is completely smooth

TPE products are mostly produced by injection molding whereby the formation of weld lines can hardly be avoided. Therefore effects of cold weld lines should be studied. Note that so called “cold” welding line develops at the impingement of two opposed melt streams (e.g. [115]). The cross section of the dumbbells was 10 x 4 mm (width x thickness). These dumbbells served not only to determine the tensile properties but also to derive other ones (set properties, dynamic-mechanical thermal analysis, DMTA, hardness). For some tests often sections cut from the “neck” of the dumbbells were used.

4.3 Characterization of the TPEs

4.3.1 Mechanical Properties

4.3.1.1 Tensile

The injection molded dumbbells or punched ones from the compression molded sheets (ISO 37 or its equivalent ASTM D 412) were subjected to uniaxial tensile test on a Zwick universal testing machine (type 1445, Zwick, Ulm, Germany). The deformation rate was 200 mm/min and the related test performed at RT and 45 % relative humidity. The personal computer controlled testing allowed us to register and store the whole “testing history”, i.e. to capture the force-displacement behavior. As the ultimate strain of (thermoplastic) rubbers may reach several hundred %, the stress values read at given strains (100, 200, 300 % etc.) in the corresponding stress-strain curves are read. They are usually reported as E-moduli at selected strain values.

4.3.1.2 Hardness

Shore Hardness (either the A or D scale) is the preferred method to group rubbers (ISO 48 or its equivalent ASTM D 1415). The hardness value is inversely related with the penetration of a standardized indenter in the rubber without causing its surface damage. Because of the resilience of rubbers the indenter penetration changes with the time. Therefore the hardness is read at 3 s of loading where the deformation is usually “stabilized”.

4.3.1.3 Set properties

Compression and tension set are very important measures of rubbers. Their values reflect the ability of rubber to return into their initial shape after being deformed in compression or tension modes for a given time at a specified temperature.

When performing the compression set test on rubbers within the Shore A hardness range, first the thickness of the disc-shaped specimens is measured. Then the disc is clamped in a test fixture that compresses the thickness of the disc by 25%. After keeping at a given time and temperature (usually 22 h at 70 °C) the fixture is opened

and the rubber disc is allowed to relax for 30 min. Afterwards the thickness is measured. The compression set is expressed by the percentage of thickness loss and lies between 0 (full recovery) and 100 % (no recovery, full plasticity).

To determine the tension set at suitable piece of rubber (strip, dumbbell) is subjected to a certain amount of deformation for a given period of time at a specified temperature (usually at 75 % of the ultimate strain, 10 min, RT). The percentage of length (strain) increase after ceasing the deformation is the tension set (ISO 12244 and ISO 2285). For TPEs the tension set seems to be a key issue. It is often referred in the literature that the definition of TPE requires that the tension set value is lower than 50 % (e.g. [80-81]).

4.3.2 Thermal properties

4.3.2.1. Differential Scanning Calorimetry (DSC)

The melting and crystallization behaviour was studied by differential scanning calorimetry (DSC) in a DSC 821^e device of Mettler Toledo (Giessen, Germany). In the Al crucibles 8-12 mg material was placed and DSC scans were registered from -100 up to 200 (PE-based) and 250 °C (PP-based systems) at 10 °C/min heating rate. The same temperature interval was covered during cooling at the same rate. The melt and crystallization enthalpy values were calculated using the “STARe” software of Mettler Toledo.

4.3.2.2. Dynamic Mechanical Thermal Analysis (DMTA)

The viscoelastic behaviour of the TPEs was investigated using an Eplexor 25 N device of Gabo Qualimeter (Ahlden, Germany). Rectangular bars cut of the injection molded dumbbells were subjected to oscillating tensile loading (static and dynamic stresses were 4 and ± 2 MPa, respectively). Measurements were made at 10 Hz frequency and 1 °C/min heating rate over the temperature range -100 to melt softening of the corresponding material. The outcome of this test was the change of the complex E-modulus and its constituents (viz. storage and loss moduli; E' and E''), respec-

tively) as a function of the temperature (T). Note that the mechanical loss factor, $\tan\delta = E''/E'$, represents that part of the energy which turned into heat in each cycle.

4.3.2.3. Heat Aging

Aging of materials refers to the variation of their properties over the time. Heat aging in air is a key issue of rubbers and standardized accordingly (ISO 188, ASTM D 573). Heat aging is usually performed at 70 or 100 °C for several days (1, 3, 7 and 7+ n7). After aging the residual mechanical properties, such as hardness, tensile stress and strain, tension set, are determined.

4.3.3 Rheological Characterization

4.3.3.1. Plate-Plate Rheometer

The plate-plate rheometer used was an ARES device of Rheometric Scientific (Piscataway, NJ, USA). The samples (circular discs) punched from compression molded sheets of ca. 1 mm thickness. These discs with 25 mm diameter and 1 mm thickness were mounted in the gap between the plates. Rheological tests were performed at various temperatures in strain and frequency sweeps in order to conclude the viscoelastic range. The ARES rheometer allowed us to monitor the following parameters under isothermal conditions: torque, complex shear modulus (G^*) and its constituents (G' , G'' , $\tan\delta$), complex viscosity (η^*) and its constituents (η' , η'').

4.3.3.2. Capillary Rheometer

Capillary rheometer measurements were done on a Rheo-Tester 1500 device of Göttfert (Buchen, Germany). Tests were carried out at various temperatures (for PE and PP-based TPEs usually $T = 180$ and 230 °C, respectively, were selected) using tungsten die of 1 mm diameter and 30 mm length (L/D ratio = 30). The apparent shear viscosity of the compound, was determined at shear rates, $\dot{\gamma} > 500$ s⁻¹. Note that this shear rate range is effective during injection molding.

4.3.4 Morphological Characterization

Scanning electron microscopy (SEM) was used to study the appearance of the GTR particles, their embedment in the thermoplastic matrix and to conclude the failure behavior of GTR containing TPEs. SEM inspection was done in a JSM-5400 apparatus of Jeol (Tokyo, Japan). To visualize the adhesion between GTR and the surrounding matrix various preparation methods were tried. Fracture of the specimens at liquid nitrogen temperature delivered no information. SEM pictures were taken from fracture surfaces after side grooving with a razor blade proved to be more informative. In order to avoid electrostatic charging, the surface of the samples was sputtered by an Au/Pd alloy coated. This occurred in a Balzers SCD-050 device (Balzers, Lichtenstein) for ca. 150 s. The thickness of the resulting coating was ca. 100 nm. The acceleration voltage during scanning with the electron beam was 15 kV.

5 Results and Discussion

5.1 Moisture- induced crosslinking via vinylsilanes

It was presumed that vinyltrimethoxy silane (VTMS) can be grafted on both GTR surface and LDPE chains during melt compounding in a peroxide initiated process. If grafting is successful then the additional cocrosslinking via action of water (giving siloxane crosslinks) should result in a compound of rubbery characteristics as mentioned before (cf. section 4.1.3.2). The idea was borrowed from the cable industry where this grafting/crosslinking process for PEs is well established. As the thermoplastic character of the compound is lost by this way, moisture-induced crosslinking should be performed for the final, molded part. Irrespective to this disadvantage, the process may be economic as the GTR particles require no pre-treatment.

In Table 5.1 we can observe the composition codes and the basic mechanical properties.

Table 5.1. Composition codes and basic mechanical properties of the moisture-crosslinked LDPE/GTR systems. Designations: *¹ phr, GTRc and GTRf – coarse and fine GTR fractions, respectively

Designation	Composition	Parts
R1, R2, R3	LDPE/EPDM/GTRc	50/15/35, 50/25/25, 50/35/15
R4, R5, R6	LDPE/EPDM/GTRf	50/15/35, 50/25/25, 50/35/15
A1, A2, A3	LDPE/EPDM/GTRc (DCP, VTMS, TMTD)	50/15/35, 50/25/25, 50/35/15 (0.15, 3, 0.05) * ¹
A5, A6, A7	LDPE/EPDM/GTRf (DCP, VTMS, TMTD)	50/15/35, 50/25/25, 50/35/15 (0.15, 3, 0.05) * ¹
P1, P2, P3	LDPE/EPDM/GTRc (PEarl 31)	50/15/35, 50/25/25, 50/35/15 (5) * ¹
P4, P5, P6	LDPE/EPDM/GTRf (PEarl 31)	50/15/35, 50/25/25, 50/35/15 (5) * ¹
x2-A2, x4-A2	LDPE/EPDM/GTRc (DCP, VTMS, TMTD)	50/25/25 (0.3, 6, 0.1);(0.6, 12, 0.2) * ¹
x4-A5	LDPE/EPDM/GTRf (DCP, VTMS, TMTD)	50/25/25 (0.6, 12, 0.2) * ¹
x2-P2	LDPE/EPDM/GTRc (PEarl 31)	50/25/25 (10) * ¹

Code	Modulus at Elongations		Tensile Strength	Ultimate Elongation	Hardness	Compression Set
	100% [MPa]	300% [MPa]	[MPa]	[%]		[%]
R1	5.2 (5.6)	-	5.4 (5.7)	170 (151)	89 (88)	61 (61)
R2	4.7 (5.1)	4.9 (-)	5.0 (3.5)	365 (316)	89 (88)	57 (56)
R3	4.5 (4.8)	4.9 (5.1)	8.1 (7.8)	755 (744)	89 (87)	65 (43)
R4	5.3 (5.9)	-	5.7 (6.2)	242 (216)	89 (90)	77 (39)
R5	4.9 (5.3)	5.3 (-)	6.0 (6.0)	515 (491)	86 (88)	64 (33)
R6	4.5 (4.8)	5.0 (5.2)	9.5 (8.9)	860 (834)	88 (87)	68 (48)
A1	5.7 (5.9)	-	5.9 (6.1)	154 (180)	89 (89)	41 (38)
A2	5.0 (5.5)	-	5.3 (5.7)	319 (243)	89 (89)	40 (29)
A3	4.7 (5.2)	4.7 (5.2)	6.8 (7.5)	682 (714)	88 (89)	41 (44)
A4	5.6 (6.2)	-	5.7 (6.4)	171 (172)	89 (90)	40 (36)
A5	5.2 (5.6)	-	5.3 (5.7)	323 (255)	88 (90)	44 (32)
A6	4.5 (5.0)	4.8 (5.1)	9.3 (9.6)	870 (882)	88 (90)	72 (50)
P1	5.7 (6.0)	-	5.9 (6.1)	185 (175)	88 (89)	41 (37)
P2	5.3 (5.6)	-	5.6 (5.9)	296 (268)	89 (89)	46 (42)
P3	5.0 (5.5)	5.5 (6.0)	7.6 (7.9)	669 (640)	88 (89)	37 (33)
P4	5.9 (6.3)	-	6.1 (6.4)	196 (175)	89 (90)	78 (72)
P5	5.3 (5.9)	2.3 (3.0)	5.7 (6.0)	364 (338)	89 (89)	65 (61)
P6	5.0 (5.4)	5.4 (6.1)	8.7 (8.9)	762 (720)	88 (88)	68 (62)
x2-A2	5.4 (5.5)	-	5.6 (5.7)	269 (240)	89 (90)	
x4-A2	5.1 (5.9)	6.2 (6.4)	6.7 (6.9)	468 (452)	89 (90)	
x4-A5	5.6 (5.7)	6.5 (6.7)	8.5 (8.5)	642 (559)	90 (90)	
x2-P2	6.3 (6.5)	-	6.5 (6.6)	253 (223)	85 (88)	

("") values after aging, (T = 70 °C, 22 h).

To check the feasibility of this method, samples of various compositions were compounded in a Brabender kneader (T = 200 °C, 60 rpm, mixing time: 6 min). Sheets of 2 mm thickness were produced by hot pressing (T = 180 °C, pressure 1.25 MPa, holding time: 5 min, fast cooling to RT). The pressed sheets were immersed in hot water (T = 80 °C) for 3 days (d) to accomplish the crosslinking. Mechanical tests were performed on dumbbell (type S3A, ISO R 37) specimens punched from the crosslinked sheets. The results are listed in Table 5.1.

5.1.1 Effects of grafting composition

Based on Table 5.1 one can recognize that neither the ready-to-use PEarl, nor the DCP-initiated VTMS grafting/crosslinking resulted in the expected property improvement. The effects measured are marginal even if the fourfold amount of the usual grafting recipe was used.

This finding is very surprising from several aspects. If VTMS is not grafted onto the GTR surface, the grafting reaction should be still effective for both EPDM and LDPE yielding the expected property upgrade (i.e. increase in both stiffness and strength eventually at cost of the ductility). On the other hand, it should be born in mind that the major effect of crosslinking in PEs is the improvement in the thermal resistance. The DMTA traces in Figure 5.1 clearly show that with increasing VTMS amount, in fact, a crosslinked structure developed. The plateau in the storage modulus (E') above the initial melting temperature is a clear indication for the crosslinking.

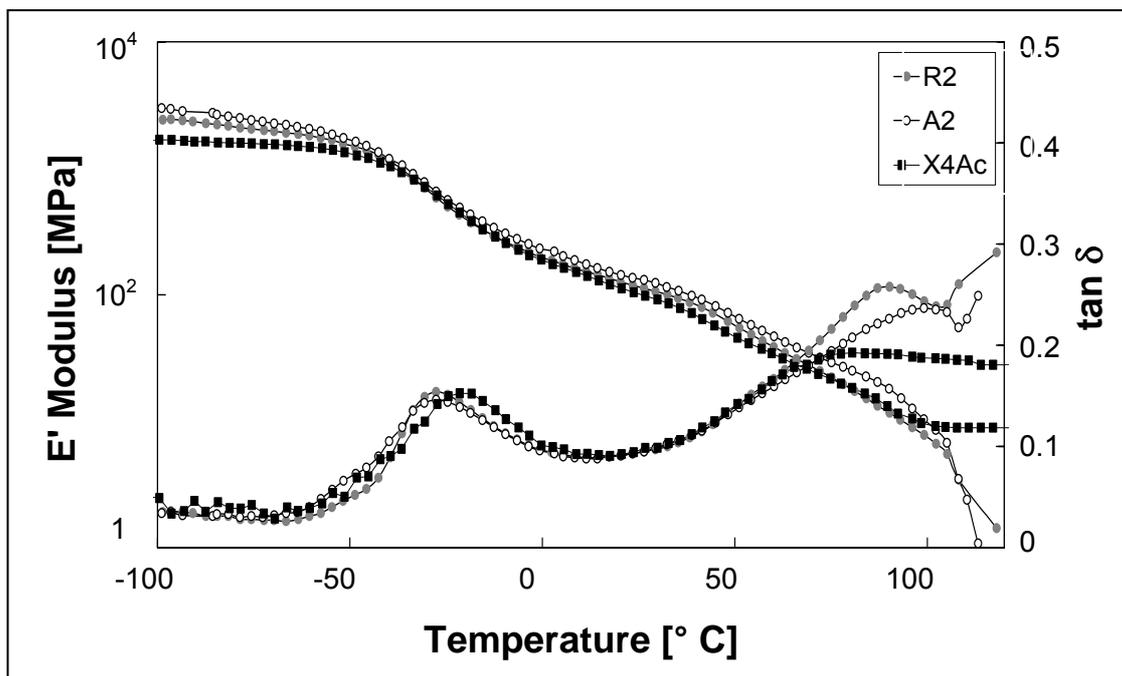


Figure 5.1. Storage modulus (E') and mechanical loss factor ($\tan \delta$) as a function of temperature for the compounds R2, A2 and x4AC. Notes: for coding see Table 5.1. The above compounds differ only in the content of VTMS to be grafted

Note that the onset of the rubbery plateau (see E' above 100 °C) means at the same time that the compound is no more melt processable.

5.1.2 Effects of GTR size

Table 5.1 contains some further valuable information. Note that the ultimate properties which reflect the “technological compatibility” of the systems do not change much as a function of the GTR particle size (c and f, respectively). This is opposed to the usual belief that the finer the GTR fraction, the better the ultimate properties are. Though the difference in the particle size of the GTR particle size of the GTR fractions is not very large, the above finding, viz. small effect of GTR particle size on the properties, should be assigned to the role of EPDM. As supposed, the EPDM may work as a dual-phase compatibilizer in respect to both LDPE and GTR. This is a very important result for the further research strategy of this work.

Anyhow, the moisture-induced cocrosslinking technique did not meet the expectations. The targeted crosslinked structure was achieved at substantially higher VTMS dosage than usual. This is likely due to the “poisoning” effect of the GTR for this sensitive vinylsilane grafting technique. Further, this procedure is quite expensive, especially if multiple amounts of the VTMS have to be used. In addition, to crosslink the product in its final shape means a strong limitation in respect to product versatility. Last but not least, the melt processability is lost. Owing to the results achieved and considering the above aspects this recycling strategy was dropped.

5.2 GTR devulcanization/reclamation

5.2.1 RegentTM – Agent- S

This devulcanizing agent was added in 6 phr to GTR following the recommendations taken from the literature [112-113]. Thermochemical decomposition was made in heated (T = 60 °C) laboratory open mill for 10 min. After 10 min mastication of GTR with RegentTM – Agent-S fresh rubber (NR, SBR and EPDM) was added and

mastication followed for additional 10 min. Note that this masterbatch procedure (GTR/fresh rubber ratio = 1/1) was adopted in order to avoid/reduce the recrosslinking of GTR (“sulfur partitioning”). In addition, introduction of fresh rubber was very beneficial to get sheeted rubber on the rolls.

The efficacy of devulcanization was determined by the change in the “net” sol content. Net sol content means that the acetone solubility of both RegentTM – Agent-S and fresh rubber – after the same treatment - has been considered. Note that the solubility in acetone and in some other solvents (e.g. toluene) is the usual way to assess changes in the crosslinked structure of rubbers [88-89]. The results are summarized in Table 5.2.

Table 5.2. Acetone solubility (net sol content) of the GTR devulcanized by RegentTM – Agent-S

GTR (coarse)	Sol content [%]
As received	12.1 ± 0.7
Devulcanized by Regent TM Agent in the presence of:	
NR	18.5 ± 1.2
SBR	17.0 ± 0.9
EPDM	16.4 ± 1.1

Notes: composition of the masticated blends – GTR/fresh rubber/ RegentTM – Agent-S = 50/50/6 parts. Results deduced from 3 parallel extractions.

Data in Table 5.2 are in agreement with those reported by Radheskumar et al. [89]

It is interesting to note that the RegentTM – Agent worked slightly better on GTR in combination with NR compared to SBR and EPDM. Recall that this devulcanization agent is usually recommended for NR- based gums. Nevertheless ca. 5 % increase in the acetone solubility can hardly be considered as an effective devulcanization for the GTR. Therefore our interest was next focused on an alternative way, viz. GTR reclamation in bitumen.

5.2.2 Reclamation in bitumen

The effects of bitumen on GTR reclamation were studied in both discontinuous and continuous operations at various processing conditions.

5.2.2.1 Batchwise

GTR/bitumen (ratio 1/1) was stored at $T = 120\text{ }^{\circ}\text{C}$ for 4 h (A), at $T = 120\text{ }^{\circ}\text{C}$ for 4 h followed by rolling on the open mill at $T = 40\text{ }^{\circ}\text{C}$ for 40 min (B) and $T = 170\text{ }^{\circ}\text{C}$ for 4 h (C), at $T = 170\text{ }^{\circ}\text{C}$ for 4 h followed either by rolling as in case B (D1) or masticating in the Brabender chamber at $T = 170\text{ }^{\circ}\text{C}$ for 5 min (D2).

The sol content (acetone extractable) increased in respect to the initial untreated GTR as follows:

$$A (<1\%) < B (1-2\%) < C (7.1-8.3\%) < D1 (11.1-13.9\%) < D2 (13.0-15\%)$$

Note that in order to get the overall sol content of the corresponding reclaimed GTR ca. 12 % (cf. Table 5.2) should be added.

One can recognize that an efficient reclaiming of GTR in bitumen is linked to a threshold temperature. In addition, the reclaim efficiency is increasing in presence of severe shear stresses (Brabender kneader).

5.2.2.2 Batchwise in plate/plate rheometer

In order to study the reclamation more detailed, time sweep rheological tests were performed at $180\text{ }^{\circ}\text{C}$ on ground rubber/bitumen (ratio: 1/1) mixes. The ground rubbers involved were GTR (coarse fraction of Scanrub), cryogenically ground truck tyre rubber (GTR ultrafine of UMSICHT) and cryogenically ground peroxide-cured EPDM rubber (EPDM of UMSICHT). As depicted in Figure 5.2 the rubber particles in bitumen behave differently as a function of time. The GTR particles present a constant viscosity up to about 4 h. Then, the viscosity starts to increase constantly for the 10 h duration of the time sweep experiment. On the contrary, in the mixture with the mixture with the ultrafine GTR particles the viscosity decreases for the first two hours and increases rapidly after this period.

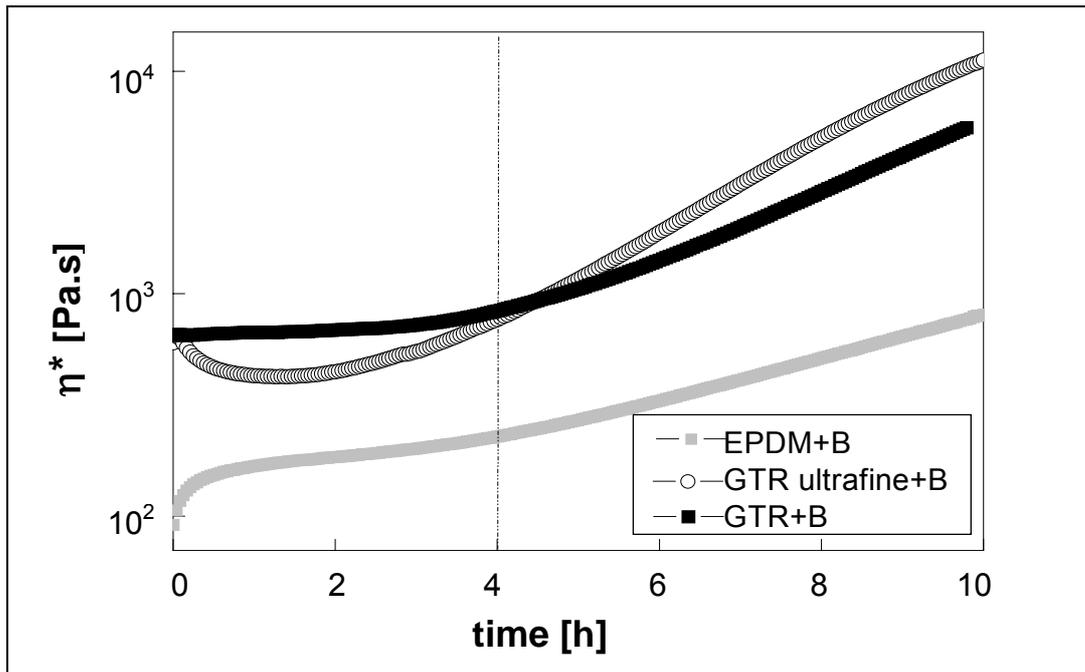


Figure 5.2. Viscosity vs. time curves for the bitumen-rubber particles mixes at $T=180$ °C, strain 1% and frequency 10 rad/s

For the EPDM/bitumen mixture, three slopes in the viscosity-time can be resolved. The first steep increase is at the beginning, then the viscosity slightly increases up to the first 4 h and shows afterwards a steeper slope (range 4 to 10 h). The high slope within the first thirty minutes can likely be related with the wetting of these fine particles (i.e. creation of a core-shell structure). It should be mentioned that the slope value after the first four hours has an order of $GTR\ ultrafine > GTR > EPDM$ for the rubber particles.

In Figure 5.3 the storage modulus (G') versus time is presented. It is obvious that the G' change upon the time follows the same trend as the viscosity time curves.

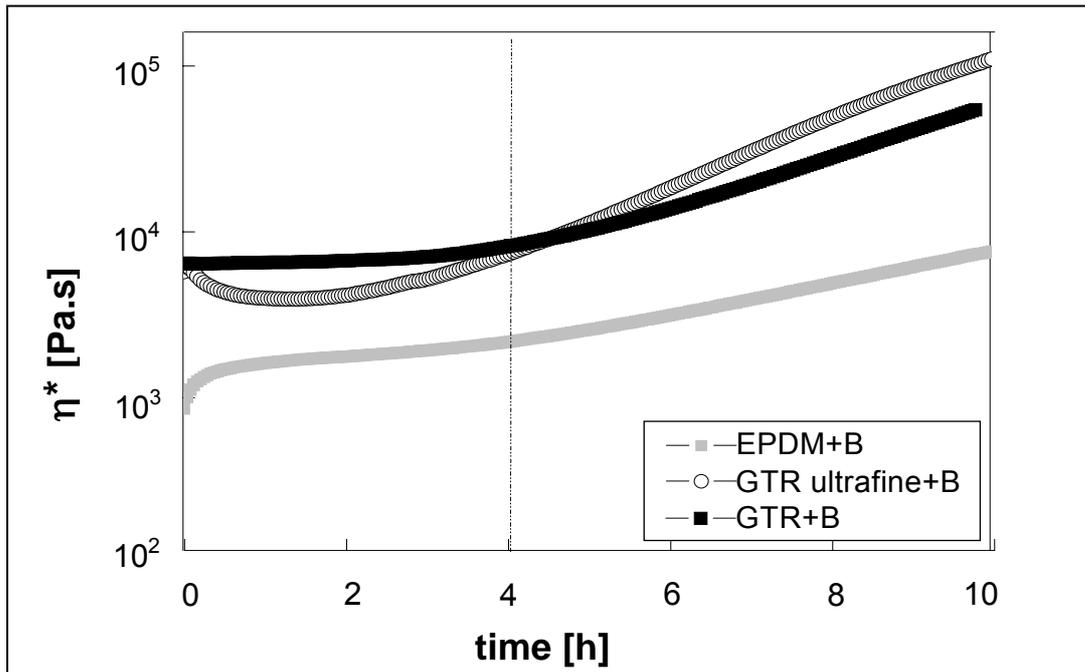


Figure 5.3. Storage modulus a function of time for the bitumen-rubber particles mixes at $T = 180\text{ }^{\circ}\text{C}$, strain 1% and frequency 10 rad/s

The higher value of the G' for the GTR particles for the first 4 h of the experiment can be related to the higher particle size and higher crosslinking degree compared with GTR ultrafine. For the particles with the smallest particle size (i.e. EPDM; $< 100\text{ }\mu\text{m}$) the G' of the dispersion lies always at low G' values. For the GTR ultrafine/bitumen dispersion (particle diameter $< 200\text{ }\mu\text{m}$, cf. Figure 4.4) the decrease of the G' may indicate a prominent softening of the rubber particles. This is a hint for a lower crosslinking degree. The latter was supported by the acetone extract of ultrafine GTR laying at $14.9 \pm 1.0\%$ initially.

All these three types of particles present totally different behaviour in the bitumen. First the low viscosity bitumen (at $T = 180\text{ }^{\circ}\text{C}$) will diffuse into the rubber particles. This phenomenon should be directly related with the crosslinking density of the rubber particles. The EPDM dispersion seems to be rather insensitive to bitumen upon heating. After a rapid G' and viscosity increase in the first thirty minutes (cf. Figures 5.2 and 5.3), these values slightly increase furtheron. The G' and viscosity decrease for the GTR ultrafine/bitumen mix the first 2 h can be likely related to the diffusion of bitumen molecules inside these rubber particles. This enhances the

viscous character of this dispersion (soft particles easily deformed upon strain). The abrupt G' and viscosity increase indicate a “gelation” behaviour of the mixes that can be assigned to the course of reclamation. So the GTR particles present a low degree of swelling and lower G' and viscosity increment compared to GTR ultrafine containing ones. This may be related to the inner structure of the rubber particles (e.g. higher crosslink density and less un-reacted double bonds in GTR compared to the ultrafine grade).

To continue the above-mentioned analysis, the mechanical loss factor ($\tan\delta$) of the mixes as a function of time can supply interesting information. As presented in Figure 5.4, the peak onset of the different dispersions varies by time and shows also various intensities. A $\tan\delta$ increase is related with enhanced viscous character of the dispersion. For the GTR a smooth increase is observed up to 3 h. Then $\tan\delta$, decreased and reached almost the initial $\tan\delta$ value. For the GTR ultrafine particles the high bitumen diffusion can be observed from the increase of the $\tan\delta$ peak during the first 2 h. After this point $\tan\delta$ starts to decrease.

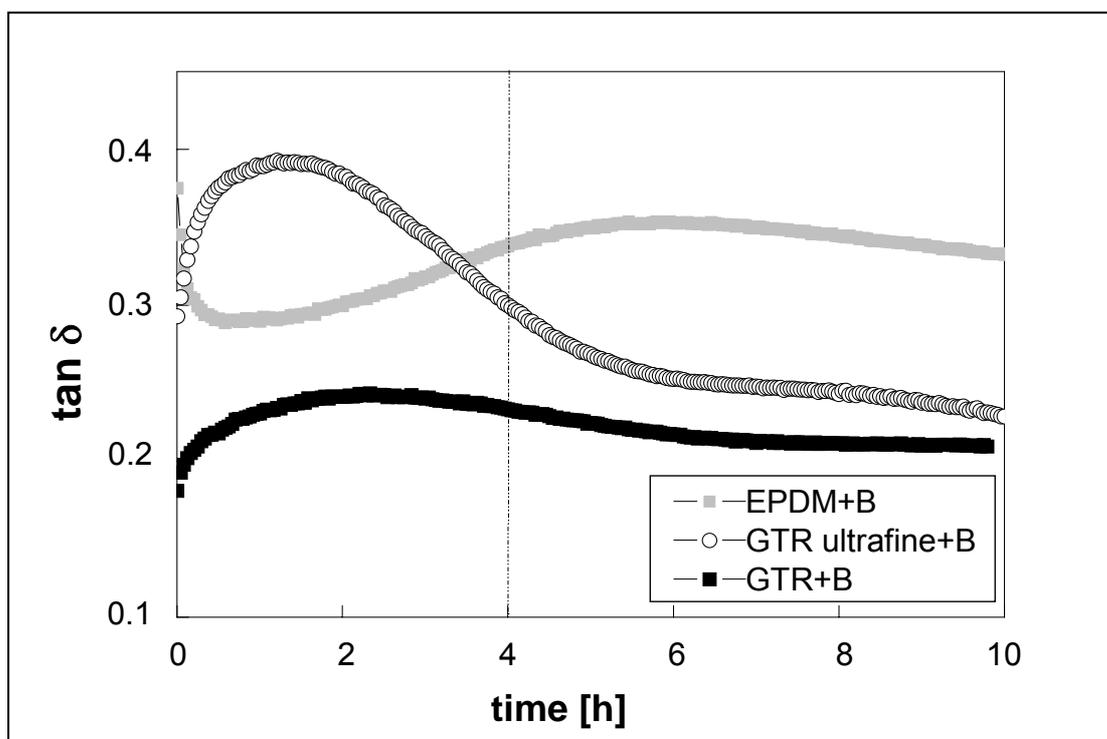


Figure 5.4. $\tan\delta$ as a function of time for the bitumen-rubber particles mixes at $T = 180\text{ }^{\circ}\text{C}$, strain 1% and frequency 10 rad/s

In the EPDM/bitumen blend, the late $\tan\delta$ increase can be linked to the low swelling ability and thermomechanical resistance of the peroxide linkages present in this EPDM waste. The smooth $\tan\delta$ decrease after 6 h of treatment is possibly related with the change of the bitumens' behaviour.

As shown in Figure 5.5, after 6 h at 180 °C the torque of plain bitumen is increasing constantly. It should be mentioned that the torque development is far below the limit of the 2 g.cm that the transducer of the ARES rheometer can measure. Irrespective to the low torque values, the relative increase is quite high. This affects, however, marginally the mixtures with GTR and GTR ultrafine, since bitumen here already developed its full action by contrast to the EPDM particles.

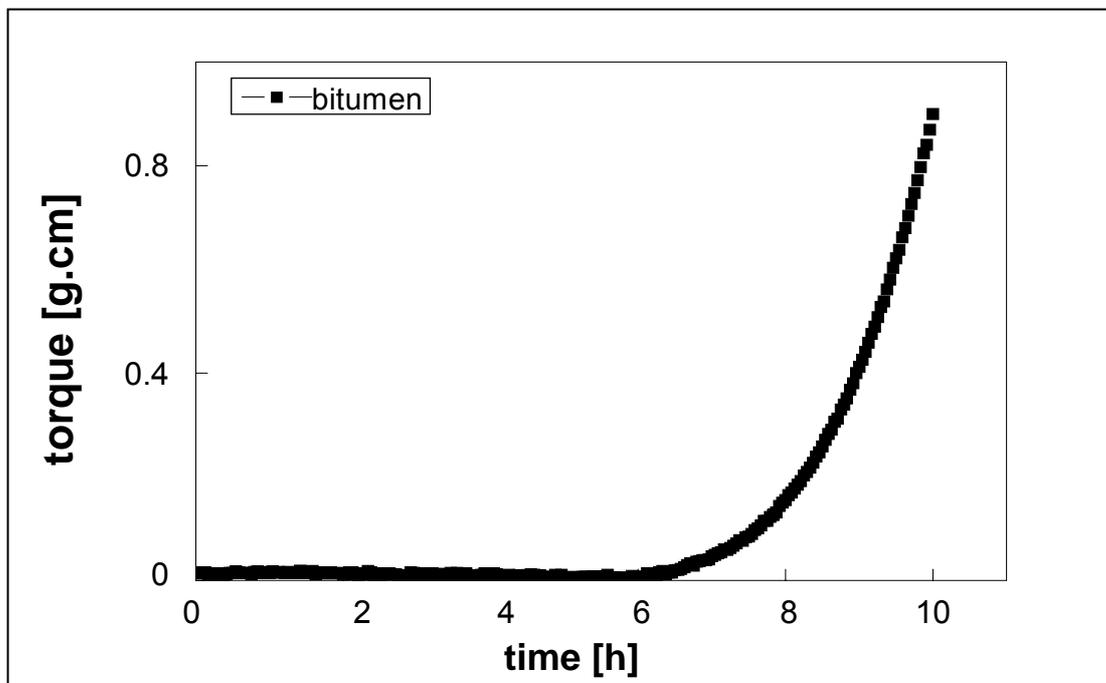


Figure 5.5. Torque development as a function of time for the bitumen used at $T = 180$ °C, strain 1% and frequency 10 rad/s

Recall that these mixtures have to be blended with selected polyolefins. For that purpose, the time of 4 h mixing of the rubber particles with the bitumen was chosen (see section 5.2.2.1). The results achieved in plate/plate rheometer justify this mixing/treating time. The “gelled” GTR particles can be easily disrupted upon high shear during extrusion compounding. In case of EPDM, the treatment is also rather optimum since at the time of four hours the mixture is at the end of its low slope for

the viscosity and G' curve (cf. Figures 5.2 and 5.3). For the GTR ultrafine particles, the situation is a bit overdue. Considering the above rheological analysis, the gelation (or reclamation representing a complex inter- and intra- particle procedure) with bitumen is well advanced at high temperatures.

5.2.2.3 Continuous

The batch tests (cf. section 5.2.2.1) already indicated a prominent effect of melt shearing. As this is even more pronounced in a extruder, attempts were made to reclaim GTR in a twin-screw extruder.

GTR was reclaimed in the co-rotating laboratory twin-screw extruder (Brabender DSE 25). The GTR/bitumen composition (1/1) was passed trough the extruder (temperature profile: 90/110/120/150, screw speed 40 rpm, residence time: 1-2 min). The registered maximum melt temperature was between 170-180 °C (recall that this temperature was set for the batchwise reclamation – cf. sections 5.2.2.1 and 5.2.2.2). The increase in sol content (compared to the initial GTR) was between 7.1 and 8.9 %. The same sol content change was also achieved when LDPE (ca. 10 wt %) was added to the mixture to avoid stickiness of the resulting material. The rather large difference in the reclamation efficiency between batch and continuous techniques based on the sol fraction is obviously an effect of the residence time. When interpreting the results one has to keep in mind that the batchwise reclamation of GTR (additional acetone extract ca. 15 %) was double that of the continuous extrusion (additional acetone extract ca. 8%). Attention should be paid to the fact, however, that the bituminuous reclamation was markedly better than the treatment with RegentTM Agent – S (cf. section 5.2.1).

The reclamation efficiency of bitumen strongly depended on the treating (mastication) temperature, residence time and additional shearing/kneading. The effect of residence time could not be compensated by more prominent shearing achieved by extrusion. One can thus speculate that the reclamation of GTR is a diffusion-controlled process during which the sulfur partitions between GTR and bitumen. This scenario is supported by results of the rheological tests (cf. section 5.2.2.2). Accordingly, the bitumen acts not only as a plasticizer (i.e. swelling the GTR particles

and thus enhancing their chain flexibility) but also as a sulfur absorbing agent. If this arguing is correct then low-sulfur content bitumens should be more beneficial for GTR reclamation than high-sulfur containing grades.

5.3 Preliminary Studies to Produce Olefinic TPEs

5.3.1 Selection of "fresh" rubber

Based on the learning from the literature it is obvious that the prerequisites of producing GTR-containing TPEs are: add fresh elastomer and/or reclaim/devulcanize the GTR at least partially. The outcoming morphology should be similar, as depicted schematically in Figure 5.6.

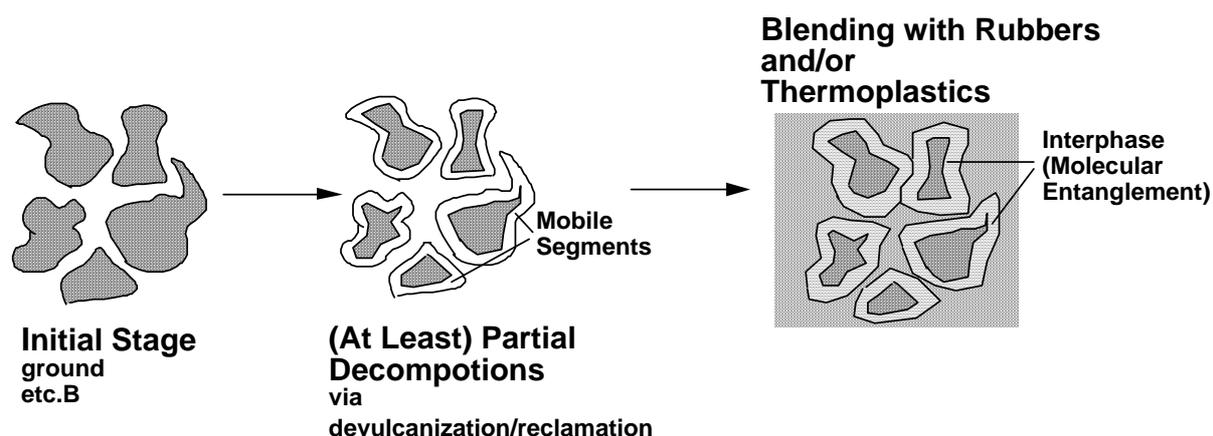


Figure 5.6. Scheme of the supposed morphology of GTR-containing TPEs

When selecting a fresh rubber to “encapsulate” the GTR particles, the rubber components of the GTR (cf. section 4.1.1.2) should be the first choice. Recall that this was already disclosed in Table 4.1. On the other hand, rubbers which are compatible with the polyolefin matrix have to be taken into account, too. From the above reasons three different rubbers were involved in the screening works, viz. NR, SBR, and EPDM.

The above fresh rubbers are added to the GTR which was thermomechanically degraded in the tight nip of the laboratory mill for 10 min at 60°C. The composition of these masterbatches, homogenized for additional 10 min rolling, was 50/50. The related GTR is denoted GTR^{TD}. For reference purpose GTR was added to the fresh rubber without previous mastication (GTR^R). TPEs were produced by melt blending of the above masterbatches with LDPE (ratio 1/1 which corresponds to LDPE: rubber: GTR = 50:25:25) in the Brabender kneader (130°C, rotor speed 60 rpm, mixing time 5-6 in).

Table 5.3 contains the ultimate tensile properties. Recall that good compatibility manifests in both improved tensile strength and elongation at break values.

Table 5.3. Effect of fresh rubber type on the ultimate tensile properties of LDPE: fresh rubber:GTR blends containing coarse GTR with and without thermomechanical degradation

Compositions	Tensile Strength [MPa]	Ultimate Elongation [%]
LDPE/SBR/GTR ^R	3.1	40
LDPE/SBR/GTR ^{TD}	3.4	20
LDPE/NR/GTR ^R	3.2	40
LDPE/NR/GTR ^{TD}	3.5	50
LDPE/EPDM/GTR ^R	3.7	150
LDPE/EPDM/GTR ^{TD}	4.1	230

Results in Table 5.3 show that EPDM is likely a better compatibilizer than SBR and NR.

5.3.2 Effect of blend composition

The initial strategy was to encapsulate the GTR particle by the fresh rubber and create a co-continuous morphology. Co-continuous means that both polyolefin and

rubber (GTR included in fresh rubber) form continuous phases. Therefore, attention was paid next on the fresh rubber/GTR ratio. Two series of TPEs were produced (see section 4.2). The selected compositions were:

LDPE: (EPDM+GTR) = 40:60 and 50:50

The EPDM/GTR ratio in those blends was varied as follows: 25/75, 35/65 and 50/50. The tensile strength and elongation at break (E_b) data of these blends are displayed in Fig. 5.7.

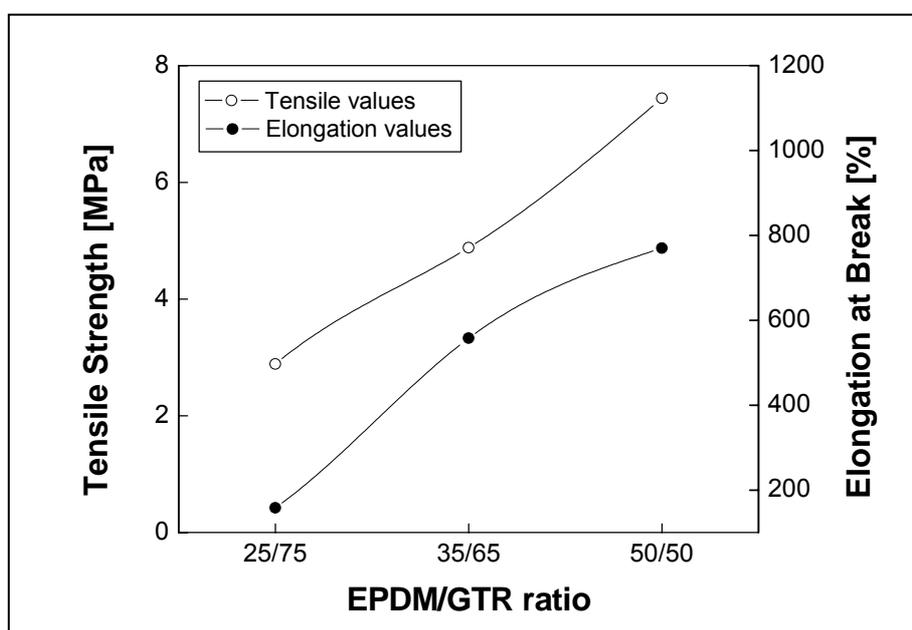


Figure 5.7. Tensile properties of TPEs produced (cf. section 4.2)

As expected, the higher the relative amount of the fresh rubber, the better the ultimate tensile properties are. Therefore, during the further work with PEs the LDPE content was fixed in a rather small range (40-50 wt %). Selective chemical etching of EPDM via n-heptane corroborated that in this composition range a co-continuous structure is present and GTR particles are preferentially encapsulated by the EPDM (cf. Figure 5.8).

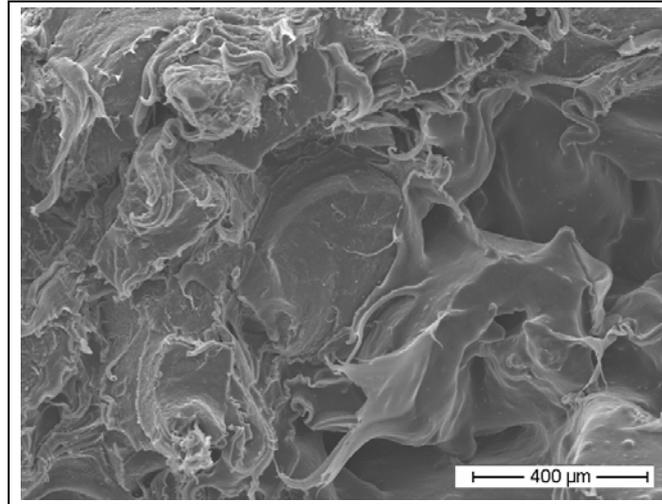


Figure 5.8. Fracture surface after chemical etching

5.3.3 Effect of dynamic curing

As show in the literature survey ([72, 74, 77] and references therein), dynamic curing is often performed when producing TPEs. This option was checked also in this work on the examples of blends containing thermochemically decomposed GTR. GTR was devulcanized by adding RegentTM Agent as described in section 4.2. The selected GTR is denoted as GTR^D. For the EPDM curing the following efficient vulcanization system were used:

Table 5.4. Curing recipes used for dynamic vulcanization

Curing System	Additives	Amount (phr)
Sulfuric (S)	ZnO	5
	Stearic Acid	1
	Sulfur	2
	MBTS	0.5
	TMTD	1
Peroxide (DCP)	DCP	1.2

Dynamic curing of the blends: LDPE:EPDM:GTR = 50:25:25 occurred in the Brabender kneader under the same conditions described in section 4.2. The mechanical test results are listed in Table 5.5.

Table 5.5. Mechanical properties of LDPE:EPDM:GTR systems with and without dynamic curing.

Compositions	Tensile Strength	Ultimate Elongation
	[MPa]	[%]
LDPE/(EPDM:GTR ^R) 50/50(50:50)	3.5 ± 0.27	150 ± 12
LDPE(EPDM:GTR ^{TD}) 50/50(50:50)	4.7 ± 0.38	320 ± 26
LDPE(EPDM:GTR ^{TD}) S 50/50(50:50)	4.5 ± 0.33	430 ± 37
LDPE(EPDM:GTR ^{TD}) DCP 50/50(50:50)	5.0 ± 0.33	600 ± 37
LDPE/EPDM/(GTR/bitumen) 50/20/(20/10)	6.5 ± 0.42	820 ± 59
LDPE/EPDM/(GTR/bitumen) 50/20/(20/10) S	5.2 ± 0.31	580 ± 23
LDPE/EPDM/(GTR/bitumen) 50/20/(20/10) DCP	5.9 ± 0.28	710 ± 39

One can see that the effect of dynamic curing is marginal on the ultimate properties at least for sulfuring curing. Table 5.5 contains also data measured in such systems which contained GTR reclaimed in bitumen (cf. section 4.2). One can recognize that in that case peroxidic curing yields some property degradation, whereas sulfuric curing has practically no effect. The latter is likely due to the initial sulfur content of the bitumen - cf. Table 4.3.

The learning from this work package can be summarized as follows:

- The strategy to encapsulate (“bind”) the partly decomposed GTR using fresh rubber that forms a continuous phase is viable. This requires, however, a considerable amount of fresh rubber.

- The most suitable fresh rubber is EPDM. This is due to its dual technological compatibility with both GTR and LDPE.

- Dynamic curing has a negligible effect on the mechanical properties. This is the reason why this method will not be applied for the compositions reported furtheron in this work furtheron.

The above findings directed the work in two directions:

a) Combination with polyethylenes

Here the major goal was to produce a TPE of co-continuous morphology by encapsulating the bitumen-reclaimed GTR in the EPDM phase which is, like the PE, also continuous. Note that the bitumen itself works as a dual phase plastizicer. By using this strategy for both LDPE- and HDPE-based TPEs information in respect with the PE crystallinity (HDPE is markedly more crystalline than LDPE) was expected.

b) Combination with polypropylene (PP)

Here the following aspects have been considered: increase the GTR content and elimination of the EPDM in the TEP compositions.

Attention should be paid, however, on the “common denominator” in the approaches a) and b) GTR reclamation by bitumen treatment.

5.4 TPE with recycled LDPE

Based in the knowledge gained in the screening phase, a TPE grade of ca. Shore A 80 hardness has been produced as described below. GTR/Bitumen (40/60 ratio) was kept at $T = 170\text{ }^{\circ}\text{C}$ for 5 h. Afterwards 10 %wt. LDPE (from the total LDPE amount) was added to this mixture prior to compounding; on the laboratory twin-screw extruder. By the addition of LDPE the sticking during pelletizing of the compound could be circumvented. The temperature profile set was $T = 125/135/145/155\text{ }^{\circ}\text{C}$, and the screw speed was 20 rpm. The net acetone solubility of the GTR in this product was $20.9 \pm 1.3\%$. The TPE itself was produced in a subsequent extrusion run ($T = 135/145/155/165\text{ }^{\circ}\text{C}$, 20 rpm). Its composition was LDPE-EPDM-(GTR-B) = 40-20-(20-20).

The properties of this LDPE-based TPE (furtheron denoted TPE (LDPE)) were compared with those of a commercial PP-based one (Santoprene 201-80 denoted as TDV) of the same hardness. The compatibility of TPE(LDPE) with Santoprene was also checked. For that purpose a compound composed of TPE (LDPE) and Santoprene in 1/1 ratio was produced during injection molding.

For the tests reported below injection molded dumbbells (Type 1A, ISO 527-2) as well as their sections were used. The molding conditions were already described in section 4.2.3.2. Note that both single and double-gated (with weld line) dumbbells specimens were injection molded. The effects of reprocessing on the properties of TPE (LDPE) were determined after 5 subsequent extrusion runs. The selected processing parameters agreed with those from the production compounding.

5.4.1 Mechanical properties

5.4.1.1 Tensile properties

The tensile properties before and after reprocessing are collated for the single gated injection molded specimens in Table 5.6.

Table 5.6. Effect of the reprocessing on the mechanical properties of TDV, TDV/TPE (1/1) ratio and TPE (LDPE). Note: N= virgin material, Y = material 5 times reprocessed

Material	Modulus at Elongations		Tensile Strength [MPa]	Ultimate Elongation [%]
	100% [MPa]	300%		
TDV _N	6.0	7.4	8.2	464
TDV _Y	5.7	7.4	8.0	399
TDV/TPE (LDPE)(1/1) _N	5.3	6.7	6.8	348
TDV/TPE (LDPE)(1/1) _Y	6.1	-	6.9	186
TPE (LDPE) _N	4.8	-	5.4	198
TPE (LDPE) _Y	5.4	-	6.0	176

Based on data in Table 5.6 one can recognize that the mechanical properties did not change practically with reprocessing. This note does not hold for TDV/TPE (LDPE) combination where a considerable reduction in the ductility occurred.

Table 5.7 shows the mechanical properties as a function of reprocessing and aging. Aging occurred in air at 70 °C for 22 h.

Table 5.7. Effect of aging and reprocessing on the mechanical properties. Note: N/N= no aging, no reprocessing; Y/N=aging, no reprocessing; Y/Y=aging and reprocessing

Material	Modulus at Elongations		Tensile Strength [MPa]	Ultimate Elongation [%]
	100% [MPa]	300%		
TDV _{N/N}	6.0	7.4	8.2	464
TDV _{Y/N}	5.9	7.6	7.8	407
TDV _{Y/Y}	5.8	7.6	7.9	350
TDV/TPE (LDPE)(1/1) _{N/N}	5.3	6.7	6.8	348
TDV/TPE (LDPE)(1/1) _{Y/N}	5.4	-	6.7	307
TDV/TPE (LDPE)(1/1) _{Y/Y}	6.4	-	7.1	191
TPE _{N/N}	4.8	-	5.4	198
TPE _{Y/N}	4.4	-	5.4	236
TPE _{Y/Y}	5.9	-	6.6	162

The combined effects of aging and reprocessing result in a slight decrease in the ultimate properties for TDV. On the contrary, this treatment has some beneficial effect on the properties of TPE(LDPE). The ductility of the TDV/TPE(LDPE) blend has been reduced by aging and reprocessing.

As emphasized before, good weld line strength is of great importance for injection molding thermoplastics. This note is especially relevant for polyolefin/elastomer blends [117,118].

Accordingly, the weld line behaviour of the compounds was assessed using double-gated injection molded specimens. The tensile response of them as a function of reprocessing and aging are summarized in Table 5.8, respectively.

Table 5.8. Effect of weld line on the mechanical properties of the thermoplastic rubbers before and after reprocessing. Note: N/N= no weld line, no reprocessing; Y/N=weld line, no reprocessing; Y/Y=weld line and reprocessing. TPE (LDPE)* - contained "ultrafine" GTR fraction

Material	Modulus at Elongations		Tensile Strength [MPa]	Ultimate Elongation [%]
	100% [MPa]	300% [MPa]		
TDV _{N/N}	6.0	7.4	8.2	464
TDV _{Y/N}	4.7	-	5.4	192
TDV _{Y/Y}	3.8	-	4.8	178
TDV/TPE (LDPE)(1/1)	5.3	6.7	6.8	348
TDV/TPE (1/1) _{Y/N}	2.4	-	2.6	129
TDV/TPE (1/1) _{Y/Y}	-	-	4.0	46
TPE _{N/N}	4.8	-	5.4	198
TPE _{Y/N}	-	-	3.1	36
TPE _{Y/Y}	-	-	4.2	58
TPE* _{N/N}	5.0	6.7	7.2	370
TPE* _{Y/N}	4.1	-	5.8	210
TPE* _{Y/Y}	4.2	-	5.6	190

Tables 5.8 and 5.9 demonstrate that all compounds possess poor weld line strength. Fortunately, this is not further reduced by aging. Nevertheless, this aspect has to be considered during design and mold construction of injection molded parts. It will be shown later that the poor weld line strength is caused by GTR particles enriched in the central region of the dumbbells. This phenomenon, often observed for filled and reinforced injection molded parts, is explained by the migration in the direction of the higher melt velocities (e.g. [119] and references therein).

To overcome this problem by using GTR of finer particle dispersion (“ultrafine”) was successful – cf. Table 5.8.

Table 5.9. Combined effect of welding line, aging and reprocessing on the mechanical properties of thermoplastic rubbers. Note: N/N= no weld line, no aging, no reprocessing; Y/Y/N= aging, weld line, no reprocessing; Y/Y/Y=weld line, aging, reprocessing

Material	Modulus at Elongations		Tensile Strength	Ultimate Elongation
	100% [MPa]	300% [MPa]	[MPa]	[%]
TDV _{N/N/N}	6.0	7.4	8.2	464
TDV _{Y/Y/N}	4.9	-	5.5	173
TDV _{Y/Y/Y}	5.0	-	5.0	166
TDV/TPE (LDPE)(1/1) _{N/N/N}	5.3	6.7	6.8	348
TDV/TPE (LDPE)(1/1) _{Y/Y/N}	-	-	3.9	83
TDV/TPE (LDPE)(1/1) _{Y/Y/Y}	-	-	3.9	44
TPE (LDPE) _{N/N/N}	4.8	-	5.4	198
TPE (LDPE) _{Y/Y/N}	-	-	3.7	83
TPE (LDPE) _{Y/Y/Y}	-	-	4.7	53

5.4.1.2 Set properties

Figure 5.9 displays the change in the compression set with aging and reprocessing

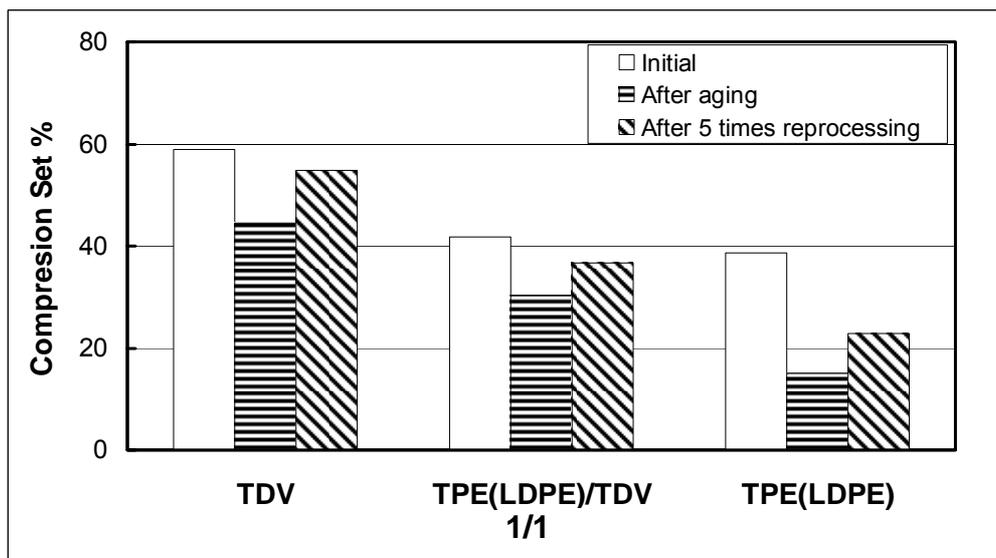


Figure 5.9. Variation of the compression set with aging and reprocessing

One can see that aging reduced the compression set whereas reprocessing increased its value. The very good compression set (low value) of the TPE(LDPE) is obviously due to its co-continuous morphology. The further improvement in compression set after reprocessing is likely an indirect hint for the GTR reclamation strategy followed. Note that during reprocessing the bitumen furtheron acts as reclaiming agent. Accordingly, some broken sulfuric linkages of the GTR are recrosslinking with the EPDM. The sulfur present and absorbed by the bitumen may crosslink the EPDM selectively etc. This scenario, i.e. crosslink partitioning mostly between the rubber components, results in some homogenization of the crosslink density, the macroscopic outcome of which is a reduced compression set.

5.4.2 Thermal behaviour

5.4.2.1 DSC

The difference in the polyolefin component of the thermoplastic rubbers becomes obvious based on the DSC traces presented in Figure 5.10.

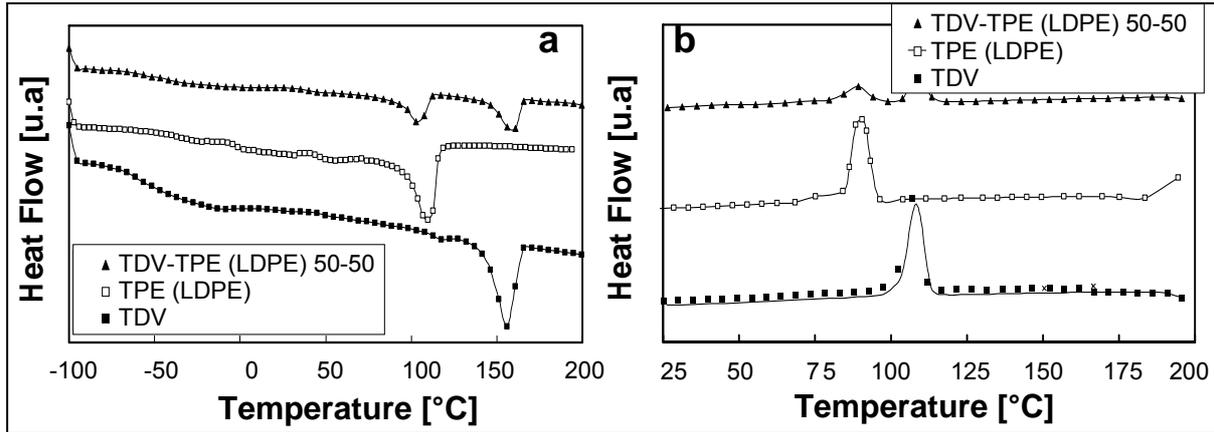


Figure 5.10. DSC traces of TDV, TDV/TPE(LDPE) 1/1 and TPE(LDPE) registered during heating (a) and cooling (b), respectively

In the DSC heating traces the T_g of the EPDM (ca. $-50\text{ }^{\circ}\text{C}$), the melting of the LDPE (ca. $115\text{ }^{\circ}\text{C}$) and PP (ca. $165\text{ }^{\circ}\text{C}$) are well resolved.

One can also assume that the rubber component of TDV is an EPDM-like rubber. Irrespective to this common component, the TPE (LDPE) + TDV blend may possess some compatibility (if any) only in the amorphous phase. The melting and crystallization peaks of the LDPE and PP are not affected by the blending. The crystallinity of the LDPE in the blend (scatters between 38 and 41% based on its net amount) agreed with that of the initial plain LDPE (43 %). This value calculated by assessing 283 J/g to the 100% crystalline LDPE.

5.4.2.2 DMTA response

To the complex phase morphology some further information can be deduced from the DMTA spectra. Figure 5.11 a and b. show the stiffness (complex E- modulus, E^*) and mechanical loss factor ($\tan \delta$) vs temperature curves for TPE (LDPE), TDV and their combination, respectively.

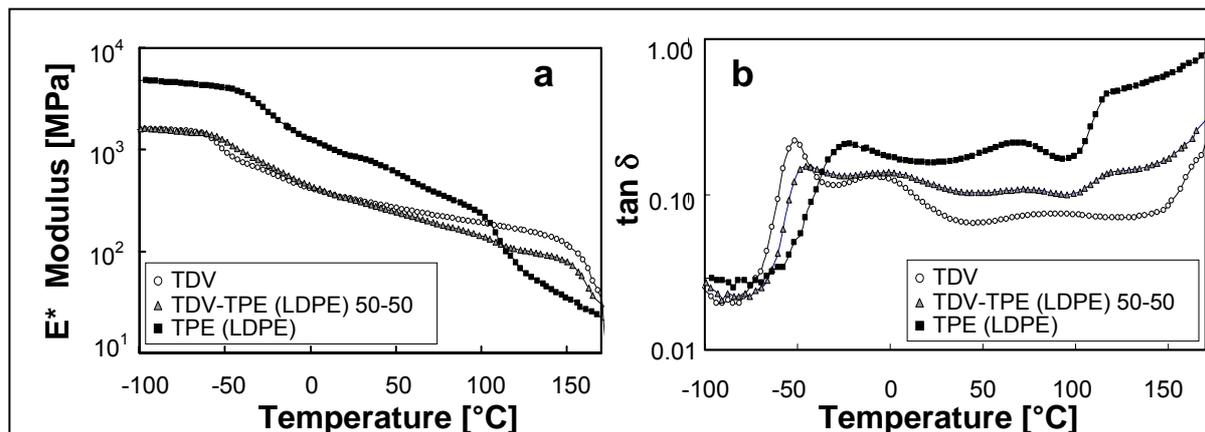


Figure 5.11. E^* vs. T (a) and $\tan \delta$ vs. T (b) curves for TPE (LDPE), TDV and TPE (LDPE)/TDV = 1/1. Measuring conditions: tension, 10 Hz, heating rate $1^\circ/\text{min}$, Temp. range -100 to 170°C , static and dynamic force 4 and ± 2 N, respectively

The E^* vs T curves show the basic difference between TPE (LDPE) and TDV. The latter has a lower T_g and substantially higher temperature resistance than TPE (LDPE). The lower T_g is due to an EPDM-like additive, whereas the thermal resistance is given by the PP matrix. The T_g of our compound appears at higher temperature (at about -30°C) and the related peak is less pronounced. This can be attributed to the fact that this peak reflects the segment movement in a complex amorphous phase composed of EPDM, GTR and LDPE. The most important aspect is that the EPDM and GTR peaks are not separated. This hints for a good compatibility between them. This manifests at the same time the efficient reclamation of GTR. Otherwise no molecular entanglement between GTR and EPDM might occur and thus the related T_g peaks would appear separately. The relaxation transition at ca. 70°C in TPE(LDPE) – see Figure 5.11b is likely linked to the bitumen constituent.

One other feature of the DMTA traces is merit of further discussion. Note that the stiffness of TDV steeply drops after reaching the melting temperature of PP. However, this is not the case with TPE(LDPE). This is a clear hint for the presence of a co-continuous structure. The sudden sagging is hampered by the EPDM+GTR phase which is likely continuous and even partly co-crosslinked. Co-crosslinking means that the reclaimed GTR is either co-crosslinked to the fresh EPDM or the EPDM, is partly crosslinked or, both.

Considering the TDV/TPE (LDPE) compound one can see that the DMTA response abbeys to the rule of mixture (additivity). This is in harmony with the tensile mechanical results reported in section 5.4.1.1.

5.4.3 Rheology

5.4.3.1 Low shear rate

The shear viscosity vs. frequency curves for the TPEs studied are depicted in Figure 5.12.

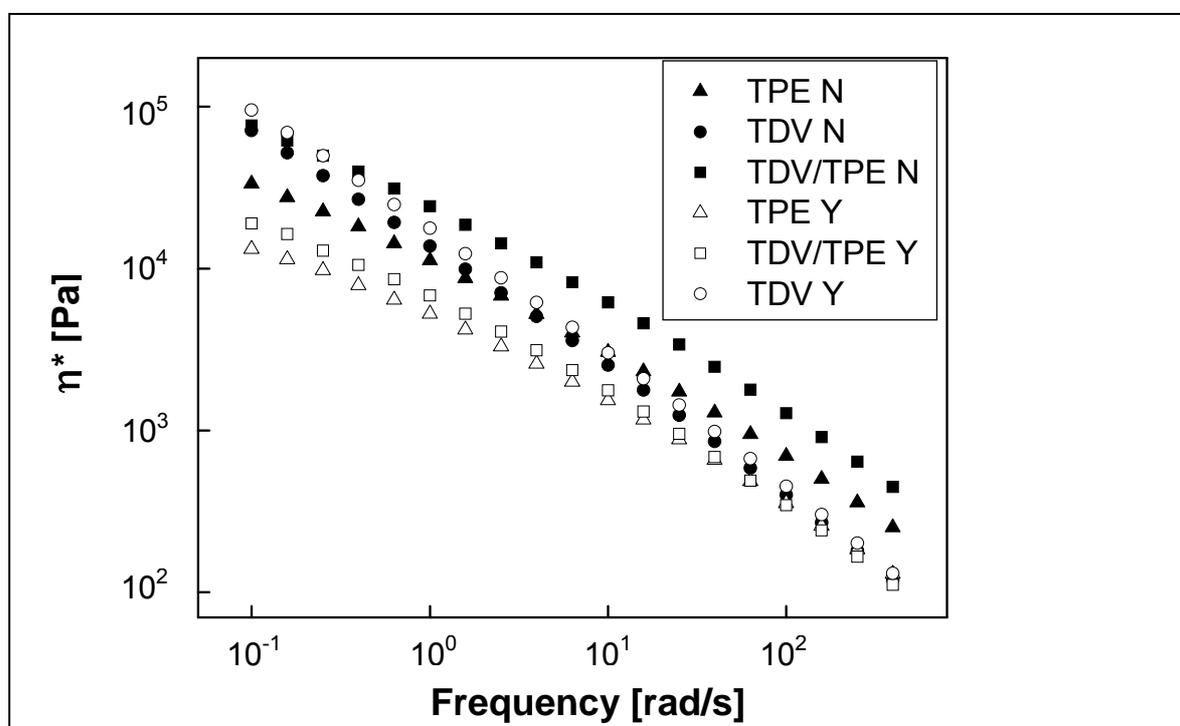


Figure 5.12. Complex shear viscosity (η^*) vs. angular frequency (ω) for the TPEs before and after reprocessing at $T = 180\text{ }^\circ\text{C}$. Designations agree with those in Table 5.6

Note that the zero shear viscosity, if any, should lie at even lower frequency range than the studied one for all TPEs. This is likely an effect of the processing oil in TDV and reclamation agent (bitumen) in TPE (LDPE). The effect of reprocessing is negligible for TDV, by contrast to the TPE(LDPE) and TDV/TPE(LDPE) blend. For the latter systems a prominent change can be revealed at low frequencies. This effect is owing to the ongoing reclamation of GTR in bitumen that happens during reprocess-

ing. This process influences the compatibility between TPE(LDPE) and TDV as well, which manifests in a similar decrease in the viscosity at low frequencies (cf. Figure 5.12).

5.4.3.2 High shear rate

Figure 5.13 shows the apparent viscosity (η_{app}) as a function of shear rate ($\dot{\gamma}$) for the compounds as assessed by capillary rheometry at $T = 180\text{ }^{\circ}\text{C}$.

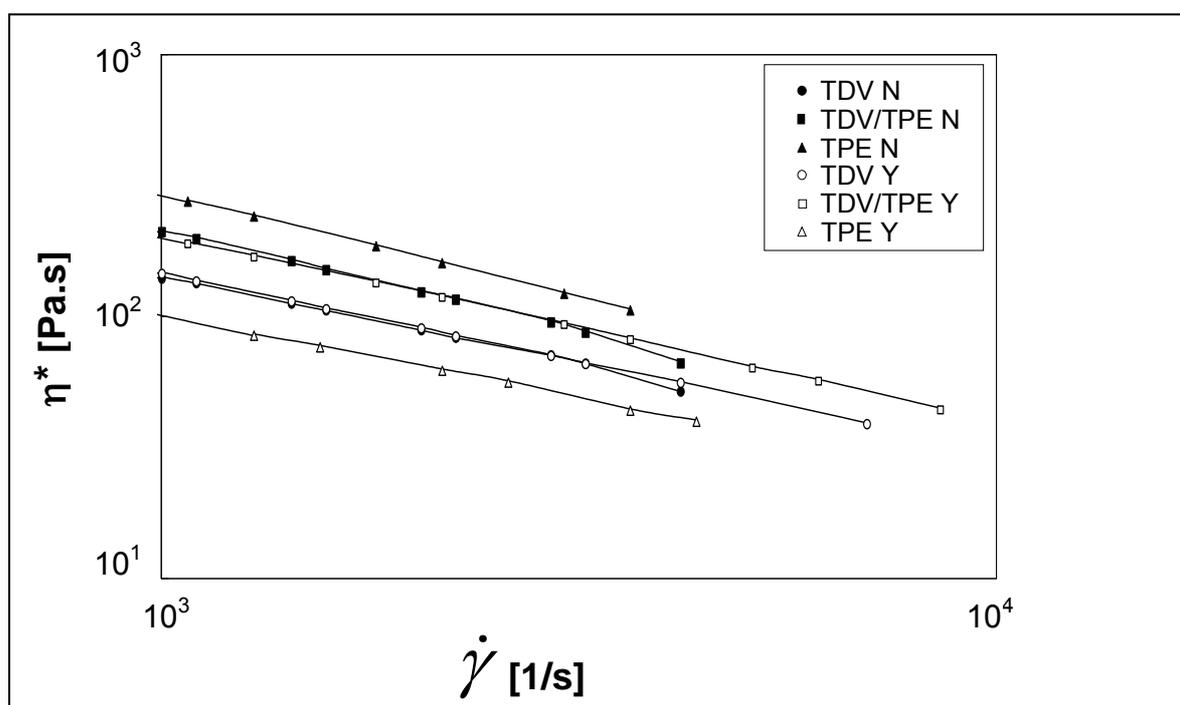


Figure 5.13. η_{app} vs $\dot{\gamma}$ for the thermoplastic elastomers studied at $T = 180\text{ }^{\circ}\text{C}$. Designations agree with those in Table 5.6

Albeit the viscosity range of the compounds is quite similar, some characteristics features can be deduced. First, the effect of reprocessing on the viscosity of TDV is negligible. This is, however, well discernible for both TPE(LDPE) and TDV/TPE(LDPE) blend. In their case the viscosity is further reduced owing to reprocessing. This suggests that a portion of the bitumen acts as external lubricant in the corresponding compounds. This is very beneficial from the viewpoint of melt processing provided that this is not accompanied later with some migration phenomenon. If this happens

the amount of bitumen should be reduced. Anyhow, the reprocessing-caused change in the melt viscosity of TPE (LDPE) is tolerable. This means in other words that no special thermostabilizers should be incorporated in the TPE(LDPE).

5.4.4 Morphology

The tensile fracture surfaces of the thermoplastic rubbers at low magnification are composed in Figure 5.14.

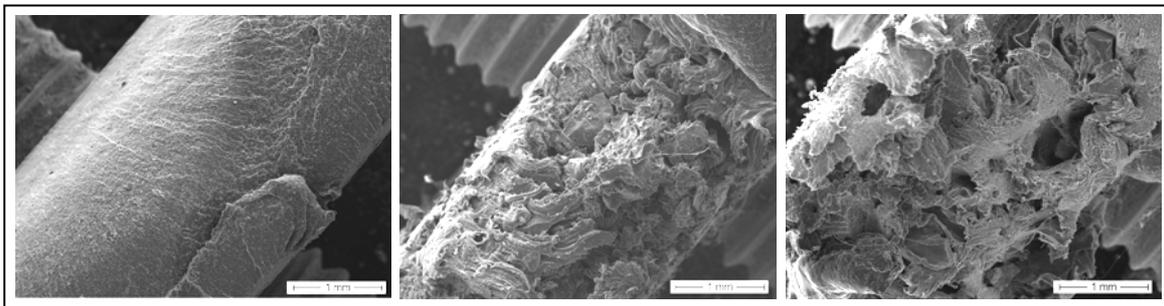


Figure 5.14. Tensile fracture surfaces of TDV (a), TPE (LDPE) (b) and TDV/TPE (LDPE) blend (c), respectively

The fracture surface of TPE(LDPE) is strongly rugged. The matrix failed very ductile owing to the good compatibility between LDPE and EPDM – see torn bands in Figure 5.14b picture. This picture also suggests that the earlier discussed co-continuous structure is present. SEM pictures taken at high magnifications evidence the formation of the interphase bonding as targeted (cf. arrow in Figure 5.15).

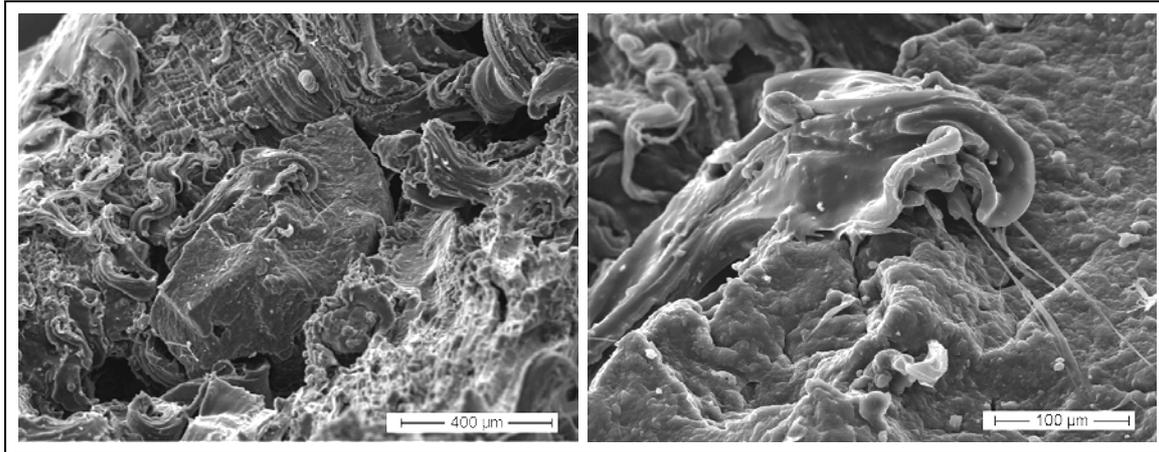


Figure 5.15. Fracture surface of a single-gated injection molded TPE(LDPE) specimen at various magnifications. Note: arrow indicates for interphase bonding via entangled chains

On the fracture surface of TDV at high magnification the finely dispersed rubber particles are well resolved. They cause cavitation and fibrillation of the matrix – cf. Figure 5.16.

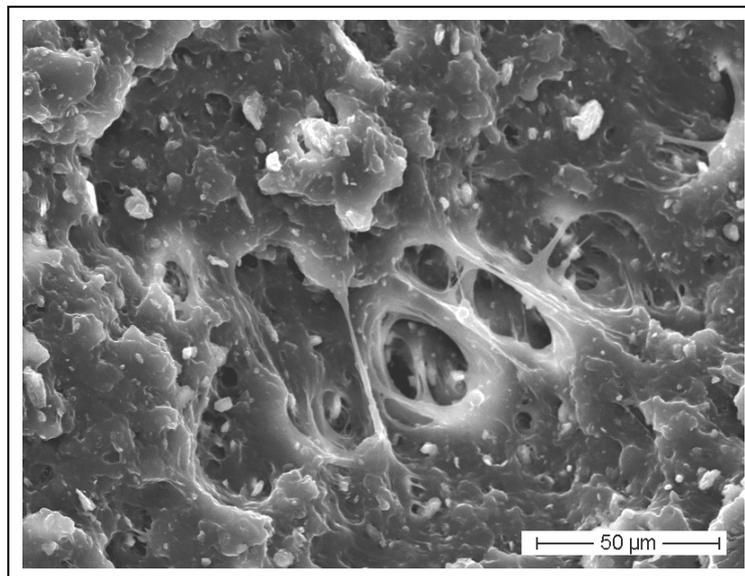


Figure 5.16. Fracture surface of a single-gated injection molded specimen of TDV

The compatibility between TPE(LDPE) and TDV is poor based on the fracture surfaces. The fresh EPDM is likely migrated in the PP-phase of TDV not fulfilling its role as interphase compatibilizer (cf. Figure 5.17).

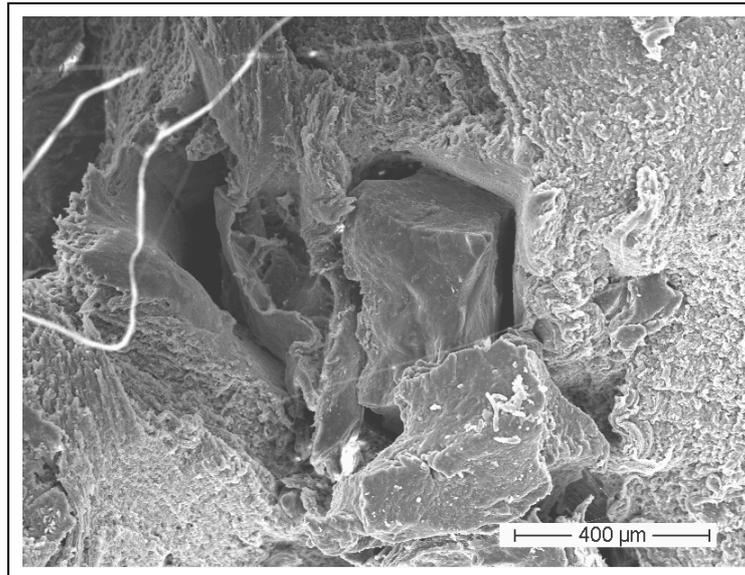


Figure 5.17. Fracture surface of a single gated injection molded specimen of the TPE (LDPE)/TDV (1/1) mix

One can see that the GTR particle easily debonds from the matrix and this extensive debonding is not associated with ductile tearing of the material. The fracture surface of the specimens with weld line is less rugged for both TPE (LDPE) and TPE (LDPE)/TDV than for the single gated versions – cf. Figures 5.18 and 5.14.

On the other hand, the failure mode of TDV is the same for specimen with and without weld line.

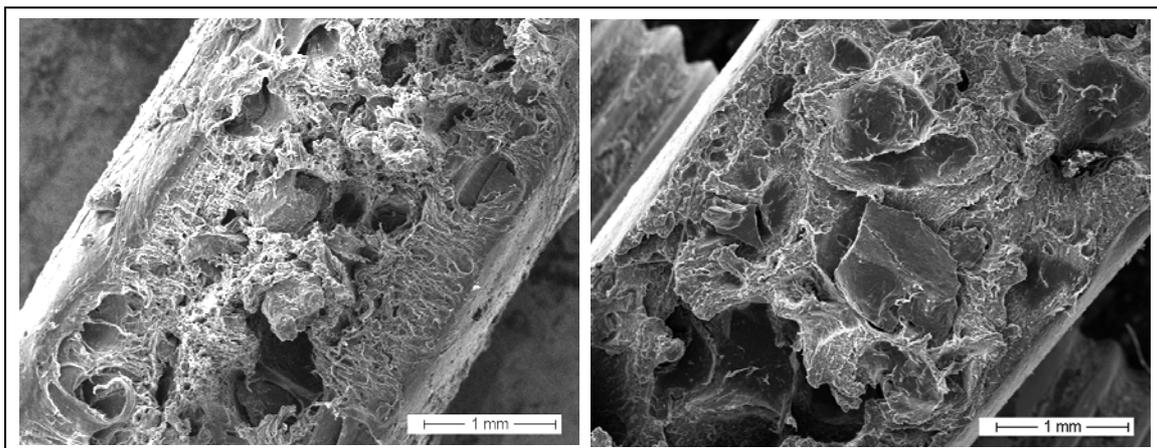


Figure 5.18. Fracture surface of double gated injection molded specimens of TPE(LDPE)-left and TPE(LDPE)/TDV 1/1-right

In Figure 5.18 one can also see that the GTR particles are likely enriched in the mid part of the cross section. Less rugged fracture surface means that the ultimate strain is markedly lower for specimen with than without weld line. This is in agreement with the tensile mechanical results listed in section 5.4.1 (cf. Table 5.6)

5.5 TPE with recycled HDPE

A TPE grade of ca. Shore A 90 hardness has been produced as described for TPE(LDPE) in section 5.4. The composition and processing conditions were also identical except that instead of LDPE, HDPE was used. The higher hardness of this TPE(HDPE) can be ascribed to the HDPE being more crystalline than the LDPE. This TPE(HDPE) was not combined with TDV as it is even less compatible with TDV than TPE(LDPE). Aging and reprocessing of TPE(HDPE) were done similar to TPE(LDPE), too. Unlike to TPE(LDPE) the mechanical properties of TPE(HDPE) were determined on specimens cut of compression molded sheets of ca. 1 mm thickness.

5.5.1 Mechanical properties

5.5.1.1 Tensile properties

The tensile properties of TPE(HDPE) before and after reprocessing and aging are summarized in Table 5.10.

Table 5.10. Effects of aging and reprocessing on the tensile mechanical response of TPE (HDPE)

Material	Modulus at Elongations		Tensile Strength	Ultimate Elongation	Hardness	Compression Set
	100% [MPa]	300% [MPa]	[MPa]	[%]		[%]
TPE(HDPE)						
-virgin	4.6	-	5.0	107	83	58
-aged	4.6	-	5.3	120	86	56
-reprocessed	5.1	-	6.2	138	87	47

Comparing the data in Table 5.10 and those in Table 5.7 one can see that the mechanical response of TPE(LDPE) and TPE(HDPE) are very similar except the ultimate elongation. The latter is markedly lower for TPE(HDPE) compared to TPE(LDPE) which is a direct manifestation of reduced compatibility.

5.5.1.2 Set properties

The compression set of TPE(HDPE) was 58%. Its value changed slightly due to aging (56%) and more prominently after reprocessing (47%) – cf. Table 5.10. Note that these values are higher than the related one measured on TPE(LDPE) – cf. Figure 5.9. This suggests that the high crystallinity of HDPE (accompanied with low compatibility towards GTR) prevents the formation of a co-continuous morphology. So in the TPE(HDPE) likely HDPE is the matrix in which both EPDM and GTR are dispersed and bitumen acts as selective plasticizer for GTR and EPDM.

5.5.2 Thermal behaviour

5.5.2.1 DSC

The DSC traces registered during heating and subsequent cooling for TPE(HDPE) along with its ingredients are depicted in Figure 5.19.

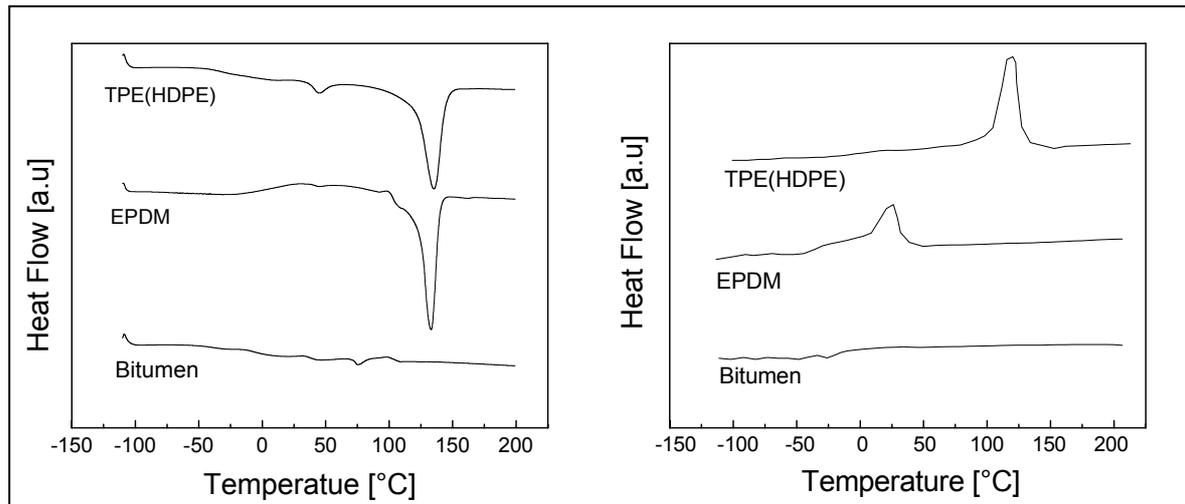


Figure 5.19. DSC traces of TPE(HDPE), EPDM, GTR and bitumen monitored during heating (a) and cooling (b) respectively. Note that heating and cooling rates were 10 °C/min

In the melting traces the T_g of GTR and EPDM are not well resolved. Their common peak appears at ca. -40 °C high magnifications. The melting peak of EPDM and HDPE appears at ca. 50 °C and 135 °C, respectively. The melting peak of EPDM is in line with the high ethylene content of this grade. The PE segments in this EPDM can crystallize, however the actual crystallinity depends on the cooling, storing (physical aging) conditions. The bitumen shows numerous endothermic peaks (also at high magnifications) due to its various ingredients. Comparing the melting and cooling traces of the HDPE and TPE(HDPE) no difference in the HDPE-related peaks can be observed.

5.5.2.2 DMTA response

The E^* vs. T and $\tan\delta$ vs. T curves for TPE(HDPE), EPDM, GTR and HDPE are displayed in Figure 5.20 a. and b., respectively.

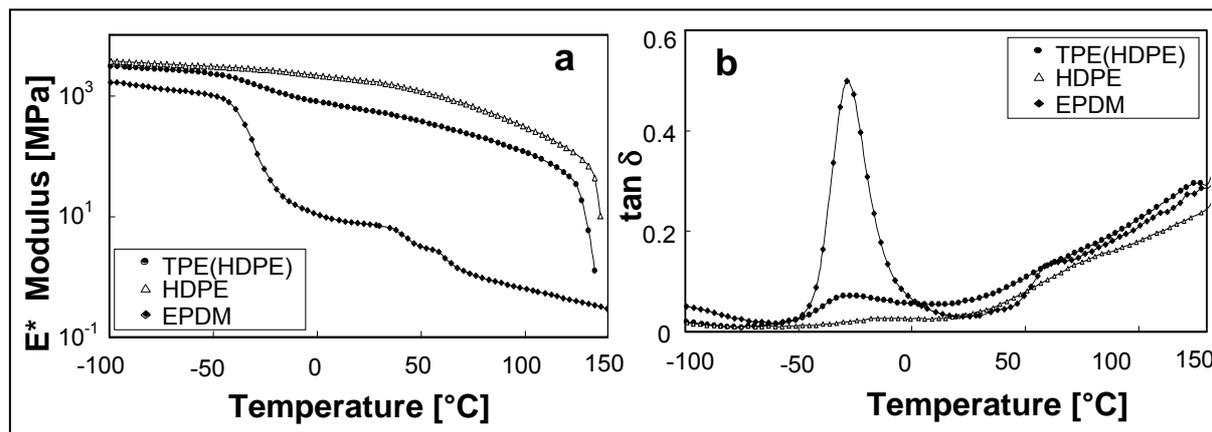


Figure 5.20. E^* vs T (a) and $\tan \delta$ vs T (b) curves for TPE(HDPE), EPDM and HDPE. Notes: DMTA tests performed in tension at 10 hz

The T_g values defined by the temperature of the E'' peaks in Figure 5.20 b are listed in Table 5.11.

Table 5.11. DMA data for the individual components and blends produced. T_3 is overlapped with T_2

Composition	T (°C / E'' (MPa) for phases rich in:			
	GTR	EPDM (amorphous)	HDPE (amorphous)	HDPE (crystalline)
	T_1 / E''	T_2 / E''	T_3 / E''	T_4 / E''
HDPE	-	-	-15 / 65	60 / 100
EPDM	-	-36 / 102	*	-
HDPE/EPDM/ GTR+bitumen	-49 / 121	-35 / 158	*	42 / 35

EPDM has one sharp relaxation peak at -36 °C (α -transition), corresponding to the T_g of its amorphous phase (cf. Figure 5.20). Some rise in E' and $\tan \delta$ values around ~ 50 °C (cf. Figures 5.20 a and c) can be attributed to the melting of residual PE crystallites that is confirmed by the DSC data (cf. Figure 5.19). HDPE has two broad relaxation peaks (cf. Figure 5.20 c) at -15 °C (β -transition) assigned to the T_g of its

amorphous phase, and the peak around ~ 60 °C (α_c -transition) relating to the vibration and rotational motion of $-\text{CH}_2-$ groups in crystalline phase due to recrystallization of smaller and less perfect crystallites [120]. For both EPDM and HDPE the low temperature transition below -100 °C is due to the crankshaft mechanism of $-\text{CH}_2-\text{CH}_2-$ polyethylene chain segments [121].

The character of E' (T) plots (cf. Figure 5.20 a) of TPE(HDPE) is quite similar to the HDPE that means that HDPE forms a continuous thermoplastic phase (matrix), while the dispersed phase is formed by the EPDM/GTR mixture. Note that this morphology differs from that of TPE(LDPE).

5.5.3 Rheology

Like TPE(LDPE), zero shear viscosity is not apparent for TPE(HDPE) even at low frequencies. (Figure 5.21). A further similarity between TPE(LDPE) and TPE(HDPE) is the prominent shear thinning behaviour. Unlike TPE(LDPE) the effect of reprocessing on the rheological behaviour of TPE(HDPE) is marginal (cf. Figure 5.12).

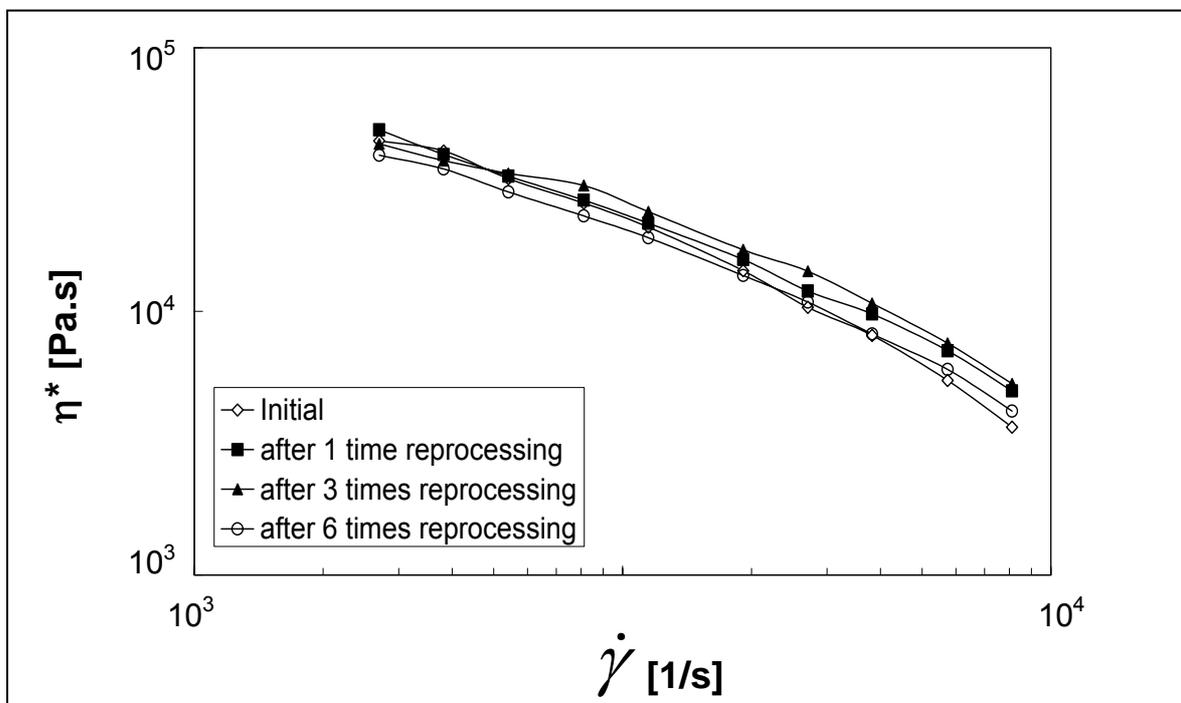


Figure 5.21. Complex shear viscosity (η^*) vs. angular frequency (ω) for TPE(HDPE) before and after reprocessing at $T = 180$ °C

One can see that owing to reprocessing the viscosity of TPE(HDPE) slightly decreases. This should be assigned to the external lubrication effect of the reclaiming bitumen. Comparing the η_{app}^* vs. $\dot{\gamma}$ traces for TPE(HDPE) (cf. Figure 5.21) and TPE(LDPE) (cf. Figure 5.13) one can recognize that the η_{app}^* values are quite similar, albeit the viscosity values for TPE(HDPE) are somewhat higher. This is due to the HDPE in the corresponding blend. Note that HDPE-based systems are usually processed at somewhat higher temperatures than $T = 180\text{ }^\circ\text{C}$.

5.5.4 Morphology

Double-side grooved specimens broken at liquid nitrogen temperature already show effects of the bitumen reclamation.

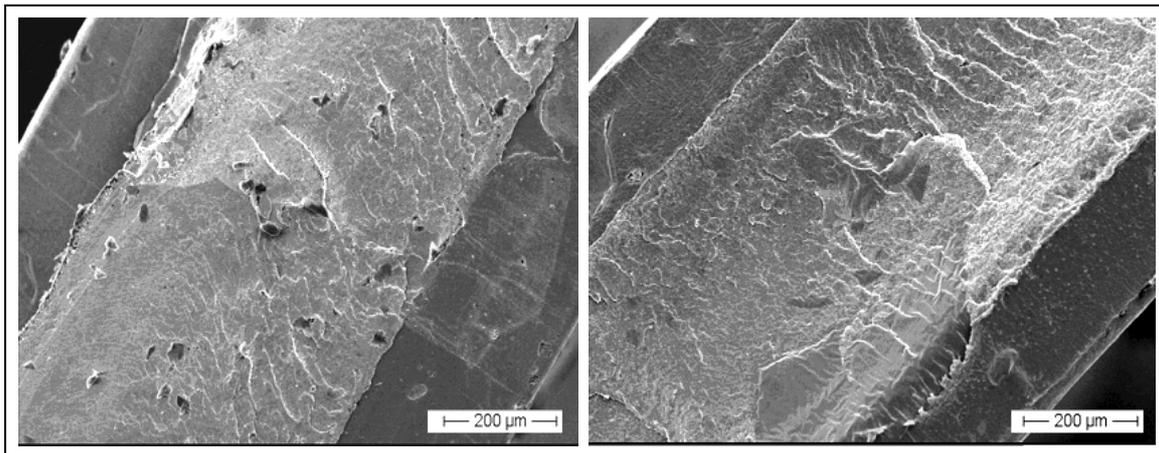


Figure 5.22. Cryogenic fracture surface of blends composed of HDPE/EPDM/GTR (40/20/40) -left and HDPE/EPDM/(GTR/bitumen) (40/20/(20-20)) -right. Note that the latter is denoted as TPE(HDPE)

One can well observe that the “homogeneity” of the blend was improved by reclamation in bitumen. The GTR particles in TPE(HDPE) are much better embedded in the matrix after bituminous treatment. So, again for the improved bonding between GTR and matrix molecular entanglement processes should be responsible.

5.6 TPE with PP

Major goals with the development of TPEs containing PP were as follows:

- Demonstrate the efficiency of GTR reclamation in bitumen
- Avoid the use of fresh rubber
- Check the effect of the GTR particle size
- Increase the amount of the GTR reclaimed in bitumen in the TPE

The related recipes contained GTR and GTR ultrafine (with and without bitumen) in 75 and 50 wt%, respectively. The GTR was reclaimed in bitumen as described in section 4.1.42. The GTR/bitumen ratio was set for 60/40. As reference TPEs those containing EPDM instead of GTR (again with and without bitumen) served. These TPEs have been produced similar as described in section 4.1.5. However, the temperature setting during extrusion was in the range from T= 180°C to 220 °C.

The recipes of the TPE(PP) grades are listed in Table 5.12. Specimens were injection molded as described in section 4.1.6.2 for TPE(LDPE). TPE(PP) + TDV 1/1 ratio blends were injection molded, too. In addition dumbbells with and without weld line were injection molded (cf. Table 5-12).

Table 5.12 Code and composition of the TPE(PP) grades produced

	TPE (PP)	Composition (parts)
TPE(PP) 50/50	PP-EPDM	50-50
	PP-GTR	50-50
	PP-GTR ultrafine	50-50
	PP-EPDM-B	50-50-30
	PP-GTR-B	50-50-30
	PP-GTR ultrafine-B	50-50-30
	TDV-B	(50)
	[PP-EPDM]:TDV	[50-50]:50
	[PP-GTR]:TDV	[50-50]:50
	[PP-GTR ultrafine]:TDV	[50-50]:50
	[PP-(EPDM-B)]:TDV	[50-(50-30)]:50
	PP-(GTR-B):TDV	[50-(50-30)]:50
	[PP-(GTR ultrafine-B)]:TDV	[50-(50-30)]:50

TPE(PP) 25/75	PP-EPDM	25-75
	PP-GTR	25-75
	PP-GTR ultrafine	25-75
	PP-EPDM-B	25-75-50
	PP-GTR-B	25-75-50
	PP-GTR ultrafine-B	25-75-50
	TDV-B	(75)
	[PP-EPDM]:TDV	[25-75]:50
	[PP-GTR]:TDV	[25-75]:50
	[PP-GTR ultrafine]:TDV	[25-75]:50
	[PP-(EPDM-B)]:TDV	[25-(75-50)]:50
	PP-(GTR ultrafine-B):TDV	[25-(75-50)]:50
	[PP-(GTR-B)]:TDV	[25-(75-50)]:50

5.6.1 Mechanical properties

5.6.1.1 Tensile mechanical properties

Figure 5.23 shows characteristic tensile stress-strain diagrams for the TPE(PP) 50/50 and 25/75 grades, respectively.

Comparing pictures a), b) and c) in Figure 5.23 the following conclusion can be drawn:

- The higher the PP amount is, the better the stress-strain properties are.
- The effect of GTR particle size is most obvious in the ductility (strain values)
- Bitumen works as an apparent plasticizer, viz. reduced the stress and increases the ductility.

The tensile mechanical data measured on single- and double-gated specimens before and after reprocessing (5 consecutive extrusion steps) are summarized in Table 5.13.

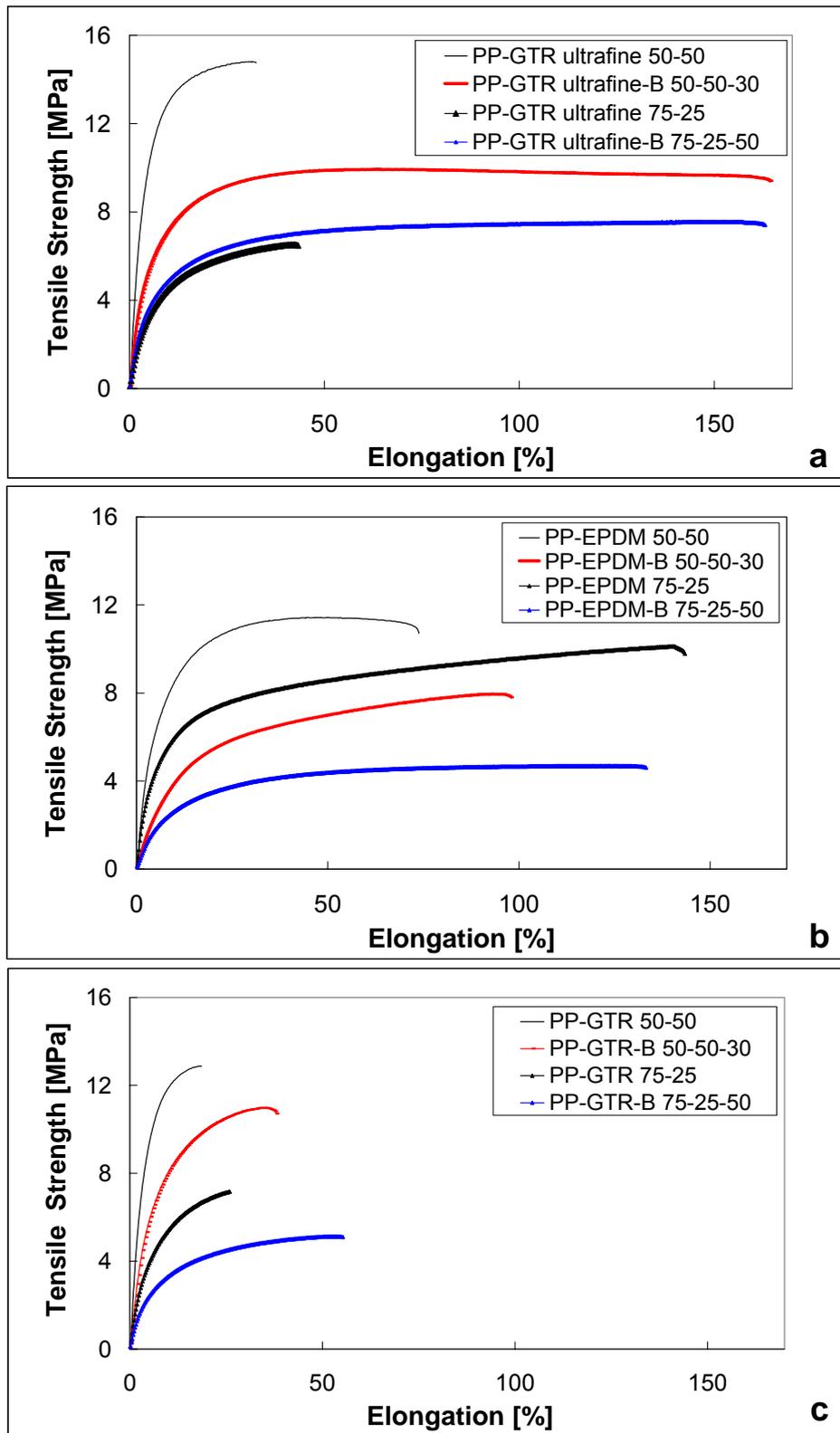


Figure 5.23. Characteristic stress-strain diagrams for the TPE(PP) compounds (cf. Table 5.12) measured on single-gated injection molded specimens

Table 5.13. Tensile mechanical properties of TPE (PP) grades with (in brackets) and without weld line. Note: reprocessing had a little effect on the measured properties. Therefore, the related data are not inserted

Material	Modulus at Elongations		Tensile Strength	Ultimate Elongation
	100% [MPa]	300%	[MPa]	[%]
PP-GTR ultrafine-B 25-75-50	6.8	-	7.0 (2.9)	196 (30)
PP-GTR ultrafine-B 50-50-30	9.6	-	9.6 (3.5)	168 (18)
PP-GTR ultrafine 25-75	-	-	6.4 (3.8)	45 (16)
PP-GTR ultrafine 50-50	-	-	14.6 (4.5)	40 (15)
PP-EPDM-B 25-75-50	4.6	-	4.7 (2.7)	165 (34)
PP-EPDM-B 50-50-30	-	-	11.5 (3.9)	72 (21)
PP-EPDM 25-75	9.5	-	10.6 (3.1)	186 (32)
PP-EPDM 50-50	16.7	-	16.7 (4.7)	144 (24)
PP-GTR-B 25-75-50	-	-	5.3 (2.4)	63 (14)
PP-GTR-B 50-50-30	-	-	11.6 (3.7)	34 (12)
PP-GTR 25-75	-	-	7.6 (2.4)	29 (13)
PP-GTR 50-50	-	-	14.0 (4.0)	21 (11)

The combination of TPE(PP) with TDV resulted in a prominent improvement of the ductility, however, at a cost of the strength behaviour (cf. Table 5.14). This is due to the fact that the Santoprene 201-80 is a soft, oil-extended TDV version. The improvement was the larger the smaller the GTR particle size was. The best performance was achieved with the EPDM/PP blends, as expected. The above results seem to be in harmony with the claim of Coran [116], viz. the incorporation of GTR into TDV yields compositions of useful properties. Table 5.14 contains also the results measured on double-gated dumbbells.

Table 5.14. Tensile mechanical properties of TPE (PP)/TDV (50/50) combinations with (in brackets) and without weld line. Note: reprocessing had little effect in the measured properties. Therefore, the related data are not inserted

Material	Modulus at Elongations [MPa]		Tensile Strength [MPa]	Ultimate Elongation [%]
	100%	300%		
[PP-(GTRultrafine-B)]:TDV [25-(75-50)]:50	4.9	6.0	6.4 (3.4)	438 (31)
[PP-(GTRultrafine-B)]:TDV [50-(50-30)]:50	6.4	7.3	8.5 (4.6)	538 (12)
[PP-GTR ultrafine]:TDV [25-75] :50	6.7	-	6.9 (4.8)	138 (57)
[PP-GTR ultrafine]:TDV [50-50]:50	8.6	-	8.9 (7.7)	209 (62)
[PP-(EPDM-B)]:TDV [25-(75-50)]:50	4.4	5.2	5.4 (3.6)	346 (61)
[PP-(EPDM-B)]:TDV [50-(50-30)]:50	6.8	7.6	8.7 (7.1)	502 (22)
[PP-EPDM]:TDV [25-75]:50	6.9	8.8	10.4 (8.7)	526 (55)
[PP-EPDM]:TDV [50-50]:50	9.5	10.7	13.2 (9.3)	629 (45)
[PP-(GTR-B)]:TDV [25-(75-50)]:50	5.5	-	5.7 (6.3)	165 (35)
[PP-(GTR-B)]:TDV [50-(50-30)] : 50	7.3	-	7.6 (6.1)	202 (24)
[PP-GTR]:TDV [25-75]:50	-	-	6.5 (3.7)	74 (29)
[PP-GTR]:TDV [50-50]:50	9.6	-	9.4 (3.1)	96 (25)

Unexpectedly, there is a steep drop in both strength and (especially) strain values in presence of weld line. It is interesting to note that the coarser the GTR fraction is, the larger the effect of the bituminous reclamation is.

The excellent stress-strain behaviour of specimens with weld line molded from PP/EPDM blends combined with TDV is likely due to a co-continuous phase structure formed.

5.6.1.2 Set properties

Table 5.15 depict the set properties of the TPE(PP) blends.

Table 5.15. Set properties of the TPE(PP) blends

	Compression Set	
	25-75-(50)	50-50-(30)
PP-GTRultrafine-(B)	62	48
PP-GTR ultrafine	55	44
PP-EPDM-(B)	60	47
PP-EPDM	57	46
PP-GTR-(B)	58	49
PP-GTR	55	46

Like in case of TPE(HDPE) the higher crystallinity of the PP compared to LDPE lead to an increase in the set properties. Reclamation of the GTR in bitumen also slightly increased the compression set.

5.6.2 Thermal response

5.6.2.1 DSC

The DSC crystallinity of the neat PP was 47,1%. This value calculated by assessing 209 J/g to the 100% crystalline PP [122]. Practically the same value was received for PP in the blends PP/GTR and PP/GTR ultrafine (scatter between 45.1 and 46.9%). However, some reduction was observed for the blends containing GTR fractions reclaimed in bitumen (scatter between 35.5 and 43.9%). Note that the large scatter for the blends PP/(GTR+ bitumen) 50/50 and 25/75 are related with material inhomogeneities. One has to consider that the material mass during DSC measurements was in the range of 10 mg.

5.6.2.2 DMTA Response

Figure 5.24 and 5.25 compare the DMTA traces of TPE (PP) 50/50 and 25/75, with various GTR fractions with and without bituminous reclamation.

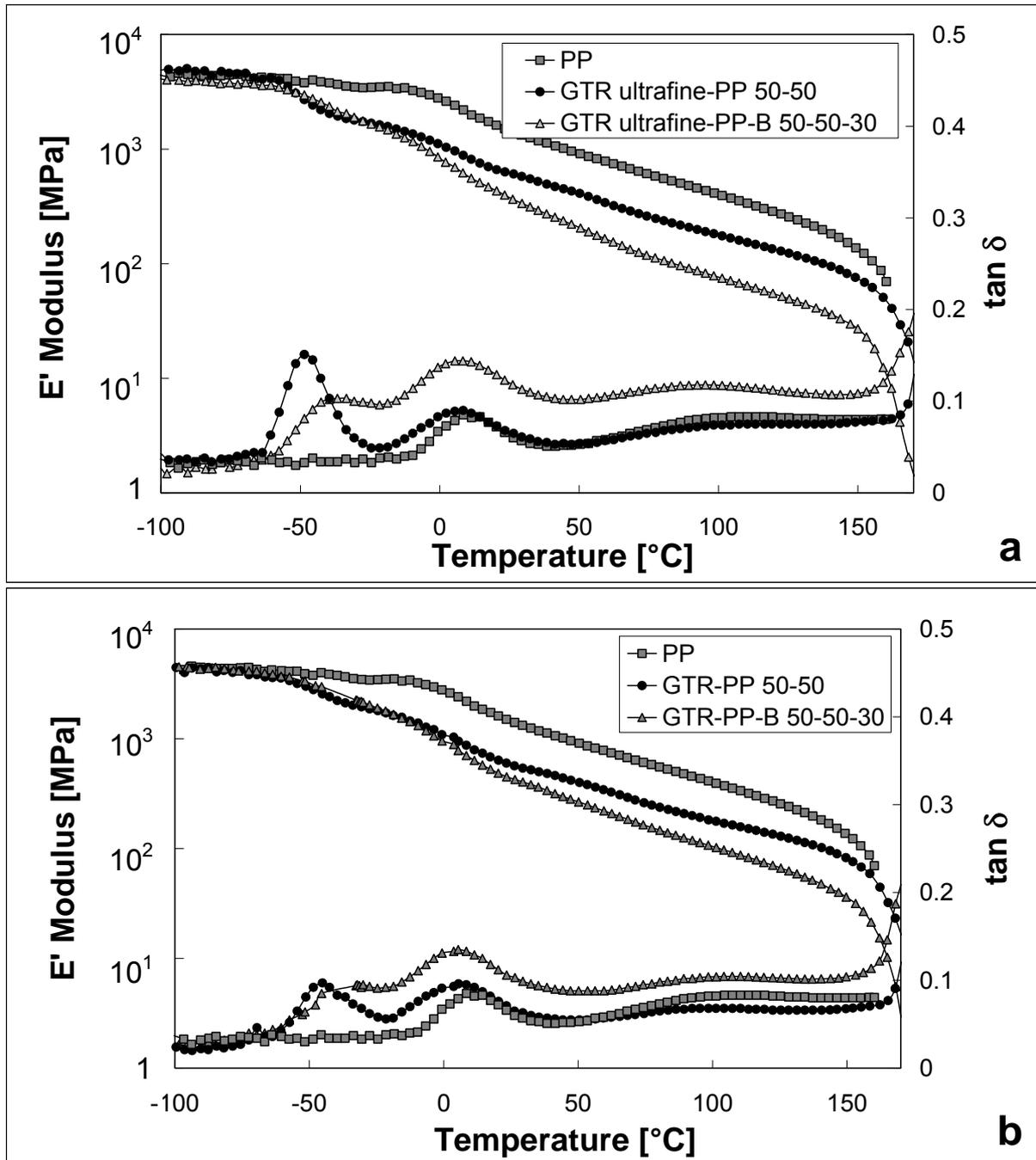


Figure 5.24. E' vs T and tan δ vs T traces for TPE(PP) 50/50 containing GTR ultrafine (a) and GTR (b) with (B) and without bituminous reclamation. Note: for sake of comparison the related traces of the neat PP are also displayed

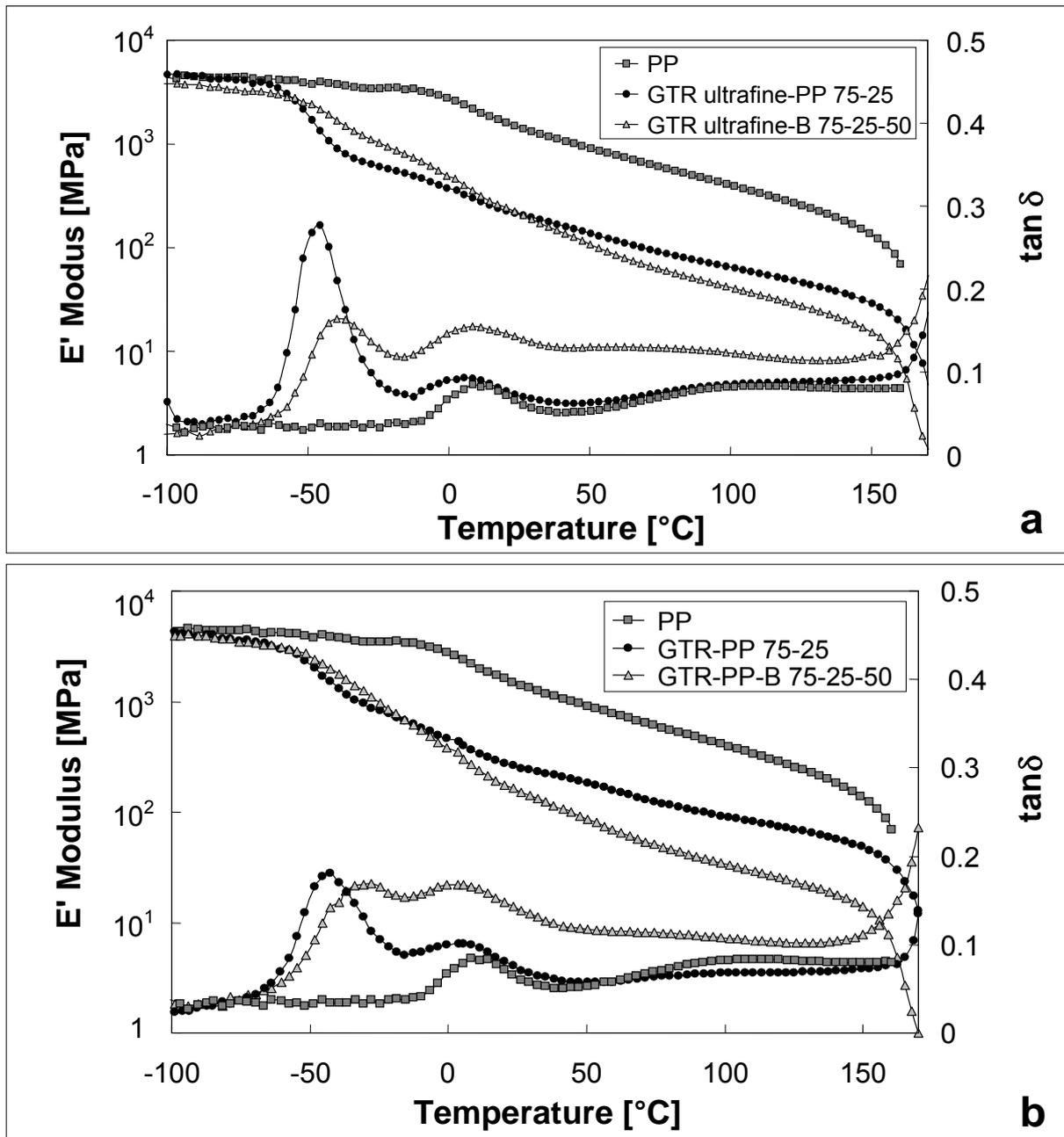


Figure 5.25. E' vs T and $\tan\delta$ vs T traces for TPE (PP) 25/75 containing GTR ultrafine (a) and GTR (b) with (B) and without bituminous reclamation. Note: for sake of comparison the related traces of the neat PP are also displayed

Albeit the bituminous treatment has a similar effect on TPE (PP) 50/50 containing GTR and GTR ultrafine (cf. Figure 5.24), there is some difference. The intensity of the β -relaxation transition (T_g) of PP at $T \cong 10^\circ\text{C}$ is increasing owing to the presence

of bitumen. This hints for lower crystallinity of the PP phase. Note that this has been found in DSC measurements. The T_g peak of the GTR is shifted towards the T_g of PP (i.e. to higher temperatures). This suggests a prominent improvement in the compatibility. So, the bitumen acts as compatibilizer for GTR and PP. The difference in the intensity of the T_g peaks of GTR and GTR ultrafine is of great relevance. The larger is the decrease in the related peak, the stronger the interphase between the particles and matrix is. So, the reclaiming of GTR ultrafine and its embedding in the PP matrix is far better than GTR (cf. the related relative changes in the T_g peak of GTR in Figure 5.24)

The same scenario holds for TPE(PP) 25/75 based in Figure 5.25. The only difference is that the inward shift in the corresponding T_g values is well resolved for the compound containing reclaimed GTR –cf. Figure 5.25.

Considering the DMTA traces of the reference compositions composed of PP and EPDM (cf. Figure 5.26), one can see the good compatibility between EPDM and PP (inward shift in the corresponding T_g peaks). It is also noteworthy that the DMTA response of TDV is very closely matched with that of the system EPDM/PP = 75/25. Accordingly, this TDV (Santoprene 201-80) should have a similar composition to EPDM/PP 75/25.

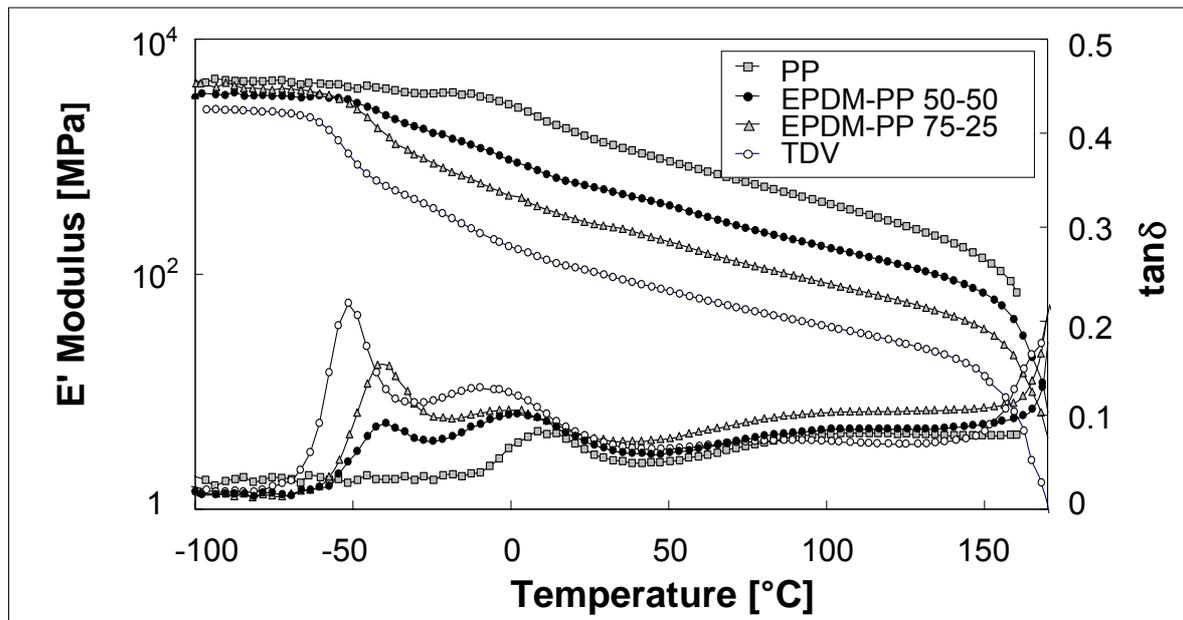


Figure 5.26. E' vs. T and $\tan\delta$ vs. T traces for PP, TDV and PP/EPDM blends (PP/EPDM ratios: 50/50 and 25/75, respectively)

There is a similar effect of bitumen in the PP/EPDM blends –cf. Figure 5.27.

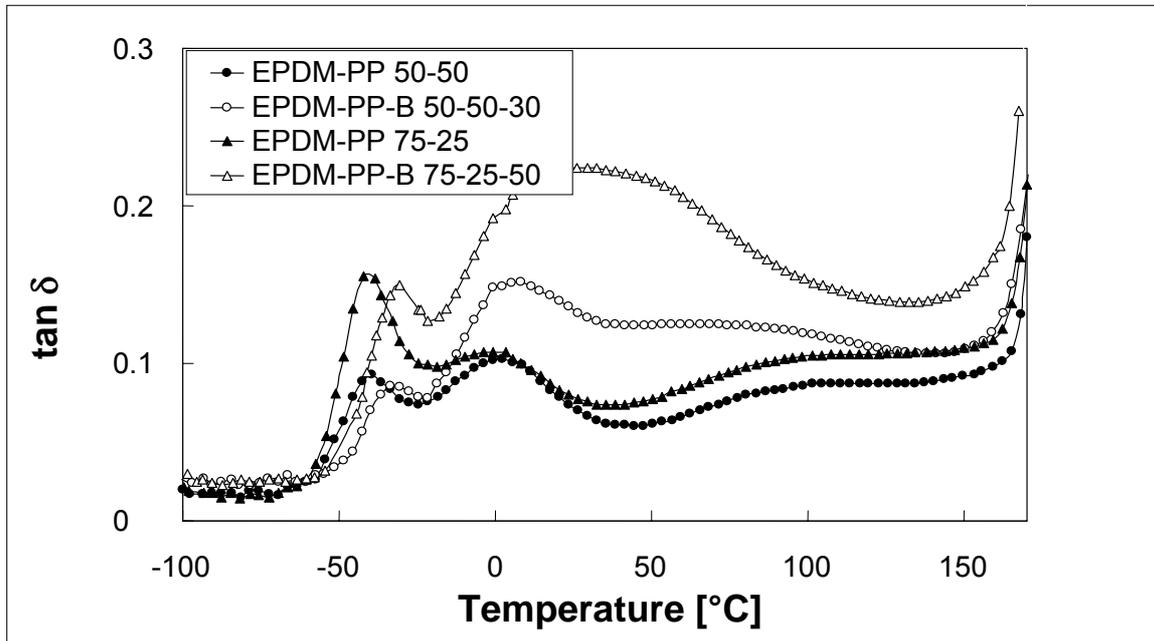
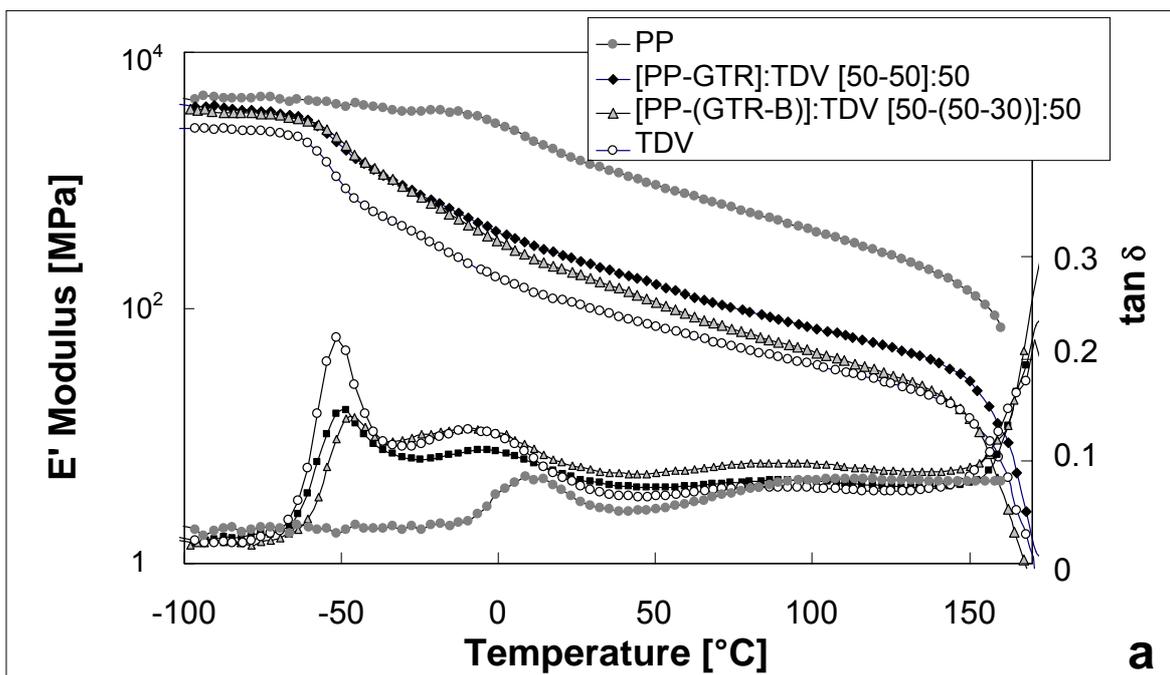


Figure 5.27. $\tan \delta$ vs. T curves for PP/EPDM 50/50 and 25/75 blends with (B) and without bitumen

Note that apart of the intensity increase of the T_g relaxation of PP, a shift toward higher temperatures occurs. The author is not aware of the reason behind this finding. The effect of compounding with TDV is shown only on the example of TPE (PP) with GTR (cf. Figure 5.28).



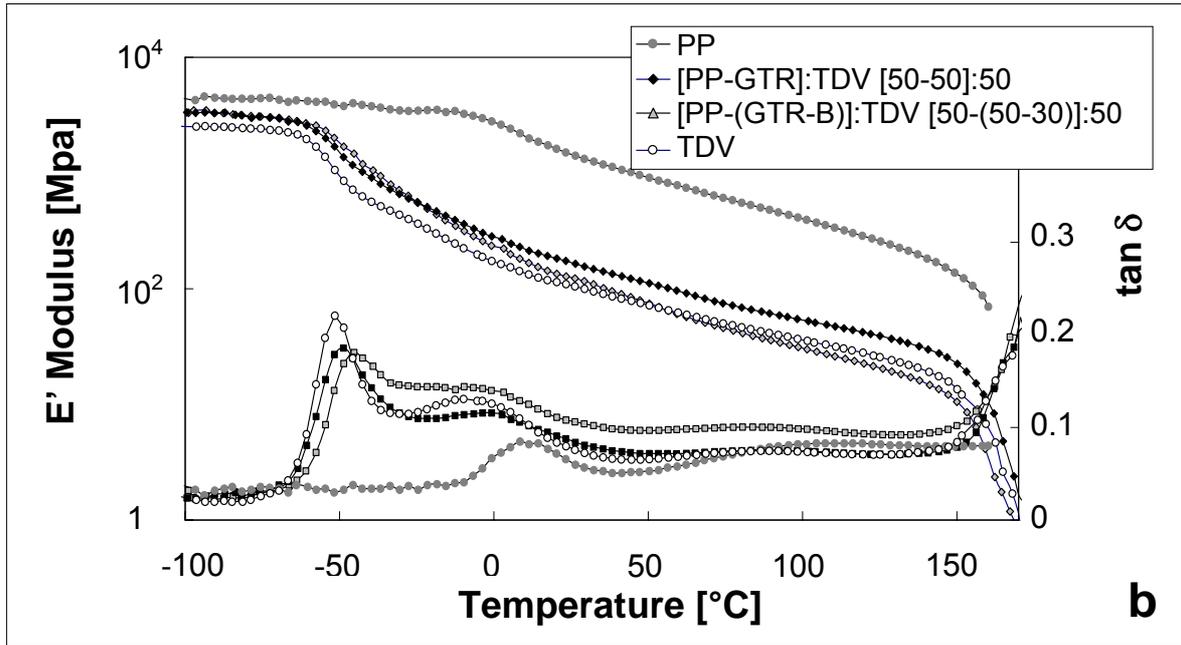
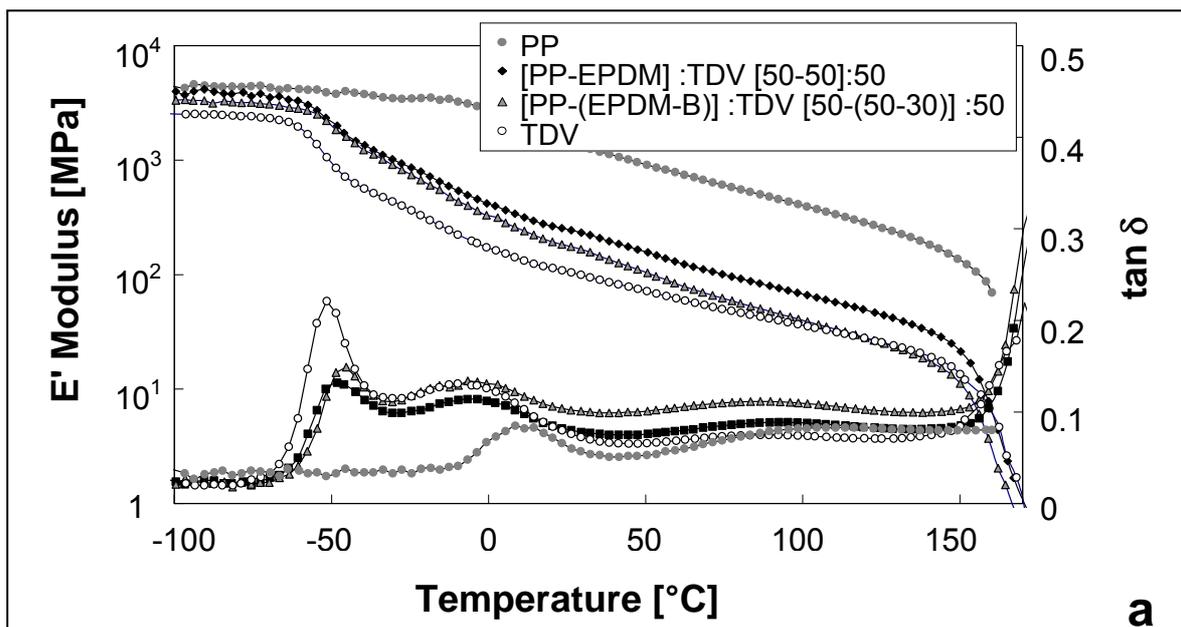


Figure 5.28. E' vs. T and $\tan\delta$ vs. T traces for PP, TDV and TPE (PP) combination with TDV. a) TPE (PP) 50/50 containing GTR with (B) and without bituminous treatment and b) TPE (PP) 25/75 containing GTR with (B) and without bituminous treatment

One can see that the stiffness response of the TPE(PP) 25/75 is very close to that of the TDV. A similar course in the DMTA traces found for the systems containing GTR ultrafine.



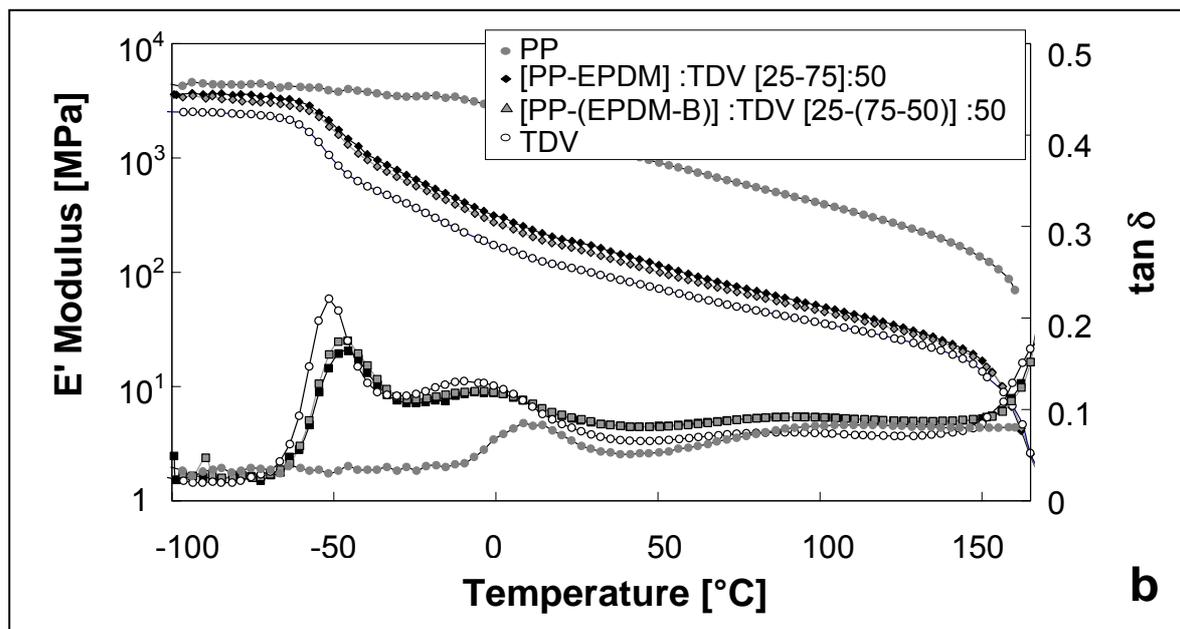


Figure 5.29. E' vs. T and $\tan \delta$ vs. T traces for PP, TDV and TPE (PP) combination with TDV. a) TPE (PP) 50/50 containing EPDM with (B) and without bituminous treatment and b) TPE (PP) 25/75 containing EPDM with (B) and without bituminous treatment

The DMTA response of the PP/EPDM blends diluted with TDV is very similar (cf. Figure 5.29) to that of the GTR containing ones shown in Figure 5.24 and 5.25.

5.6.3 Rheology

5.6.3.1 Low shear rate

Strain and frequency sweep rheological tests were performed at 200 °C. First, the mixtures at a 50/50 ratio by weight (rubber to PP) were examined in strain sweep experiment (Fig. 5.30). In all cases addition of the rubber and rubber particles, irrespective their type, resulted in an increase of the storage shear modulus (G') compared to the neat PP. At the same time the storage modulus departs earlier from linearity than in case of neat PP. The addition of bitumen acts like a plasticizer of the mixtures as their storage modulus decreases. It is interesting to observe that parallel

to the modulus decrease some extension of the linear region of G' appears for the rubber mixes containing bitumen.

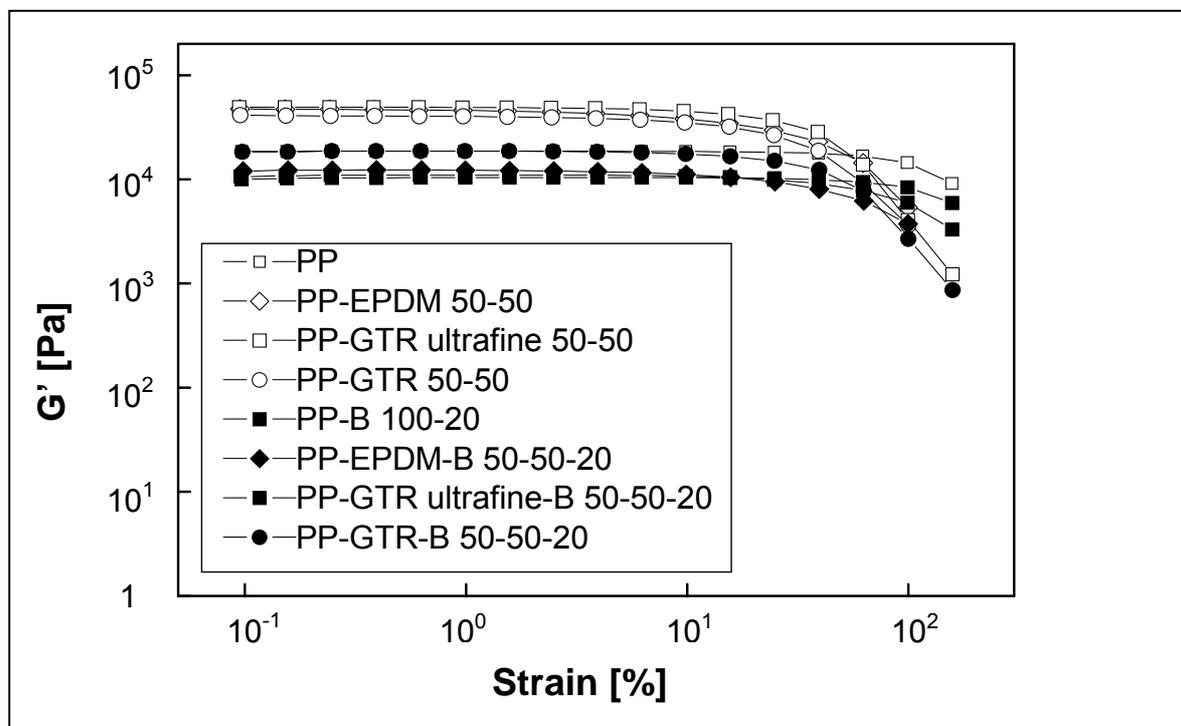


Figure 5.30. Storage modulus vs. strain for the mixtures at a 50/50 ratio by weight (rubber to PP). Note: measurement was performed at $T = 200$ °C, frequency 10 rad/s

Increasing the amount of rubber and rubber particles in the mixtures, the phenomena related to different types of the particles should be more pronounced. Curves in Figure 5.31 show that the major findings discussed in respect to Figure 5.30, are similar. Moreover, due to the higher particle amount, G' starts to decline at lower strain values. This suggests that the structure created can less withstand to high shear forces. This behaviour is obvious for the EPDM/PP blend. The particle network must be disrupted under the large oscillatory strain in order to show this non-linear behaviour. Addition of bitumen acts not only as plasticizer but also as compatibilizer as the mixes now can withstand higher strain values before their G' modulus decrease. The high modulus for GTR ultrafine and GTR containing PP (when compared to neat PP PP/bitumen), indicate that bitumen has been absorbed by these rubber particles. So the apparent amount of bitumen in the mixture became less which affected its plasticizing effect, as well.

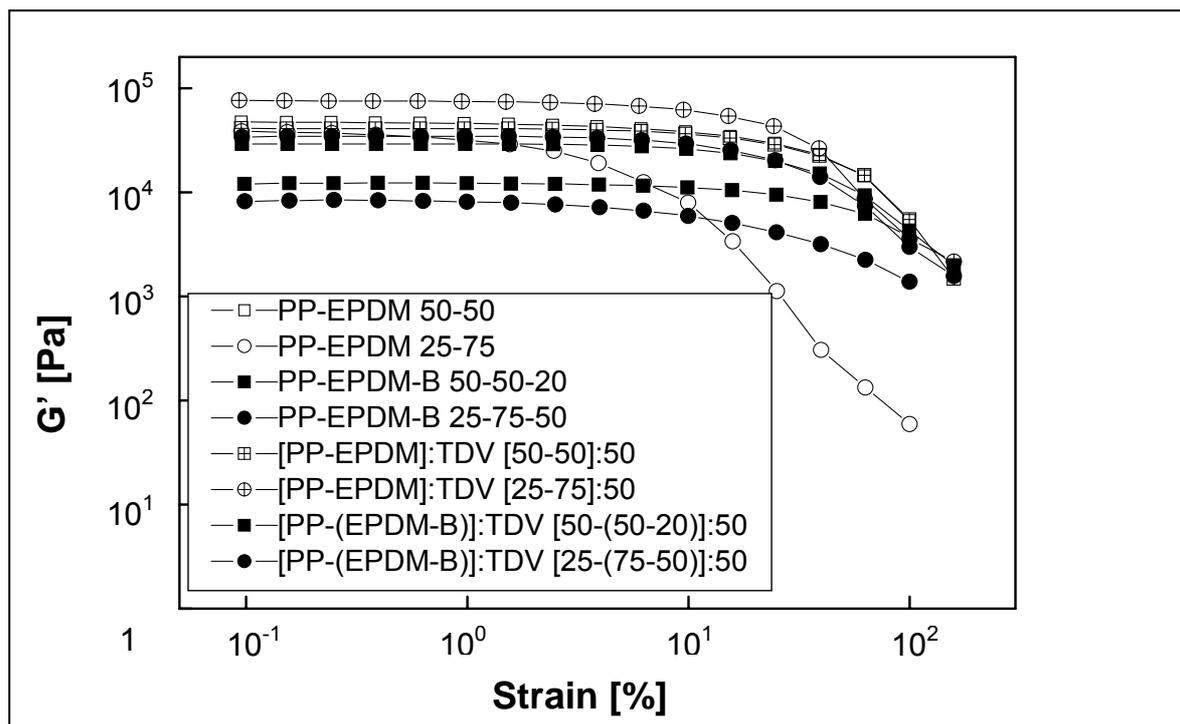


Figure 5.31. Storage modulus vs. strain for the mixtures at a 25/75 ratio by weight (PP to rubber). Note: the measurement was performed at $T = 200$ °C, frequency 10 rad/s

The behaviour of the above mixes was also examined in frequency sweep experiments. The strain was fixed at 1% in the related tests.

As shown in Figure 5.32 show the increase in the storage modulus of PP after the addition of the rubber particles was followed by a parallel decrease in G' when bitumen was incorporated. This reveals the plasticizing, more exactly the reclaiming/plasticizing effect of bitumen. By increasing the rubber content in the mixtures the difference in the melt rheology of the compounds became more prominent.

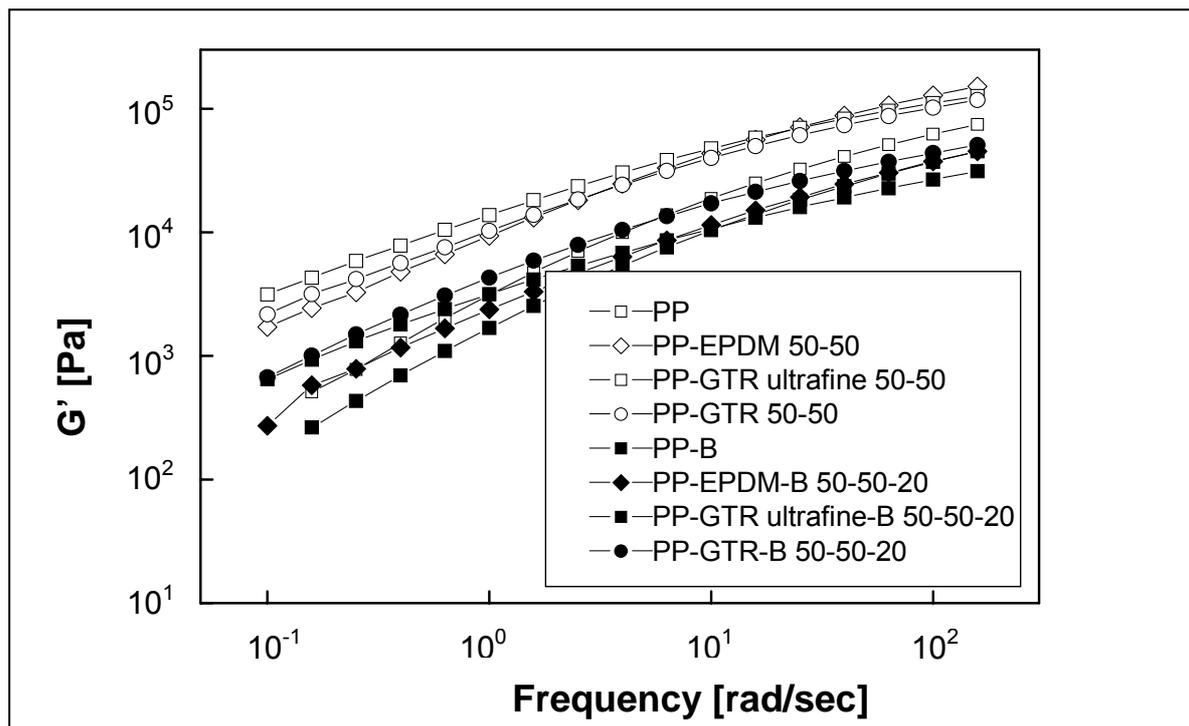


Figure 5.32. Storage modulus vs. frequency for the mixtures at a 50:50 ratio by weight (rubber to PP). Note: the measurement was performed at $T = 200\text{ }^{\circ}\text{C}$, frequency 10 rad/s

As shown in Figure 5.33, the filling of PP with rubber particles changes tremendously the behaviour of the mixes at low frequencies. The change in the respective curves (small slope) suggests their solid-like character. Addition of bitumen results in a more liquid-like behaviour but it is still far away from that of PP or PP/bitumen compounds at low frequencies.

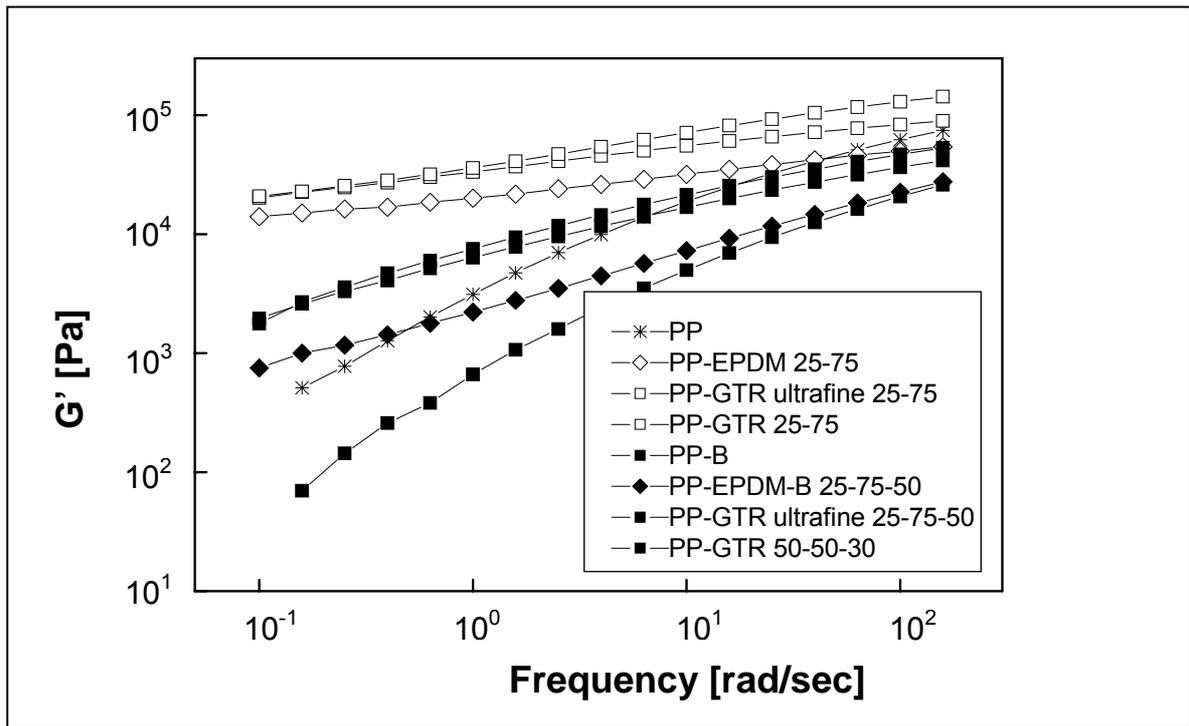


Figure 5.33. Storage modulus vs. frequency for the mixtures at a 25/75 ratio by weight (PP to rubber). Note: the measurement was performed at $T = 200\text{ }^{\circ}\text{C}$, frequency 10 rad/s

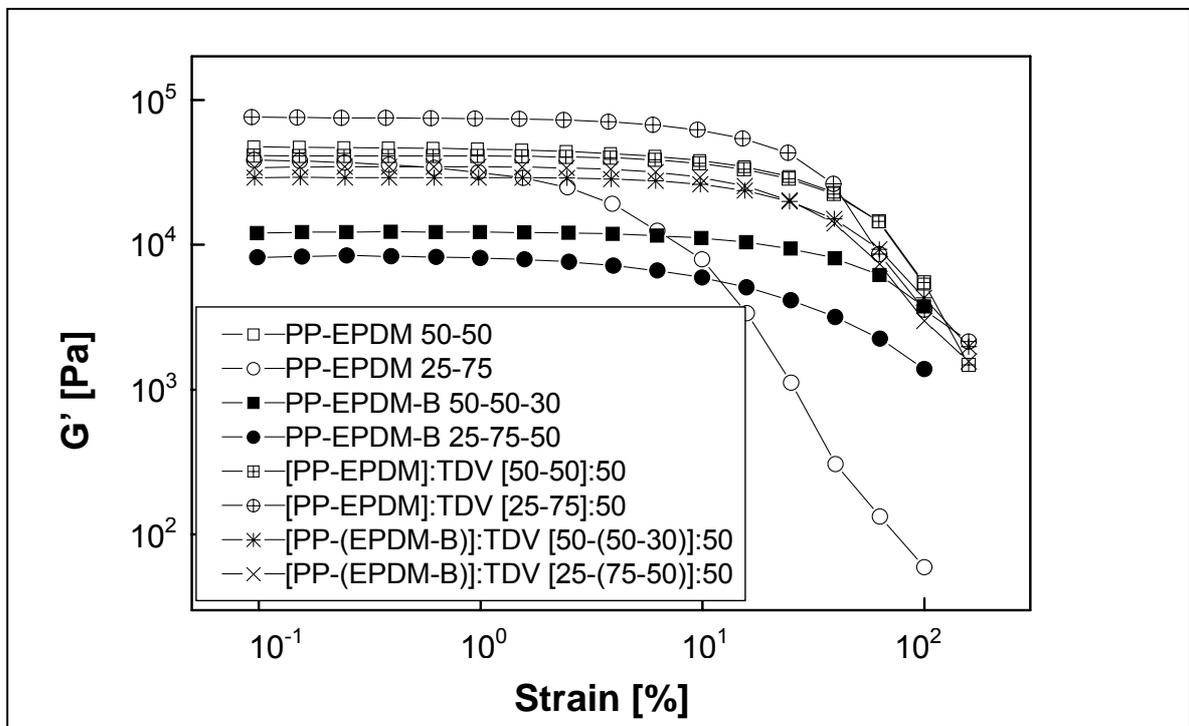


Figure 5.34. Storage modulus vs. strain for the EPDM mixtures. Note: the measurement was performed at $T = 200\text{ }^{\circ}\text{C}$, frequency 10 rad/s

For the GTR ultrafine/PP systems the results are more or less similar to the EPDM/PP blends. As shown in Figure 5.35, TDV acts again as compatibilizer.

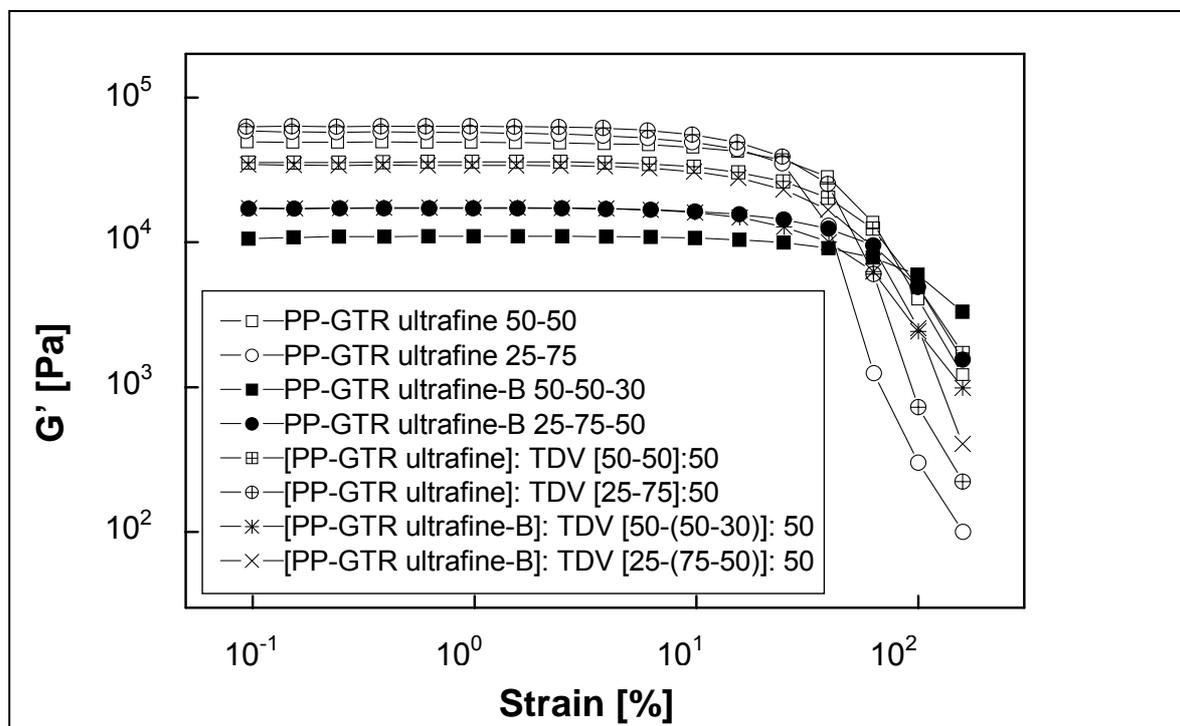


Figure 5.35. Storage modulus vs. strain for the mixtures containing GTR ultrafine. Note: the measurement was performed at $T = 200\text{ }^{\circ}\text{C}$, frequency 10 rad/s

The plasticizing effect of bitumen (for both 50/50 and 25/75 compounds) for the TDV containing blends is obvious. Note that for the mixes with GTR ultrafine/PP and TDV the addition of bitumen results in lower modulus differences than those observed in the respective EPDM samples (cf. Figure 5.34)

The rheological behavior of the mixtures containing TDV and GTR fractions strongly differs upon the type of the latter (cf. Figure 5.35 and 5.36). The decrease of the storage modulus for the PP/GTR 25/75 mixture reveals the plasticizing effect of TDV for this mix (cf. Figure 5.36). Note that this effect is negligible for the mixes containing GTR ultrafine (cf. Figure 5.35).

This phenomenon might be related with the combination of the two different particle sizes of the GTR ($400\text{--}700\mu\text{m}$) and Santoprenes' rubber particles ($<100\text{ }\mu\text{m}$). By this combination of rubber particles highly deformable structure can be created. Interestingly, the addition of bitumen has almost no effect to the GTR/PP/TDV compound (cf.

Figure 5.36). If this is the case, then the TDV behaviour alone should also be less influenced by adding bitumen.

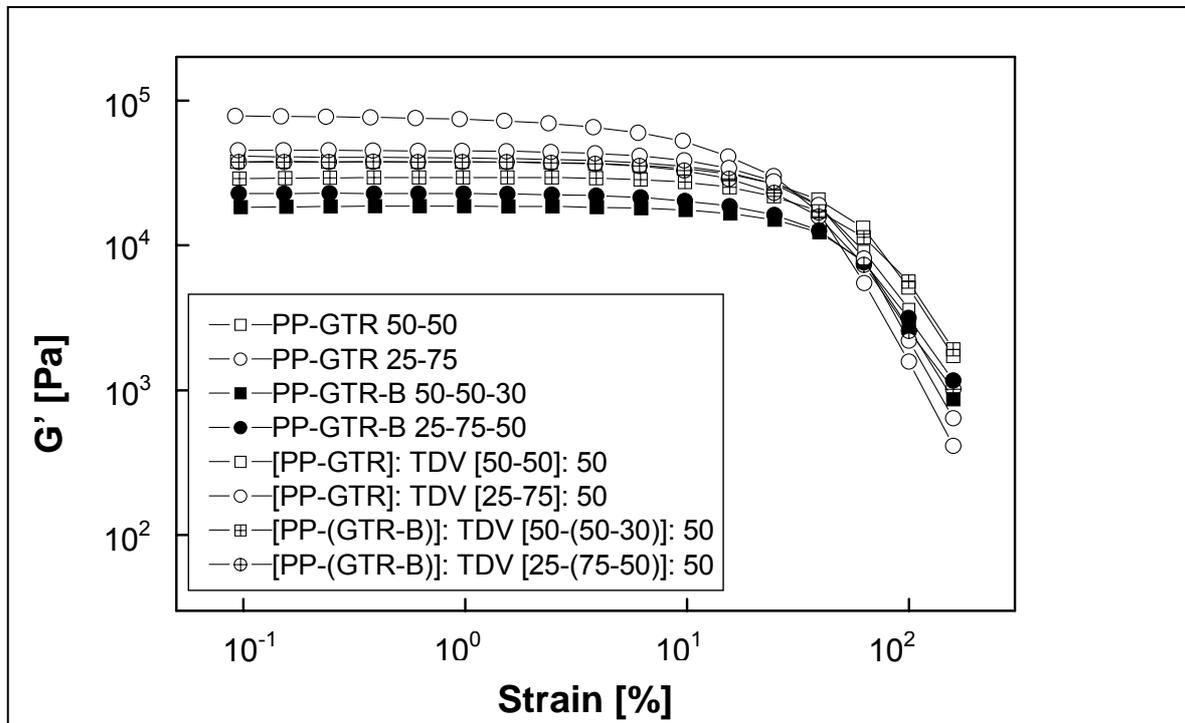


Figure 5.36. Storage modulus vs. strain for mixtures containing GTR. Note: the measurement was performed at $T = 200$ °C, frequency 10 rad/s

To check this scenario, mixtures of TDV with and without bitumen were examined. As presented in Figure 5.37, addition of bitumen in the amount used for the 50/50 and 25/75 compounding resulted in a small decrease of the storage modulus. This fact corroborates the above-mentioned comment about the role of TDV in the GTR mixture. Recall that the TDV used should be a highly plasticized grade.

Comparing the moduli for PP/EPDM (25/75) and neat Santoprene[®] samples (Figure 5.34 and 5.37) one can notice that they present similar values. The behaviour of Santoprene[®] alone does not alter in great extent by the addition of bitumen (Figure 5.37) opposed to the PP/EPDM (25/75) blend (Figure 5.34). The modulus decrease in the latter case may suggest that the bitumen enters in the EPDM phase which is likely continuous. On the contrary, G' does not decrease in GTR/PP/TDV blends after introduction of bitumen as bitumen is compatible with the TDV (Santoprene) phase. The rheological behaviour of the blends with GTR ultrafine is in between the above

mentioned two thresholds. This can be attributed to the finer particle size and less crosslinked stage of this GTR ultrafine. Recall that this was reflected in higher initial sol content of GTR ultrafine compared to GTR.

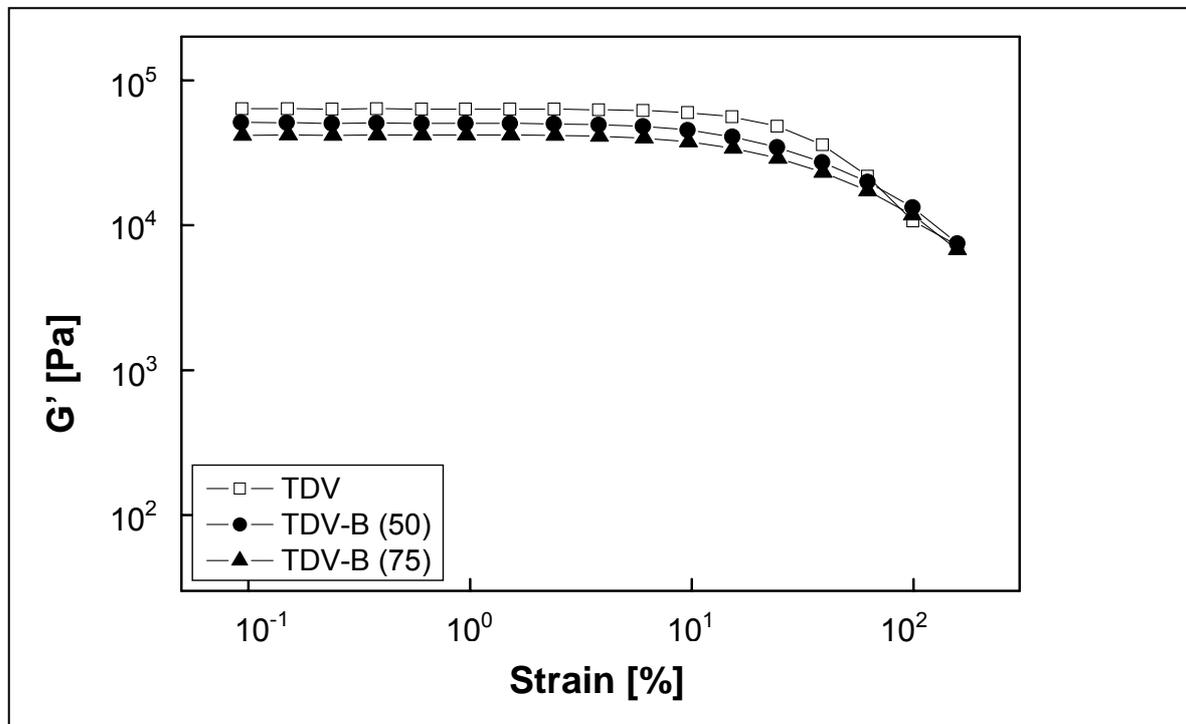


Figure 5.37. Storage modulus vs. strain for the Santoprene TDV mixtures and its blends with bitumen. Note: the measurement was performed at $T = 200\text{ }^{\circ}\text{C}$, frequency 10 rad/s

Some further information about these blends supplies the frequency sweep tests. In Figure 5.38 the effect of different rubber particles is presented. For the PP/EPDM blends (Figure 5.38 a)) the addition of Santoprene[®] strongly alters the slope of the curves, especially for the 25/75 blends. Similar scenario holds also for the GTR ultrafine containing blends (Figure 5.38b)), these, however, TDV alter the rheology of both 50:50 and 75:25 compounds owing to its plastisizing role.

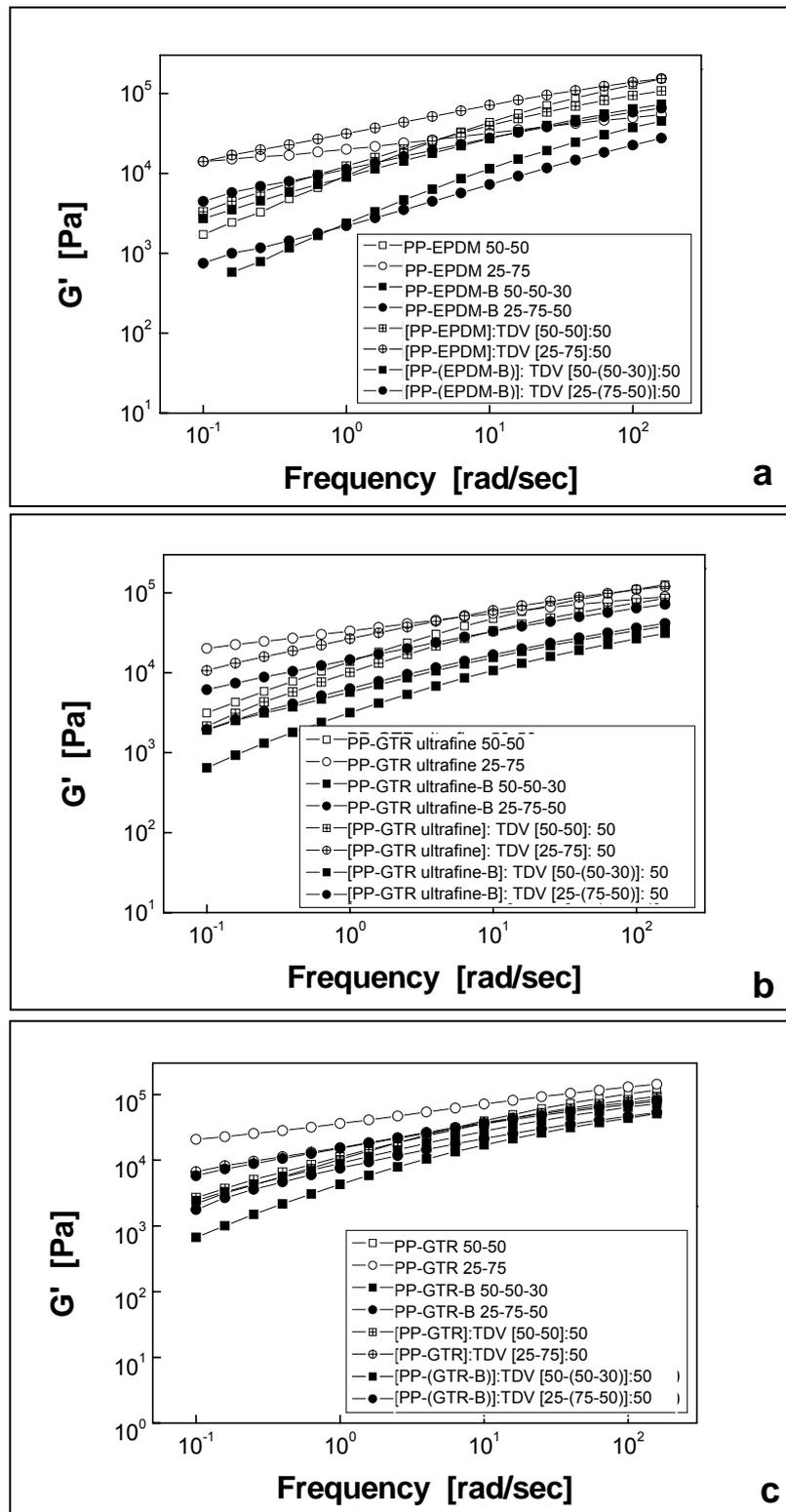


Figure 5.38. Storage modulus vs. frequency for the mixtures with Santoprene[®] for a) EPDM, b) GTR ultrafine and c) GTR rubber particles

In case of GTR containing blends (Figure 5.38 c)), addition of bitumen in the compounds with TDV (Santoprene) does not affect the frequency behaviour of either 50/50 or 75/35 blends. Continuing the above-mentioned analysis, the role of bitumen in TDV in a frequency sweep should also be examined. As presented in Figure 5.39, a marginal effect can be noticed due to the bitumen added.

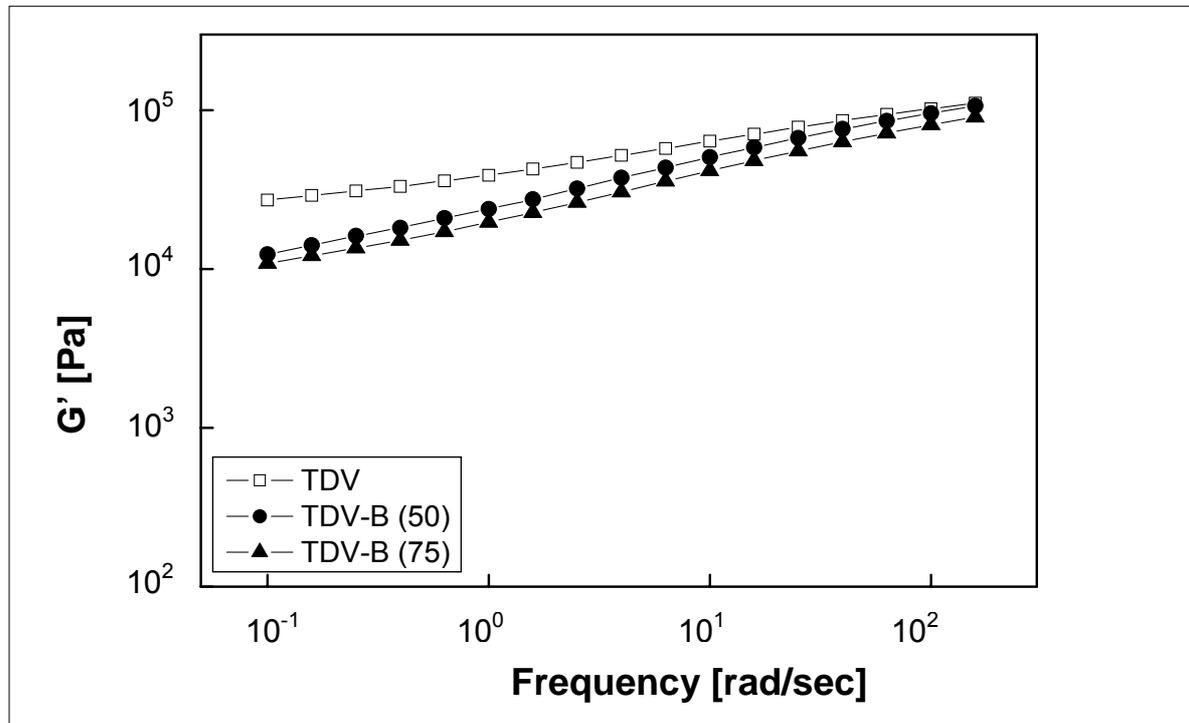


Figure 5.39. Storage modulus vs. frequency for the TDV (Santoprene[®]) mixtures

5.6.3.2 High shear rate

Figure 5.40 displays the melt viscosity as a function of shear rate for the TPE(PP) compounds with GTR with and without bituminous reclamation of the latter.

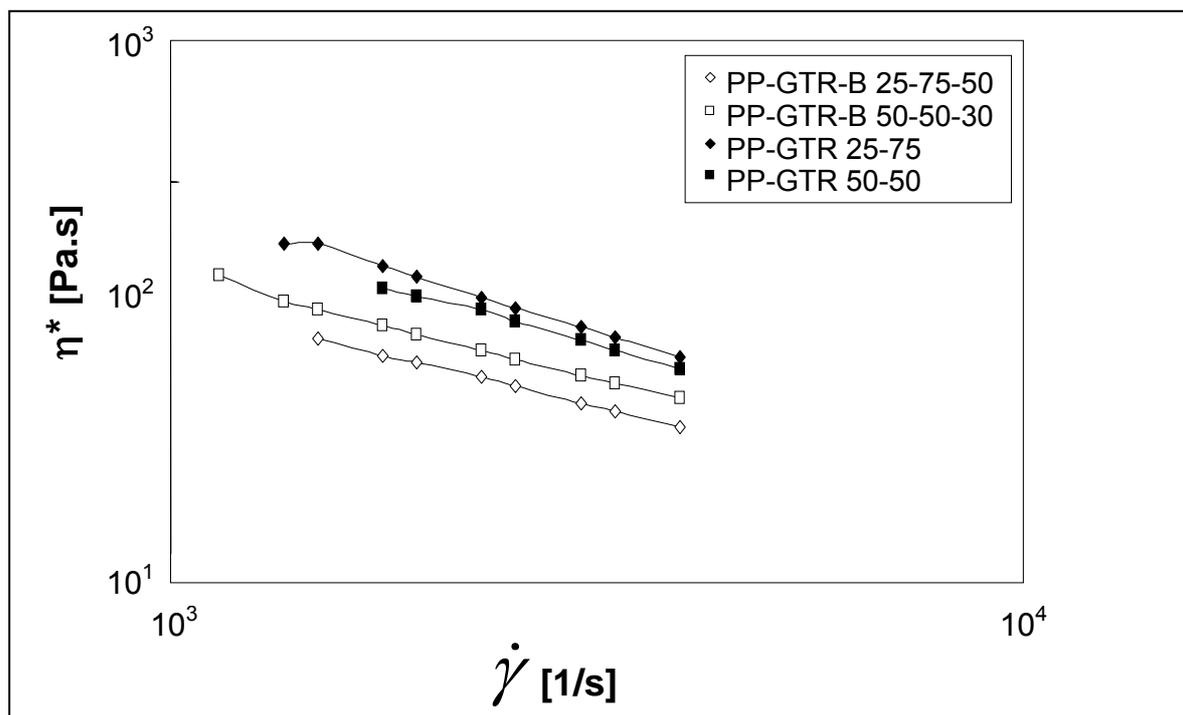


Figure 5.40. Apparent melt viscosity as a function of shear rate for the TPE(PP) compounds with GTR with and without bituminous reclamation of the latter

One can recognize that all compounds exhibit a strong shear thinning behaviour. Those TPEs containing in bitumen reclaimed GTR have markedly lower viscosities at the same shear rate than the reference PP/GTR blends. Accordingly, bitumen works as apparent plasticizer in the corresponding compounds. Recall that this is in harmony with the rheological results got at low shear rates. On the other hand, there is no clear tendency with respect of the composition of the TPE(PP)s.

Figure 5.41 compares the rheological behaviour of the TPE(PP) containing ultrafine GTR with that of the PP/EPDM blends at similar compositions. Comparing the rheological behaviour of the compounds with GTR and GTR ultrafine only a marginal difference can be found. In this shear rate range shear thinning overwrites the effect of the GTR particle size.

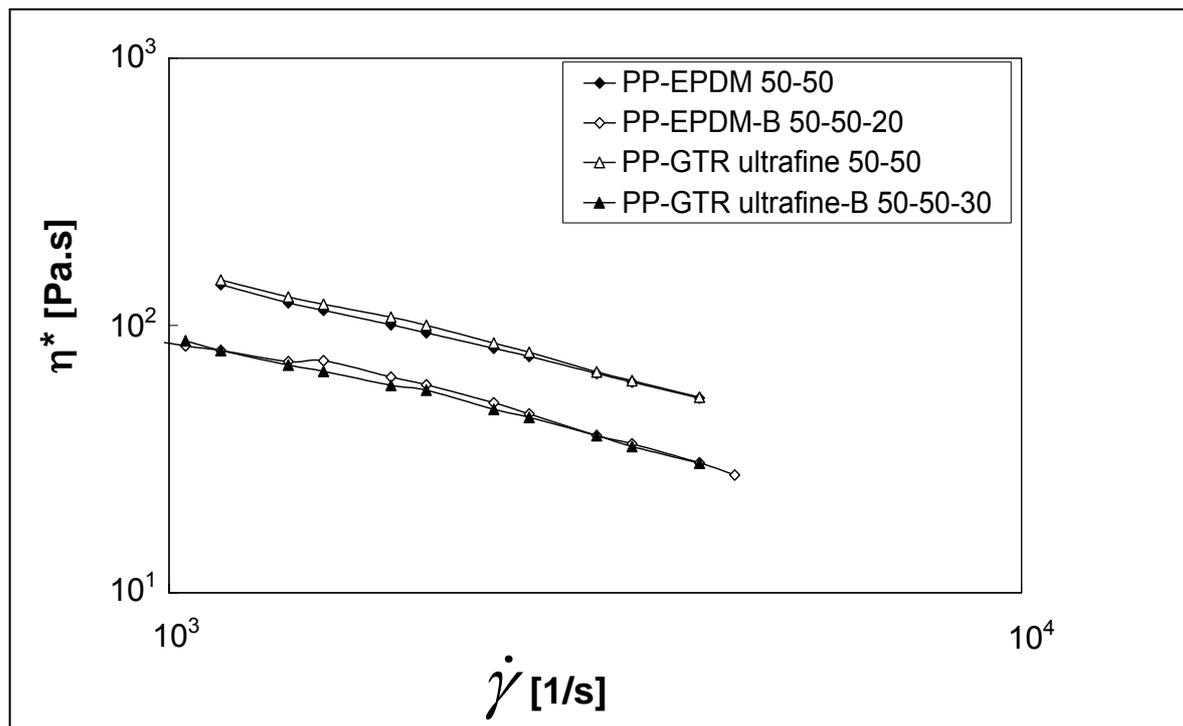


Figure 5.41. Apparent melt viscosity as a function of shear rate for the TPE(PP) compounds (50/50) with ultrafine GTR with and without bitumen reclamation of the latter. Note this figure contains the selected curves of PP/EPDM blends

The combination of TPE(PP) grades with TDV yielded some interesting effects – cf. Figure 5.42.

First, TDV shows a homogeneization effect for the GTR containing TPE(PP) compounds irrespective whether or not the GTR was reclaimed. This is a hint for the good compatibility between the extending oil of the TDV and bitumen. Second, the melt viscosity of the compounds containing more GTR becomes higher which is in line with the expectation. Third, the effect of GTR particle size “reappears” after compounding with TDV at least when the GTR is not reclaimed. One can notice the rather high viscosity of the compounds TPE(PP) 50/50 with GTR ultrafine in Figure 5.42.

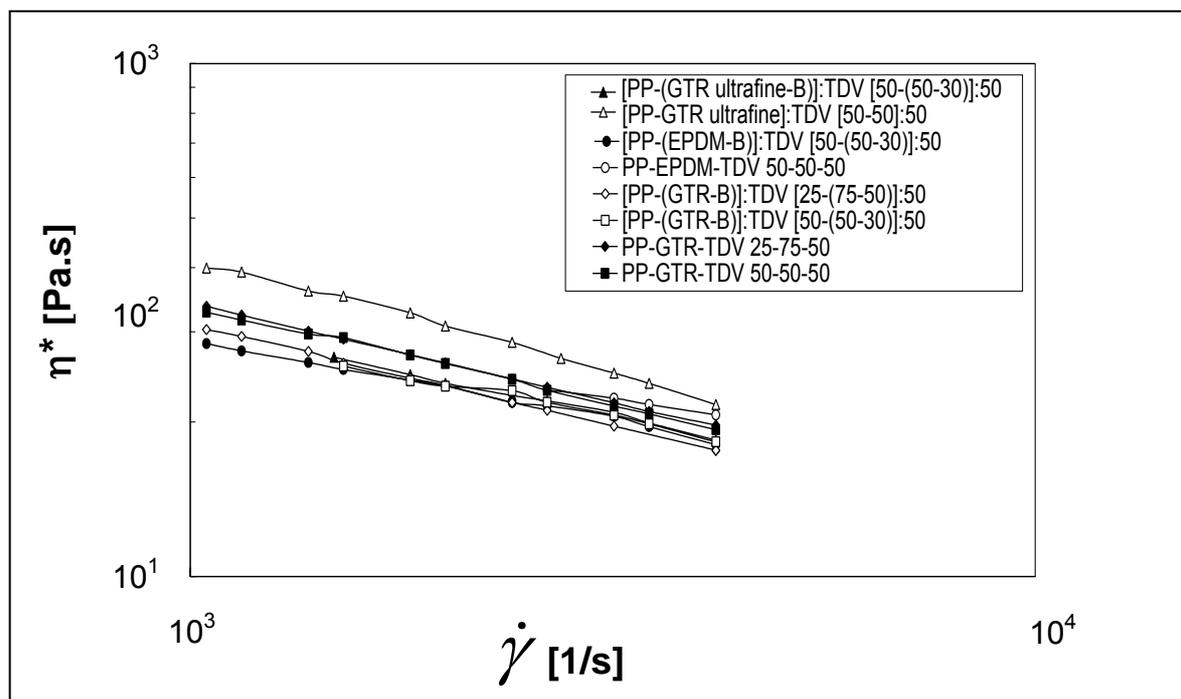


Figure 5.42. Apparent melt viscosity as a function of shear rate for the TPE(PP) grades with TDV. Note that compound with all three GTR fractions with and without bitumen reclamation are displayed in this figure

The above results suggest that GTR containing PP-based blends can easily melt processed at high shear rates as their viscosity is less affected neither by the mean particle size of the GTR nor its reclamation. This is the major reason why such processes are proposed for polyolefin/GTR blends. Attention should be paid, however, to the fact that easy processing does not yield products of good mechanical performance as demonstrated before.

5.6.4 Morphology

5.6.4.1 Cut surface

SEM inspection of cut surfaces of the TPE (PP) may deliver useful information on the morphology development. Cutting occurred at RT using a scalpel. Figure 5.43 and 5.43 compare the cut surfaces of TPE (PP) viz. PP/GTR 50/50 and PP/(GTR+bitumen) 50/(30+20) at various magnifications.

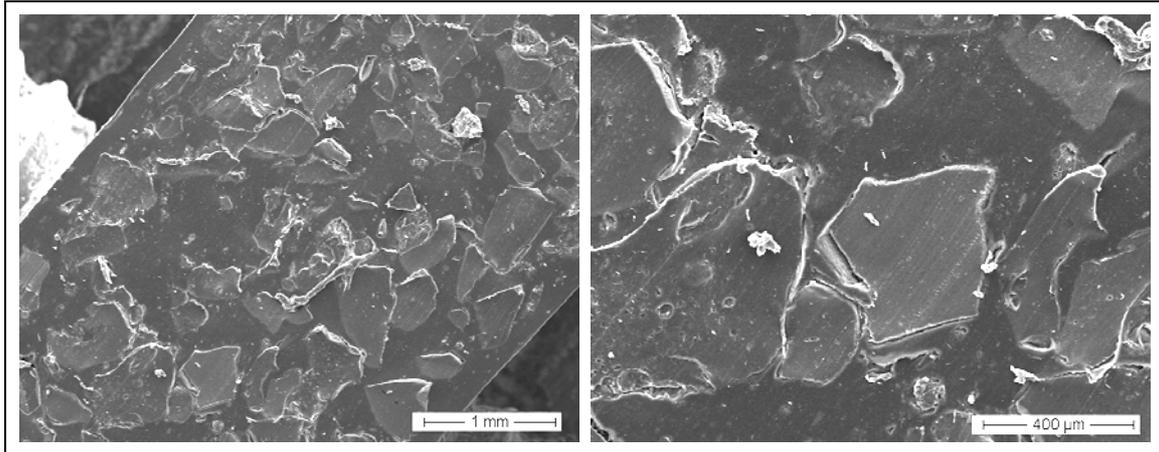


Figure 5.43. SEM pictures taken from the cut surfaces of PP-GTR 50-50

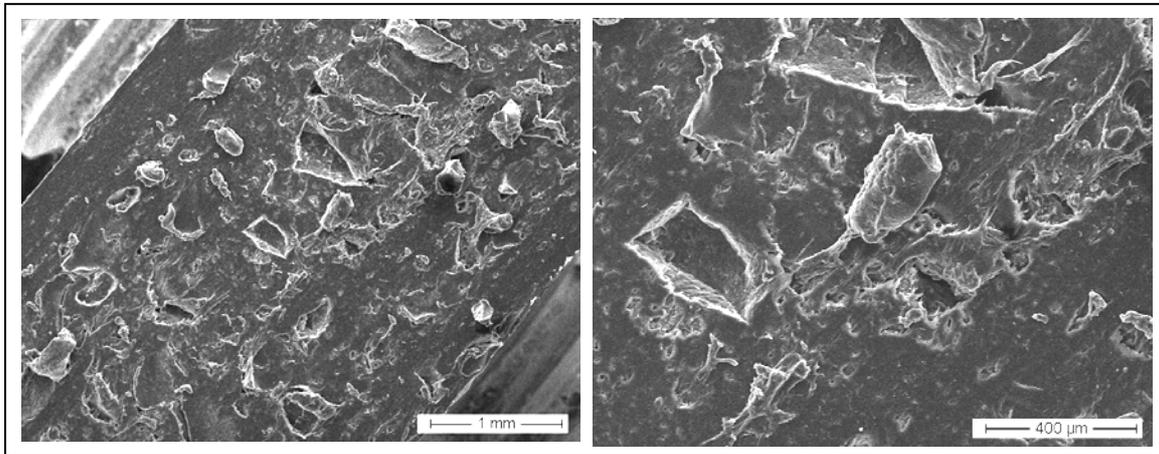


Figure 5.44. SEM pictures taken from the cut surfaces of PP-(GTR-B) 50-(50-30)

The efficient reclamation of the GTR due to bituminous treatment is obvious. The surface reclaimed GTR particles adhere to the matrix well. Further, they become well plasticized by the bitumen present. This is well resolved in the SEM pictures based on the typical “shearing effect”.

5.6.4.2 Failure of single gated injection molded specimens

Figure 5.45 shows the fracture surface of the blends PP-GTR 50-50 and 25-75.

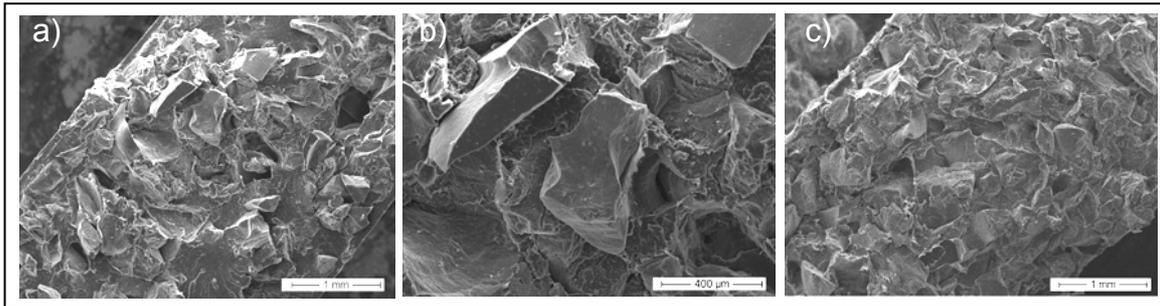


Figure 5.45. Fracture surface of the PP-GTR blends at 50-50 (a and b) and 25-75 (c) composition ratio

One can recognize the rather brittle failure mode due to the lacking interphase between the GTR and PP matrix. This is well recognizable especially at higher magnifications – cf. Figure 5.45 – b picture.

The failure mode turns to be far more ductile after bituminous reclamation of the GTR – cf. Figure 5.46.

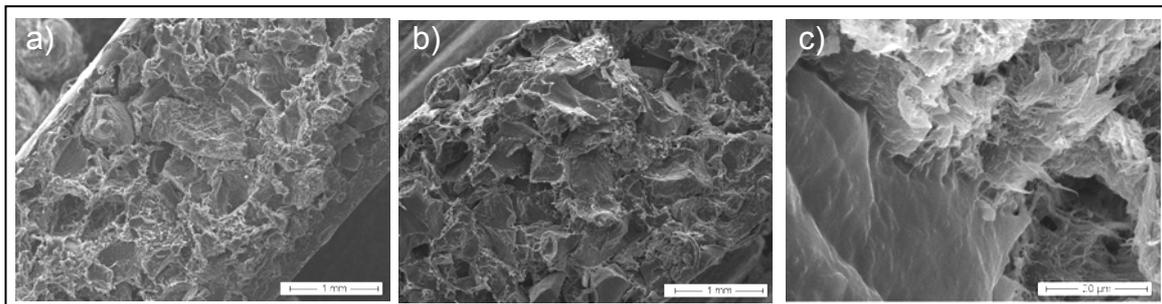


Figure 5.46. Fracture surface of TP(PP) of compositions 50-50 (a) and 25-75 (b and c) containing GTR reclaimed bitumen

At high magnification (cf. Figure 5.46, picture c) the good adhesion between the GTR particles and PP matrix is clearly visible. The fibrillar structure present (see arrow in Figure 5.46, picture c) corroborates that the interphase is mostly formed via molecular entanglements. The failure scenario is somewhat different for the TPE(PP) compounds with GTR ultrafine. The PP matrix locally fails ductilely even if the GTR ultrafine is not reclaimed in bitumen – cf. Figure 5.47. This behaviour, termed microductile deformation, is due to the small PP ligament thickness between the neighboring GTR ultrafine particles. Bituminous reclamation of GTR results in a macroscopic

ductile failure favoured also by the plasticizing effect of bitumen in the related compound.

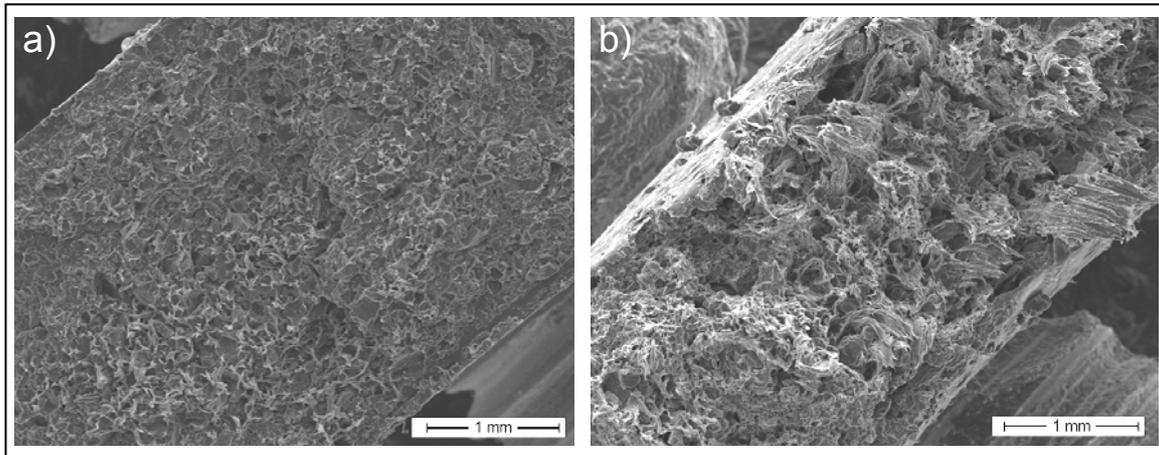


Figure 5.47. Fracture surface of the TPE(PP) compounds of 50-50 ratio containing GTR ultrafine fraction before (a) and after reclamation in bitumen (b)

Fractographic analysis sheds light also why the PP-EPDM blends exhibited far better mechanical properties without than with bitumen (cf. Table 5.12).

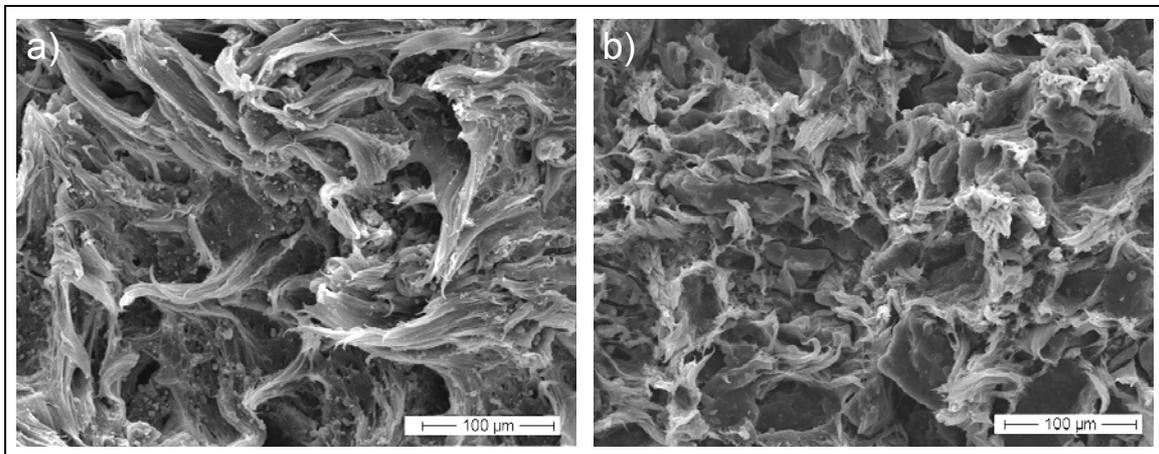


Figure 5.48. SEM pictures taken from the fracture surface of EPDM-PP blends (50/50) without a) and with bitumen b)

Figure 5.48 picture a) shows that the EPDM is finely dispersed in the PP matrix. The small particles cavitate followed by crazing and elongation (fibrillation) of the matrix ligaments in between. The bitumen added is mostly absorbed by the EPDM. This

changes both the interfacial tension and viscosity ratio of the blend components. Recall that these parameters control the particle size and its distribution in disperse blends. As a consequence of bitumen incorporation coarser EPDM particles appear in the PP matrix. This is a clear hint that bitumen reduces the compatibility between EPDM and PP.

5.6.4.3 Failure of double-gated injection molded specimens

The fracture surfaces of the TPE(PP) specimens with weld lines show the basic difference in the composition, more exactly reflect that of the GTR reclamation. Figure 5.49 compares the weld line fracture surfaces of the PP/GTR ultrafine (50/50)-TDV blends with and without bitumen reclamation.

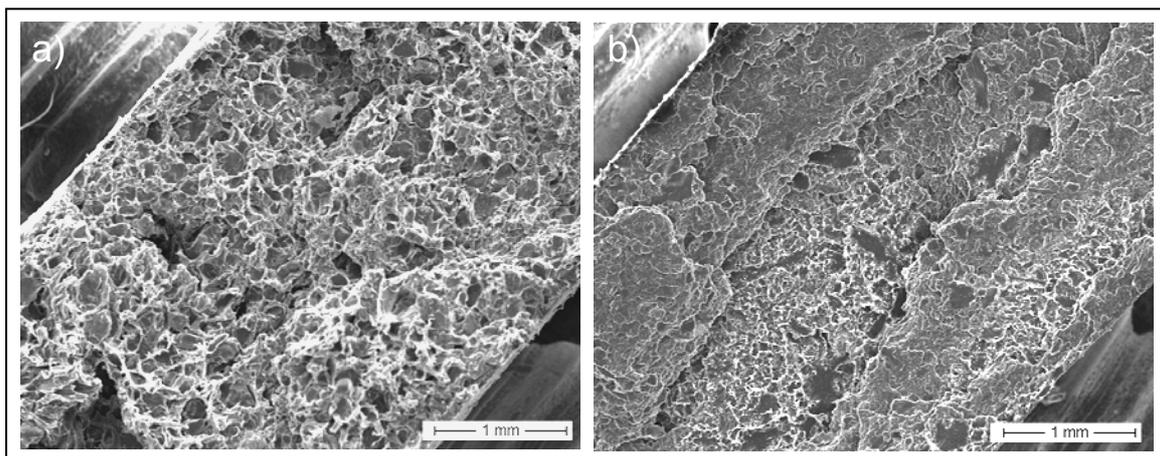


Figure 5.49. Weld line fracture surface of PP-GTR ultrafine (50/50)-TDV blends, a) without bitumen, b) bitumen reclaimed

The rough surface in the blend containing not reclaimend rubber is due to debonding. This is strongly favored owing to the missing interfacial adhesion between the PP matrix and the GTR ultrafine particles. The lacking interfacial bonding becomes obvious at higher magnifications (cf. Figure 5.50).

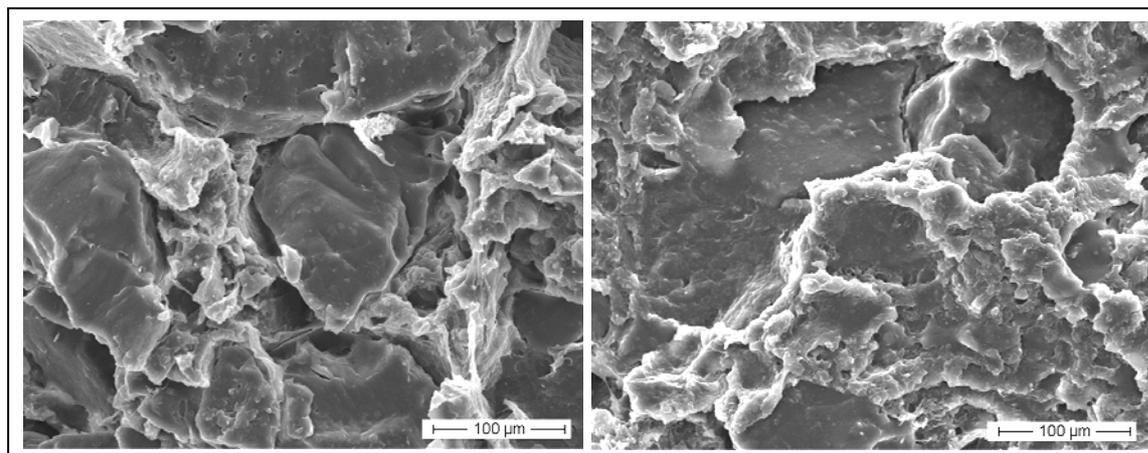


Figure 5.50. Weld line fracture surface of PP-GTR ultrafine (25-75)-TDV blends. Without bitumen –left, bitumen reclaimend –right

One can recognize that bituminous reclamation of GTR improved the bonding to the PP matrix considerably. On the other hand the bitumen present in the PP phase, altered the deformation behaviour of the PP. Their combined effect turned out in the weld line strength reported in Table 5.13.

6 Conclusions

This work was devoted to develop thermoplastic polyolefin-based elastomers (TPE) using ground tyre rubber (GTR) fractions. As polyolefins, low and high density polyethylenes (LDPE and HDPE, respectively) and polypropylene (PP), served. The LDPE and HDPE were recycled grades. Their sources were horticultural films and transportation crates, respectively.

The motivation of this research work was to find value-added products (viz. TPEs) containing GTR and recycled polyolefins.

Based in the knowledge from the literature and preliminary screening works two strategies were deduced:

- a) co-crosslinking between the polyolefin matrix and GTR particles by adopting the moisture-crosslinking of vinylsilane grafting
- b) Partial devulcanization/reclamation of the GTR fractions and their blending with polyolefins in the melt

Note that the co-crosslinking route results in products which are melt processed (shaped) but of thermoset characters. By contrast, the polyolefin blends containing devulcanized or reclaimed GTR retain their melt (re)processability.

The co-crosslinking strategy proved to be less promising as the property improvement targeted could not be reached or only at such multiplication the usual grafting recipe which can by no way considered as economic.

It turned out that the devulcanization (thermochemical treatment) of GTR by state-of-art products (RegenTM Agent) only slightly enhances the sol content (acetone soluble fraction) of GTR compared to thermomechanical treatments. Reclaiming of the GTR in bitumen, however, was well suited to increase the sol content and thus to guarantee the required partial decomposition of the GTR. The latter was considered as an essential prerequisite for creating good “bonding” between the GTR particles and polyolefin matrix. Good “bonding” is owing to entangling between molecules of the GTR and polyolefin which generates an interphase. According to the research strat-

egy the stress transfer through the interphase can be improved when suitable fresh rubber is added, that may preferentially cover (encapsulate) the GTR particles. It was established that a very efficient reclamation of the GTR by the bitumen occurs under given conditions (long term “cooking” at $T \geq 160$ °C). Simultaneous or additional kneading, extrusion mixing of the GTR/bitumen compositions are advantageous, however, the time needed for good reclamation could not be reduced by high shear mixing. This aspect should be considered when outlining an industrial scale process.

As rubber compatibilizers for PE/GTR blends natural (NR), styrene/butadiene (SBR) and ethylene/propylene/diene rubbers (EPDM) were tested and the latter was found as the most suitable one. The LDPE-based TPE of the composition TPE(LDPE) = LDPE (40)/EPDM (20)/GTR (20)/bitumen (20 parts) showing 80 Shore A hardness has been characterized on injection molded specimens with and without weld line, in detail. In addition, its combination with a PP-based commercial thermoplastic dynamic vulcanizate (TDV) of the same hardness has been investigated, too. The TPE (LDPE) produced exhibited useful engineering (tensile mechanical, set and rheological) properties even after aging and/or multiple reprocessing. Its weakness was mostly due to the moderate weld line strength. This has to be improved and parallel to that attention should be paid on how to avoid the formation of weld lines (or circumvent their negative effect) in the injection molded parts.

A comparative study was devoted to a TPE grade containing HDPE (TPE(HDPE)). The interest behind this comparison was to elucidate the possible effect of the matrix crystallinity. Recall that HDPE is more crystalline (crystallinity $\approx 60\%$) than LDPE (crystallinity $\approx 40\%$). As expected, TPE(LDPE) outperformed TPE(HDPE) with respect to the basic mechanical properties. Major conclusion from this part of the work was that low matrix crystallinity is beneficial for the TPE performance. This may be an interesting issue for the future when low crystallinity polyethylenes produced by new metallocene catalysysts will be available as “waste” (i.e. to be recycled) materials. The costs of the above TPEs (cf. Table 6.1) are about 1.5 €/kg which is below the price of commercial TDV grades (2.5-3.5 €/kg). Accordingly, these TPEs may be competitive for several applications. Note that the hardness of the TPEs developed can be tailored upon request in a given range via the composition.

Table 6.1. Estimated costs for TPE(LDPE) and TPE(HDPE)

	Materials cost (€/kg)	Ratio in the recipe (%)	€/kg
LDPE recycled	0.4	40	0.16
EPDM rubber	2.5	20	0.50
GTR	0.2	20	0.04
Bitumen	0.2	20	0.04
GTR/Bitumen treatment			0.20
Extrusion compounding including granulation			0.55
Overall estimated cost			1.49 €/kg

To round up this work efforts were dedicated to develop GTR-containing PP-based TPEs (TPE(PP)). This was triggered by the following aspects: commercial thermo-plastic elastomers are PP-based, and thus better compatibility with them can be expected, compatibilization with EPDM can be circumvented, and last but not least, the reclaimed GTR content in the recipe can be enhanced. During this work the effect of the initial particle size of GTR (GTR: 0.4-0.7 and GTR ultrafine: < 0.2 mm) was also studied.

The related TPE(PP)s, produced by extrusion melt compounding before and after the bituminous reclamation of the GTR fraction were:

PP/GTR = 50/50 and 25/75 (Shore A hardness: 88 and 83, respectively)

PP/(GTR+bitumen) = 50/50 and 25/75 (Shore A hardness: 84 and 81, respectively)
the GTR/bitumen ratio was 60/40.

The bituminous reclamation of GTR was evidenced by strongly improved ductility (ultimate strain) and set properties. It was found that the rheological terms, such as complex shear modulus, viscosity and their constituents, reflect well the bituminous reclamation caused changes in the phase structure in the viscoelastic range (low shear rate). The melt viscosity of the corresponding blends at high shear rates allows us to produce items of thin cross sections and long melt path. Figure 6.1 shows that using the same injection molding conditions the blend PP/GTR ultrafine gives short

shots (i.e. fully filled parts) whereas that one with bituminous reclamation of GTR ultrafine yielded complete parts.

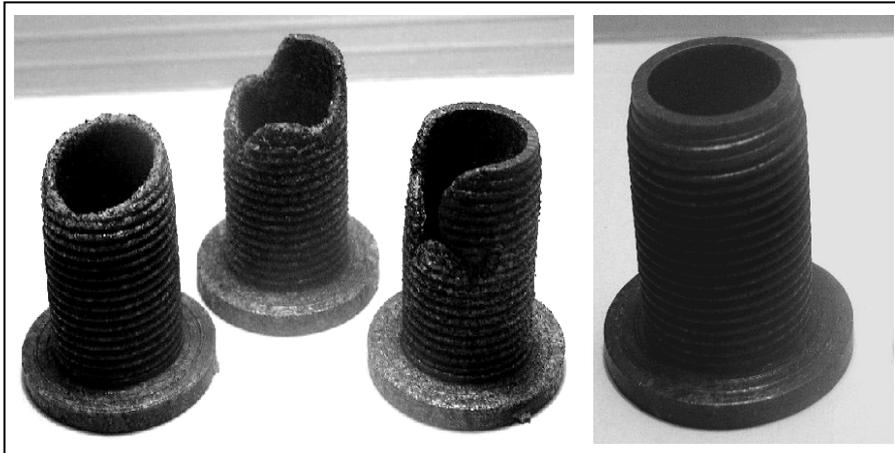


Figure 6.1. Connectors injection molded from PP/GTR (50/50; a) and PP/(GTR+bitumen) (50/50; b) under identical conditions

Summarizing this work one can claim that the GTR reclamation in bitumen followed by melt compounding with polyolefins is a promising approach to produce TPEs that should be followed furtheron. The major tasks to be solved are:

- Fit the efficient GTR reclamation (long duration, batch procedure) to the extrusion melt compounding/granulation
- Explore the overmolding, coinjection with the new TPEs to reach improved surface characteristics. This means the use of the above disclosed TPEs as cheap core material for products which are “covered” by more expensive commercial products.

Future Outlook

In order to check the possible applications of the newly developed TPEs (and thus their commercialization) further investigation are necessary. This includes both standardized (like tear behaviour) and non-standardized techniques (fracture mechanical methods). Fracture mechanical investigations may be especially relevant to assess

the fatigue crack growth. Note that rubbers usually fail by fatigue crack propagation. The related tests would yield useful information on the embedding quality of the GTR particles as these investigations are very sensitive to the interface/interphase. It is worth noting that standardized fatigue fracture tests can also be used. However, the fatigue assignment in that case is for less clear than in fatigue crack growth. Nevertheless, tensile and flexural fatigue tests can deliver some information on the long-term performance, at least when compared to those of competing TPE formulations.

7 Literature

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8 List of Publications

1. Lievana, E.; Bernal, C.; Frontini, P.: Impact fracture behaviour of rubber-modified polyamide 6. European Conference on Macromolecular Physics, Eger, Hungary (2001), pp. 162-164.
2. Lievana, E.; Wollny, A.; Mülhaupt, R.; Karger-Kocsis, J.: Impact Fracture and Failure Behaviour of In-Situ Polymerized, Ethylene/Butylacrylate Rubber Toughened Polyamide-12. *Macromol. Mater. Eng.*, Vol. 287, No. 4, (2002), pp. 266-271.
3. Lievana, E.; Karger-Kocsis, J.: Impact Modification of PA-6 and PBT by Epoxy Functionalized Rubbers. *Macromol. Symp*, Vol. 202, (2003), pp. 59-66.
4. Grigoryeva, O. P.; Fainleib, A. M.; Tolstov, A. L.; Starostenko, O.; Lievana, E.; Karger-Kocsis, J.: Phase structure, morphology and mechanical properties of novel thermoplastic elastomers (TPEs) from recycled HDPE, EPDM and ground tyre rubber. XVI^{ème} Congrès Mondial des Plastiques en Agriculture, C.M.P.A. '03, 13-17 décembre 2003, Alger, Algérie. Recueil des résumés. pp 12-13.
5. Lievana, E.; Bernal, C.; Frontini, P.: Essential work of fracture of rubber-modified polyamide 6 in impact. *Polymer Engineering and Science*, Vol. 44, No. 9, (2004), pp. 1707-1715.
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 9. Grigoryeva, O. P.; Lievana, E.; Tolstov, A. L.; Starostenko, O.; Fainleib, A. M.; Karger-Kocsis, J. Viscoelastic behaviour, thermal properties and morphology for new composites from recycled HDPE, EPDM, ground tyre rubber (GTR) and bitumen. The 4th Asian-Australasian Conference in Composite Materials, Sydney, Australia (2004), pp. 799-803.

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