Tensile and fracture mechanical properties of styrene-butadiene rubbers (SBR) filled with industrial and pyrolytic carbon blacks, and organoclay

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Abstract. In this work we examined effects of filler combinations (industrial carbon black (CB), pelletized pyrolytic carbon black (pCB_p) and organoclay (I30.P) on the tensile mechanical and fracture mechanical properties of SBR rubbers. The performance of standard N660 CB was compared with that of pCB_p when used alone or in 1: 1 blend ratio at an overall filler content of 60 part per hundred part rubber (phr). The study covered also a mix composed of 20 phr pCB, 20 phr N660 and 10 phr I30.P the hardness of which was identical to those of the (p)CB filled ones. N660 yielded better tensile properties than pCB_p. By contrast, the latter yielded higher tear and trouser tear strength values than CB. I30.P increased the storage modulus value (E') in spite of the filler content of 50 phr. Presence of organoclay and pCB_p also increased the critical value of the J-integral.

Introduction

Disposal and recycling of the increasing amount of waste tires are great challenges nowadays. Intensive research is addressing various aspects of tire recycling [1-2]. Today, worn tires are commonly used for energy generation, but value-added material-related options are in forefront of interest. For example, ground tire rubber (GTR) can be minor or major component in thermoplastic elastomers [2]. Another possibility is the partial devulcanization, after which the devulcanized, reclaimed rubber can be used, mostly as additive, again. For devulcanization ultrasonic and microwave techniques are most promising [2-3]. Pyrolytic processes produce a carbonaceous solid and a volatile fraction. The latter is a common feedstock of the pyrolysis itself [1,4]. The pyrolytic carbon black (pCB) may well be used as rubber reinforcement [5-7]. pCB contains inorganic materials from the initial rubber recipe ($CaCO_3$, ZnO, SiO_2) based on which it has a dual character [6]. The quality of the resulting carbon black depends on the "feedstock" (rubber recipe) and production conditions (temperature, pressure, atmosphere) [1,4,6], and on the post-treatment, as well. During oxygen-free pyrolysis the product has higher carbon content which when heat-treated at a high temperature may approach the quality of the commercial CBs. Additional acid treatment removes the residual minerals. These treatments are not always practical because some benefits of the dual structure (especially the silica content) are lost. According to Norris the guaranteed quality pCB is between N300-N700 standard CBs [6].

In our research we used a styrene-butadiene rubber (SBR) because it is one of the major component of tires' formulations. Two types of CBs, namely a standard N660 and a pelletized pyrolytic CB (pCB_p) were involved in this study. To check the application potential of pCB_p, these CBs were used alone and 1: 1 blend ratio at a total filler content of 60 phr. Further aim was to examine the effect of additional organoclay. Previous studies have shown that the combination of organoclay and industrial CB may show excellent reinforcing effect in rubbers [8-9]. The I30.P organoclay was added in 10 phr. Learning from the literature is that rubber combinations having the

same hardness should be produced for comparison purpose [10]. Since organoclay (I30.P) increases the hardness more strongly than CB (due to a larger specific surface weight) the overall filler content was reduced to 50 phr. So, the related SBR gum contained 20 phr pCB$_p$, 20 phr N660 and 10 phr I30.P. The SBR compounds were tested to evaluate the mechanical properties (tensile strength, elongation at break, tear strength), dynamic mechanical properties (DMTA), the softening caused by cyclical and dynamic loading (Mullins effect, Payne effect [11]), and the quasi-static fracture mechanical properties. To determine the latter single edge-notched tensile (SEN-T) and trouser-shaped testpieces were used. For fracture mechanical characterization the J-integral and CTOD (crack tip opening displacement) methods were adopted. CTOD = 0.5 mm was chosen for the critical value.

Experimental

Materials, compounding The recipe used is given in Table 1. The rubber was mixed on a laboratory two roll mill (Labtech Scientific LRM-SC-110), friction was 1.3, the temperatures of the front and back rotors were 70°C and 50°C, respectively. The time of mixing was 27 min. The samples were cured in a Collin Teach-Line Platen Press 200E laboratory press at 160°C for the t$_{0.9}$ time (time needed to reach 90% of cure in rheometer) of the compounds with 5 MPa pressure producing sheets with 2 mm thickness. Curing studies were performed using MonTech Monsanto R100S rheometer, in the isothermal time sweep mode (1.667 Hz, 1° angle) for the samples at T=160°C for 45 minutes.

Table 1. Designation and composition of SBR mixes and the hardness values of rubbers.
Designation: MBTS-2-mercaptobenzothiazole

Designation	Composition [phr]								Hardness [ShA°]
	SBR	I30.P	N660	pCBp	ZnO	Stearic acid	MBTS	S	
SBR ref.	100	-	-	-	3	2	1.5	2	40±0
I30.P	100	10	-	-	3	2	1.5	2	50±1
N660	100	-	60	-	3	2	1.5	2	67±1
pCBp	100	-	-	60	3	2	1.5	2	63±1
N660+pCBp	100	-	30	30	3	2	1.5	2	63±1
N660+pCBp+I30.P	100	10	20	20	3	2	1.5	2	65±1

Testing Specimens (DIN 53504 Type 1 for tensile and ASTM D624 Type C for tear tests) were punched from the sheets. Tensile (ISO 37) and tear tests (ISO 34-1) were performed on a Zwick Z250 universal testing machine with a crosshead speed of 500 mm/min at room temperature. Each of above tests was repeated on five specimens to deduce the mean values. Strain softening (Mullins effect) was studied on the above dumbbell specimens, which were loaded sequentially to increasing strain levels, namely to 50, 100, 150 and 200%, respectively. After reaching the lower fixed strain, the specimen was fully unloaded before starting with its subsequent loading cycle up to the next, higher fixed, strain value. DMTA spectra were registered on rectangular specimens in tensile mode at a static preload 0.1 N with 0.1% strain. The frequency was 10 Hz and the spectra were taken in a temperature range of -100 to 60°C using a Q800 device of TA Instruments. The temperature ramp was 3°C/minute. DMTA technique was used to assess the Payne effect. It was investigated also in tensile mode, 0.01N static preload, however, at 30 °C using 10 Hz frequency with a strain sweep from 0.01 to 10% strain. Fracture mechanical tests were performed on single edge-notched tensile loaded (SEN-T) and trouser tear specimens. SEN-T specimens of 100 x 25 x 2mm dimension (length x width x thickness) with 10 mm initial notch length were loaded with 10 mm/min crosshead speed on the above mentioned Zwick testing machine. The crack tip opening displacement (CTOD) has been followed by visual inspection using a digital miscroscope. The camera was positioned in front of the crack in order to focus on the internal surface generated by

blunting and growing of the crack. J-integral tests were also performed on specimens, which were loaded up to 100% deformation at 200 mm/min crosshead speed in five cycles (to eliminate the Mullins effect) and notched afterward. The fracture energy from trouser tear ($J_{trouser}$) was determined on 100 x 30 x 2mm specimens (length x width x thickness) with an initial notch length of 40 mm at 100 mm/min deformation rate.

Results and discussion

Mechanical behavior The tensile strength and ultimate tensile elongation data are displayed in Figure 1. a. The test samples have same hardness, with the exception of the unfilled SBR and SBR with I30.P, because they serve as references. The maximum tensile strength with the lowest ultimate tensile strain delivered N660. In contrast, pCB_p leads the lowest tensile strength and the largest deformability. This suggests that pCB_p is a less active filler than N660. As expected, the blend of N660 + pCBp yields intermediate results. The tensile performance of the gum with N660+pCBp+I30.P is slightly better than the mixture containing only pCBp, although the filler level in this case in only 50 phr.

In Figures 1. b. the tear strength and trouser tear ($J_{trouser}$) data can be seen. $J_{trouser}$ was determined by the Eq. 1 where 'F_{tear}' is the constant force after the onset of crack propagation, and 't' is the thickness of the specimen.

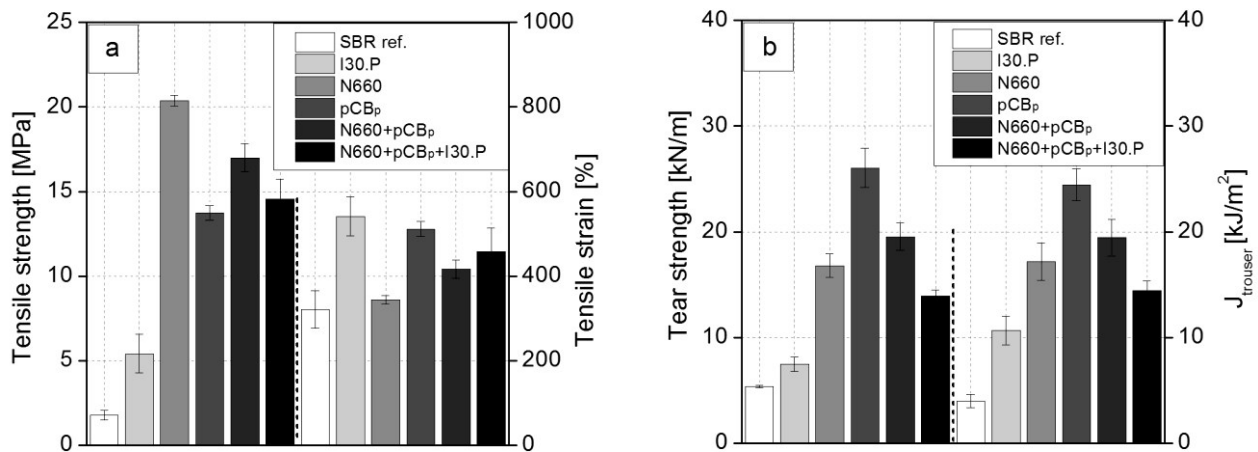$$J_{trouser} = \frac{2 \cdot F_{tear}}{t} \tag{1}$$

Figure 1. Mechanical and fracture mechanical properties of the SBR rubbers:
a.) Tensile strength and ultimate tensile strain data; b.) Tear strength and $J_{trouser}$ values

It is striking that the highest tear values exhibit the pCB_p-containing mix. This positive effect occurs also in combination with N660 and also I30.P. This effect may be linked with the wide distribution of the pCB_p particles. The large/small particles force the crack to follow a zigzag path associated with higher energy absorption. We expected good results from I30.P, because the layered structure of clay may further increase the crack propagation resistance. This effect was, however, not observed. Interesting observation is that there is a clear correlation between the various crack opening modes (tear strength - I mode, $J_{trouser}$ - III. mode), the values are numerically very similar and their units are the same.

DMTA behavior, Payne-effect, Mullins-effect Figure 2. a. shows the DMTA results (loss factor and storage modulus). In terms of loss factor, a marginal change in the glass transition temperature (T_g), read at the temperature linked to the maximum of the tan δ peak, was found. Increasing reinforcement yields decreasing tan δ peak value, because the segmental motion of the rubbers chains is hampered in the filler-rubber interphase. In this regard, the strongest rubber-filler

interaction was found for the N660+pCB$_p$+I30.P sample, which is clearly attributable to the effect of I30.P. This mixture exhibits the highest E' in the rubbery range. Between the E' values of the other CB filled mixtures a negligible difference can be observed.

Figure 2. b. shows the evolution of the Payne effect. The E' of CB filled rubbers has significant amplitude dependence. Naturally, it is influenced by the filler activity: with increasing specific surface weight of CB the related Payne effect also increases. Note that the initial E' values of the pCB$_p$ containing samples were lower than those with N660. I30.P containing (p)CB filled rubber provides the highest E', and it shows the greatest Payne-effect, as well. According to Figure 2 the layered structure organoclay has significant effect on the dynamic properties. The application of I30.P leads to enhanced rigid filler-rubber interactions which cause increasing E' at low strains. However, this effect diminishes with increasing strain values due to damage of the filler "network".
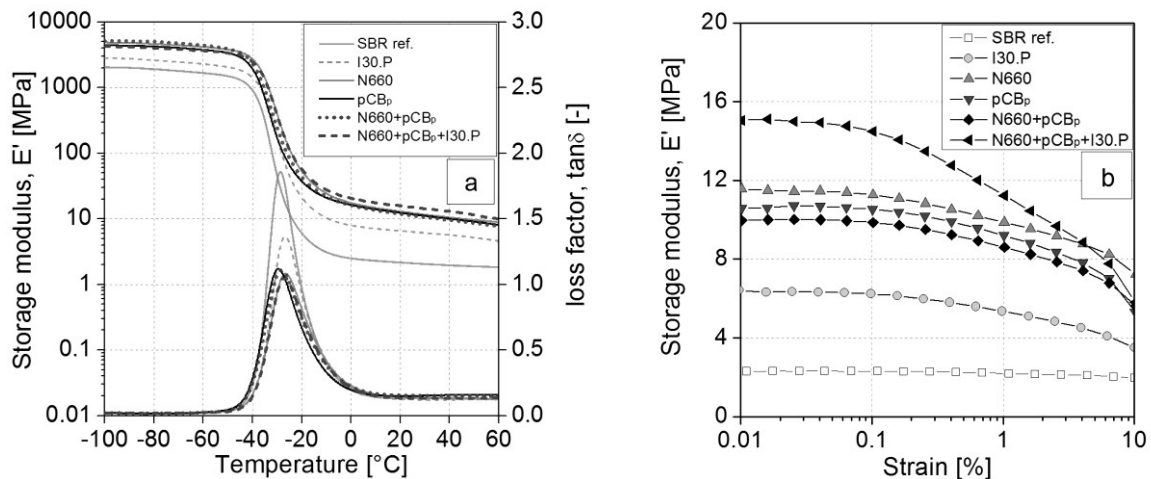

Figure 2. Dynamic mechanical thermal properties, DMTA results of the SBR rubbers:
a.) Storage modulus (E') and mechanical loss factor (tan δ) as a function of temperature;
b.) E' as a function of strain (Payne effect)

In Figure 3 we illustrate the Mullins effect schematically and also the way, how this has been considered in this work. The Mullins effect has been quantified by considering the force ratio of the cyclic and separate monotonic loading of the specimens at a given strain as a function of the loading cycles. Change in the dissipated energy (E$_{diss}$) has been considered in a similar way, i.e. the hysteresis was related to the overall energy introduced. The corresponding data are listed in Table 2. The values are quite similar for the CB containing samples. As expected, the Mullin's effect becomes more prominent with increasing load level. Furthermore, the largest softening occurred in the first cycle. It seems to I30.P slightly increased the Mullins-effect.
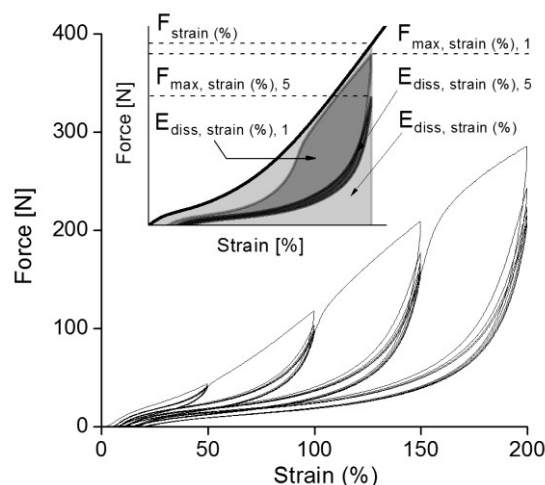

Figure 3. A typical Mullins behavior and its quantification schematically

Table 2. Mullins effect for the filled SBR rubbers. Mullins effect is quantified by $F_{max, strain (\%), cycle (number)}$ and $E_{diss, strain (\%), cycle (number)}$

Designation	Mullins-effect [%]							
	$F_{max, 50, 1}$	$F_{max, 150, 1}$	$F_{max, 150, 1}$	$F_{max, 150, 5}$	$E_{diss, 50, 1}$	$E_{diss, 50, 5}$	$E_{diss, 150, 1}$	$E_{diss, 150, 5}$
SBR ref.	85±1	83±1	92±2	90±2	8±2	6±2	6±1	5±1
I30.P	93±3	87±3	97±2	91±2	16±1	9±2	20±0	10±1
N660	92±5	90±5	97±6	92+4	20±2	13±2	35±3	14±1
pCB$_p$	93±2	88±2	95+3	85±3	19±1	12±0	34±1	12±0
N660+pCBp	88±3	83±3	95±4	83±3	18±3	11±2	24±1	10±1
N660+pCBp+I30.P	86±2	81±1	91±1	81±1	17±1	12±0	25±0	11±0

Fracture mechanical results J-integral values were calculated by Eq. 2, where η is an geometric factor with the value of 0.9, B is the thickness, of test piece, W the width of the test piece, a_0 the initial notch length, U is the area under the measured curve.

$$J = \frac{\eta \cdot U}{B \cdot (W - a_0)} \qquad (2)$$

As critical J-integral (J_c), traced to crack onset, the J-integral value at CTOD=0.5 mm has been considered. It can de stated that the cyclic preloading markedly reduced the above J_c data confirming effect of Mullins strain softening. For the SBRs with N660+pCB$_p$ and N660+pCB$_p$+I30.P a synergistic effect can be seen. It is hypothesized that an efficient stress redistribution via the fillers' dispersion occurs during crack blunting and crack onset whereby the material's resistance is enhanced.
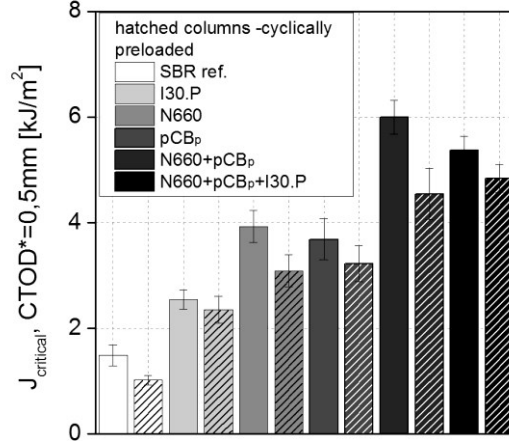

Figure 4. $J_{critical}$ values determined at CTOD*=0.5mm

Conclusion

In this work the tensile mechanical and fracture mechanical behaviors of SBR gums having the same Shore A hardness and filled with industrial CB, pelletized pyrolytic CB (pCB$_p$) and organoclay in various combinations were determined. The results can be summarized as follow.
N660 yielded higher tensile strength and lower elongation at break than pCB$_p$ confirming its higher reinforcing activity. On the other hand, the tear strength with pCB$_p$, even when combined with N660, was higher than with CB alone. This was attributed to a favorable effect of the dispersion (in macro-, micro-, nanoscale). Organoclay may improve the tensile mechanical properties, but has no impact on the tear and trouser strengths, of CB filled SBR mixes. DMTA results showed that introduction of organoclay increased the E' value in rubbery range. Consequently, the Payne-effect become also stronger. Synergistic effect with respect to crack initiation (J_c) was observed for

N660+pCB$_p$ mixture. It was traced to effects of the fillers' dispersion supporting an efficient stress transfer/relieve locally thereby enlarging the related damage zone. Related data on SBR with N660+pCB$_p$+I30.P supported this hypothesis. J$_{trouser}$ agreed with the tear strength suggesting that even under mode III-type loading mode I, i.e. crack opening, conditions prevail. J$_c$ values of the cyclically preloaded specimens were lower than those of the virgin ones. This underlines the importance of Mullins-effect on the fracture mechanical parameters.

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