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Feasible incorporation of devulcanized rubber waste in virgin natural rubber

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Abstract Devulcanized rubber waste produced from end-of-life passenger tyres by continuous shear flow stage control reaction technology was used both as filler and as part of rubber in a natural rubber matrix to develop the use of the rubber compound and lower the cost. The measurements of cure characteristics, swelling behaviour, crosslink density and dynamic and mechanical properties were carried out in our laboratory. In the present study it was found that using devulcanized rubber as part of rubber yields much better properties than using it as filler. Up to 15 phr devulcanized rubber used as filler and up to as much as 50 phr devulcanized rubber used as part of rubber can be incorporated in a new product without any noteworthy deterioration in performance arising.

Introduction

The environmental problems created by waste rubber and discarded tyres have become serious in recent years. Also the management of waste rubber has been a growing problem in the rubber industry [1]. The global consumption of elastomers has grown to a yearly production level of about 18 Mtons/2002 [2]. According to the end of life vehicle (ELV) directive (2000/53/EC), car makers must re-use or recover 85% of ELVs by weight per vehicle and by the year 2006 at least 80% of that weight must be re-used or recycled. For the year 2015 this target rises to 95% of ELVs by weight, 85% of which must be re-used or recycled [3]. Therefore, utilization of rubber waste is an urgent economic and environmental task faced by industry worldwide [4].

Many attempts to recycle waste tyres have been made for both environmental and economic reasons [5–8]. Several studies have been performed on the mechanical properties of rubber materials containing crumb rubber and regarding the possibilities of modifying crumb rubber to improve those properties using chemical, mechanical or biotechnological methods [9–14]. However, no modification method has so far resulted in materials with properties equal to those of virgin rubber materials. Partly devulcanized rubber is claimed to be compatible with the virgin material, to show advantages in processing and to lead to lower cost of compound. The technology has been found to produce high-quality devulcanized rubber in a continuous process by selectively breaking the sulphur crosslinks of rubber through shear flow stage reaction. In this technology the devulcanization can be controlled by choosing an appropriate screw configuration, operating temperature and screw speed [15].

In the present work, the devulcanized rubber produced from end-of-life passenger tyres by continuous shear reaction technology was used as filler (Dev.F) and as a part of rubber (Dev.R) in virgin natural rubber (NR) to identify the application properties of the rubber compounds obtained. The examinations of cure characteristics, swelling behaviour and crosslink density as well as dynamic mechanical analysis and analysis of the mechanical properties of the compounded materials

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were performed in our laboratory. The target was the realistic incorporation of devulcanized rubber in natural rubber matrix and the improving of the properties of these compounds.

Experimental

Materials

The virgin natural rubber (SMR5) used as a matrix in this study was prepared according to ASTM D 3184 (formula 2A). SMR5 was masticated using 0.2–0.5 phr peptising agent Struktol A86 by Schill & Seilecher. The devulcanized rubber generated from passenger tyres by applying continuous shear flow reaction treatment was supplied by Hauler Ltd, Finland. The particle size of ground rubber powder used in the devulcanizing process was around 4 mm. The processing temperatures were in the range 180–230 °C and the screw speed was 375 rpm. The yield with these conditions was 80–100 kg/h. The composition of the devulcanized rubber derived from the passenger tyres was app. 70 wt-% SBR, 20 wt-% vinyl-SBR, 10 wt-% polyisoprene and other tyre rubber additives in an unknown ratio. The form of the obtained devulcanized rubber was quite similar to that of virgin uncured rubber. It contained 3% fabrics and was metal-free. The soluble fraction of it in toluene was 32 wt-% at room temperature.

Sample preparation

The compound recipes are given in Table 1. The loading amounts of the waste rubber were 10, 30, 50 phr. In the formula of Dev.F the devulcanized rubber was used as filler and the amounts of curatives were added on the basis of the virgin rubber content; in the formula of Dev.R the devulcanized rubber was considered an elastomeric component and the amounts of curatives were added on the basis of the total rubber content. In the latter case the amount of devulcanized rubber was calculated with respect to the soluble fraction; the soluble part is considered as unvulcanized rubber.

To improve the mixing quality and to prevent prevulcanization, a two-stage mixing process was applied. The components, except sulphur, were mixed in a laboratory-size internal mixer (David Bridge & Co). The total volume of the mixer was 1.2 L and the temperature was kept around 65 °C. About 80% of the total volume of the mixer was filled.

The order and time period of mixing were as follows:

Warming NR: 1 min
Adding ZnO, stearic acid and ½ carbon black: 3 min
Adding ½ carbon black and devulcanized rubber: 2 min
Adding accelerator CBS: 1 min

The sulphur was added afterwards in a two-roll mill. At first the rubber premixture was warmed up for 1 min, after which the sulphur was added. After 3 min the sheet was drawn away from the mill and cooled down to room temperature. The nip gap was 2 mm and the temperature of the rolls was not more than 65 °C to prevent any scorch problem during the mixing step.

About 1 day after mixing the vulcameter runs were carried out to determine the proper curing conditions. The compounds were moulded into the sample slabs and buttons at 160 °C using an electrically heated compression moulding press.

Cure characteristics

A Monsanto 100S oscillating disc rheometer was used to obtain the cure characteristics at temperature 160 °C according to ISO 3417.

Swelling and crosslink density

Circular test pieces of diameter 10 mm were cut from the vulcanized sheets (2 mm thickness) and soaked in toluene at room temperature (23 °C). The specimens were removed from the solvent, blotted and weighed

Table 1 The compound recipes[a] N-cyclohexyl-2-benzothiazyl sulphenamide

Formulation (phr)	NR	Dev.F10	Dev.F30	Dev.F50	Dev.R10	Dev.R30	Dev.R50
NR	100	100	100	100	96.8	90.4	84
Devulcanized rubber	–	10	30	50	3.2	9.6	16
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
N-220	35	35	35	35	35	35	35
CBS[a]	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25

quickly at periodic intervals. The weighing was continued up to equilibrium swelling (around 72 h). The swelling degree $Q(t)$ of rubber in solvent was calculated using the equation

$$Q(t) = \frac{M_t - M_i}{M_i},$$

where M_i is the initial weight of the sample and M_t, the weight at time t. [16, 17].

For vulcanizates containing reinforcing fillers such as carbon black, the volume fraction of rubber v_r for use in the calculation of crosslink density is obtained from the following expression derived by Kraus: [18, 19]

$$\frac{v_r}{v_{rf}} = 1 - m\phi/(1-\phi),$$

where v_{rf} and v_r are the volume fractions of filled and unfilled rubber in the swollen rubber phase, respectively, m is the rubber-filler interaction parameter and ϕ the volume fraction of the filler.

The crosslink density of the gels was calculated from the Flory–Rehner equation. [16, 17]

$$v = \frac{\ln(1-v_r) + v_r + \chi v_r^2}{2V_s\left(0,5v_r - v_r^{1/3}\right)},$$

where v is the crosslink density, V_s the molar volume of the swelling solvent, v_r the rubber fraction from the Kraus equation and χ the polymer solvent interaction parameter: $\chi = 0.393$ for the NR-toluene system. [20].

Dynamic mechanical analysis

The dynamic mechanical analysis of the mixtures was performed using a dynamic mechanical thermal analyzer (DMA Perkin Elmer, Pyris Diamond). Specimens of dimension 20 × 6 × 2.3 mm were analyzed in tension mode at a constant frequency of 10 Hz under nitrogen gas in the temperature range from –100 to 170 °C. The heating rate was 2 °C/min. The temperature corresponding to the peak in the tan δ versus temperature plot was taken as the glass transition temperature (T_g).

Mechanical properties

Tensile strength and tear strength measurements were performed with a Monsanto Tensometer 10. Tensile specimens were dumbbell-shaped test pieces according to ISO 37 (Type 1) and tear resistance was determined with trousers test pieces according to ISO 34 (Type A). Testing speed in tensile tests was 500 mm/min, and 100 mm/min in tear tests. An abrasion resistance test was carried out according to ISO 4649, involving an abrasive run of 40 m with loading 10 N. Hardness was tested based on ISO 7619 using a ShoreA durometer.

Morphology

The morphology of the tensile fractured surfaces of samples was investigated using a scanning electron microscope (JEOL JSM-T100). The fractured surfaces were sputter coated with gold powder using a K550 sputter coater.

Results and discussion

Cure characteristics

The torque as a function of devulcanized rubber content is shown in Fig. 1. For the Dev.F system, the minimum torque (M_L) remains stable with the different devulcanized rubber content. However, in the Dev.R system M_L has slightly increased with the higher devulcanized rubber content. This indicates some interaction between the devulcanized rubber and the virgin rubber. The slightly lower M_L value of the Dev.F system compared with that of the Dev.R system could be explained by some rupture of main chains in the devulcanization causing a lubricating lower molar mass fraction in devulcanized material.

Maximum torque (M_H) is a measure of the elastic modulus related to the crosslink density (see Fig. 1). The maximum torque decreases in the Dev.F compounds and increases in the Dev.R compounds. This indicates that the crosslink density is lower in the Dev.F/NR than in the Dev.R/NR system. Further vulcanization occurred in Dev.R compounds because of a greater amount of curing agents. This conclusion

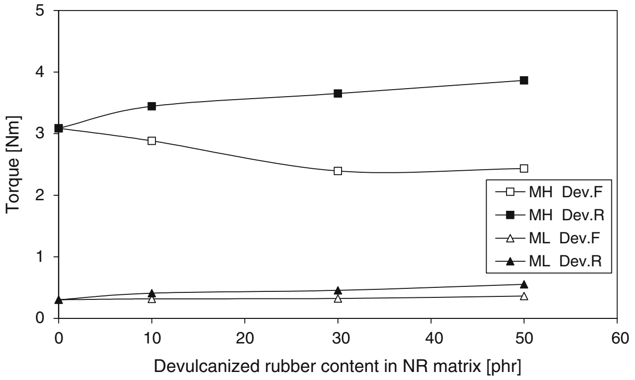

Fig. 1 M_L and M_H as a function of devulcanized rubber content

also has been proved by Isayev et al. [1]. In the Dev.F system the torque reduction can be explained by the lower concentration of sulphur in the mixtures. The devulcanized rubber acts as a plasticizer because shorter chains and smaller molecule pieces exist after the main chain breakage. This also leads to torque reduction (see Table 1).

Figure 2 gives the relationship of optimum cure time (t_{90}) and scorch time (t_{S2}) as a function of devulcanized rubber content. The shorter scorch time (t_{S2}) in the blends indicates that the crosslinking reaction starts earlier. It is suggested by Ishiaku et al. that a reaction product between the NR matrix and the devulcanized rubber might catalyze the crosslinking reaction [21]. Also, diffusion of accelerator from devulcanized rubber into virgin rubber would reduce scorch time [22]. Since the scorch time is slightly decreases in these systems, the processability does not change significantly with the devulcanized rubber loading.

Optimum cure time (t_{90}) is the vulcanization time required to obtain optimum physical properties. It can be observed from Fig. 2 that the optimum cure time changes slightly with the waste rubber content. It is concluded that the incorporation of waste rubber in virgin NR matrix does not effect the cure time significantly.

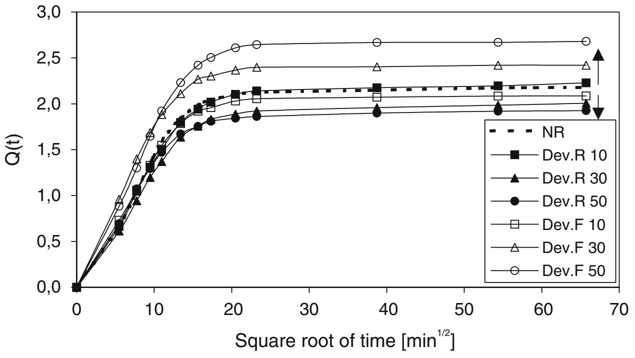

Fig. 3 Swelling degree as a function of square root of time in toluene

Swelling behaviour and crosslink density

The investigation of swelling equilibrium can help to elucidate the structure of the polymer network. Figure 3 shows the degree of swelling of the NR compounds with various Dev.F and Dev.R contents in toluene. It is found that all cases show similar behaviour. The rate of toluene uptake is relatively fast in the initial stage and reaches an equilibrium state at the same time. In the equilibrium state, the degree of swelling rises in the case of increasing Dev.F loading and decreases in the case of increasing Dev.R loading.

According to Fig. 4, the crosslink density decreases with the Dev.F compounds and increases with the Dev.R compounds as a function of waste rubber content. The maximum swelling ratio behaves in just the opposite way. There are new active crosslinking sites in devulcanized rubber, which continue to form crosslinks during revulcanization; the greater the devulcanized rubber content, the more active crosslinking sites there are. However, in the case of Dev.F, increasing waste rubber loading decreases the concentration of sulphur and the crosslink density is lower. The conclusions are consistent with the cure characteristics.

Dynamic mechanical analysis

The results of tangent delta of the dynamic mechanical analysis are shown in Fig. 5. Tan δ_{max} was found to shift to a higher temperature; namely, the glass transition temperature rose with increasing Dev.F rubber loading where the devulcanized rubber was considered as inactive filler. This is because waste

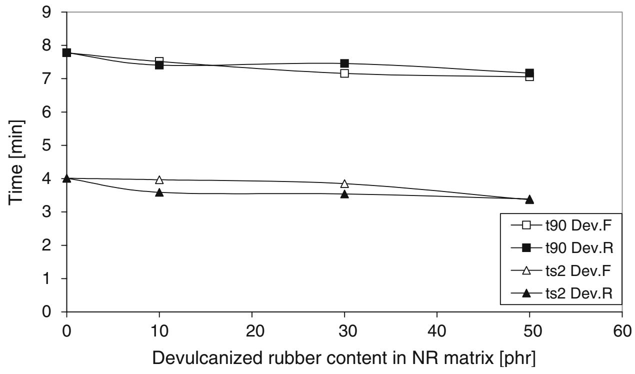

Fig. 2 Optimum cure time (t_{90}) and scorch time (t_{S2}) as a function of devulcanized rubber content

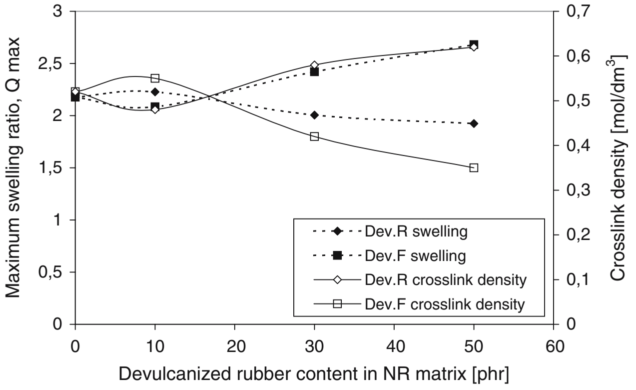

Fig. 4 Maximum swelling ratio and crosslink density as a function of devulcanized rubber content

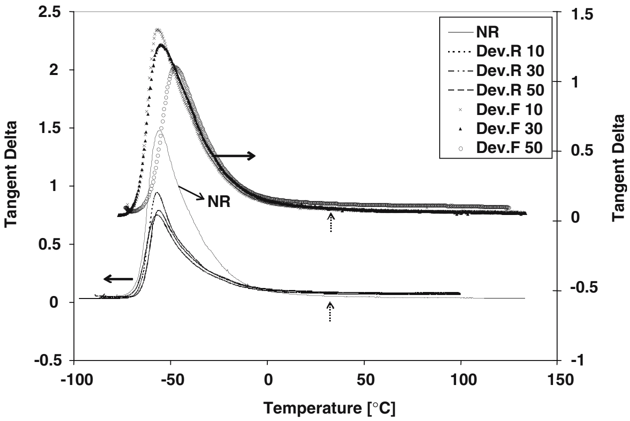

Fig. 5 Plot of tan δ versus temperature

rubber contains 70% of SBR, which has a higher glass transition temperature than NR matrix. However, in the Dev.R system the amount of devulcanized rubber is much lower than in the Dev.F system and the glass transition temperature does not change significantly with different waste rubber content.

As the waste rubber content increases, the peak height drops, especially at high waste rubber loadings. This was found both for Dev.F and Dev.R systems. The results suggest that increasing the waste rubber content causes an increase in elastic behaviour. The higher tan $\delta_{\max}$, the greater the mechanical losses. These losses are related to the high energy input required for the motion of the molecular chain of the polymer as the transition is approached [21]. The rolling resistance becomes higher with the introduction of waste rubber since the values of tan δ increase with the devulcanized rubber loading in the temperature range 30–80 °C (see Fig. 5).

Mechanical properties

Tensile strength, elongation at break, tear strength, abrasion resistance and hardness were used to evaluate the mechanical properties of the compounds. In comparing the mechanical properties of Dev.F and Dev.R compounds, the latter gave better results. If the devulcanized rubber participates in the crosslink reaction as it did in the case of the Dev.R system, the mechanical properties are improved at a loading of 10 phr and quite good properties are obtained at loadings of 30 and 50 phr loading. However, the inactive devulcanized rubber fillers generally cause a deterioration in the mechanical properties with higher filler loading, although the retention values of properties range from good to excellent at a loading of 10 phr. The mechanical properties are discussed in the following.

The effect of the waste rubber content on tensile strength and elongation at break is shown in Figs. 6 and 7. Tensile strength and elongation at break deteriorated with the loading of inactive devulcanized rubber waste. The reason is probably the uncontinuous and imperfect structure in the blends. However, much better tensile strength and elongation at break is achieved if devulcanized rubber takes part in the crosslink reaction. We assume that the devulcanization rubber has active crosslink sites and that there is a greater amount of curing agents in the Dev.R system. Revulcanization occurs between devulcanized rubber and virgin rubber and higher crosslink density is obtained in the system. In the Dev.F system the devulcanized rubber is considered as inactive filler and the concentration of curing agent is lower, even though there exists the same amount of active crosslink sites in the devulcanized rubber. The vulcanization reaction is not complete and perfect, which leads to a decrease in tensile strength and elongation at break.

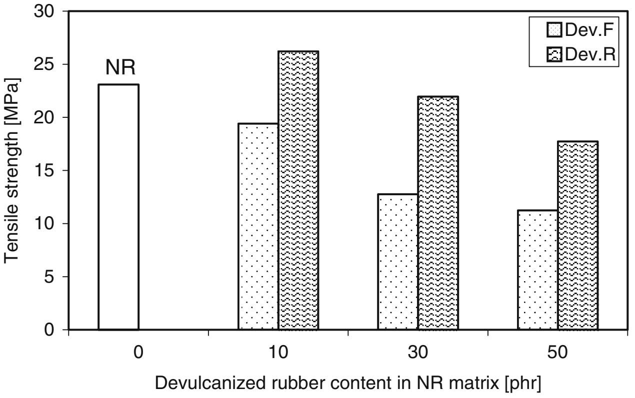

Fig. 6 Tensile strength versus devulcanized rubber content in NR matrix

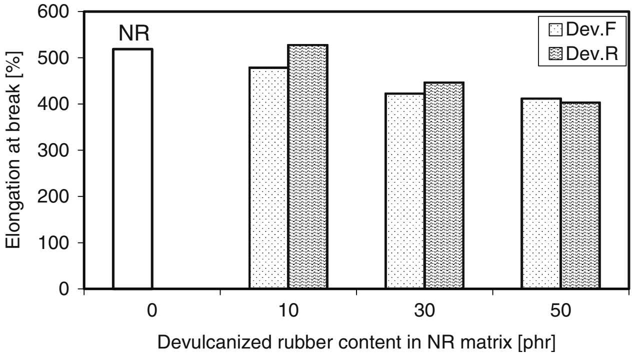

Fig. 7 Elongation at break versus devulcanized rubber content in NR matrix

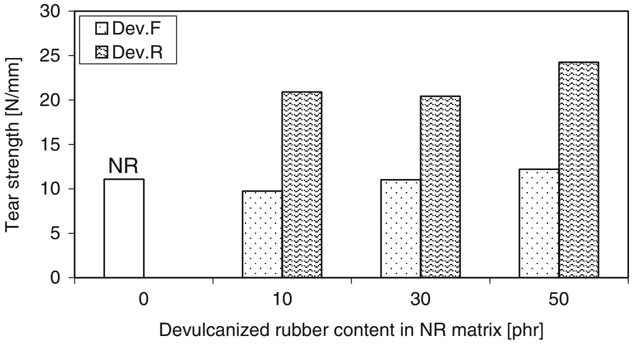

Fig. 8 Tear strength versus devulcanized rubber content in NR matrix

The effect of waste rubber content on the tear strength is given in Fig. 8. With the Dev.F compounds, tear strength decreases at a loading of 10 phr, but with a loading of over 30 phr an improvement is noticed. In the case of Dev.R compounds, the tear strength is even greater than twice that of the NR matrix with different waste rubber content. Generally, the higher the waste rubber loading, the higher the tear strength. These results indicate good compatibility and interfacial adhesion between NR matrix and waste rubber. Also, double bonds are left in the vulcanizates and even more active crosslinking sites exist after devulcanization. The improved tear strength is due to the crosslink reactions between devulcanized rubber and virgin matrix.

The variation in abrasion resistance with waste rubber content can be found in Fig. 9. It indicates that the abrasion resistance is improved with Dev.R loading but impaired with Dev.F loading. The reason for the deterioration in abrasion resistance in Dev.F compounds could be the shorter fragments and chains in the compounds and also the net decrease in network chains [21]. Complete crosslink reaction and perfect network structure can be achieved in the Dev.R system. This conclusion can be reached by comparing the results of the Dev.F and Dev.R compounds.

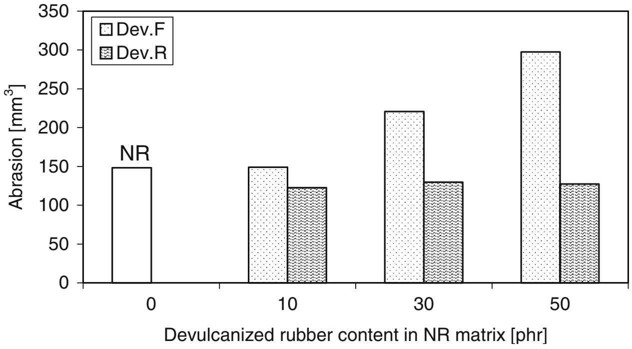

Fig. 9 Abrasion versus devulcanized rubber content in NR matrix

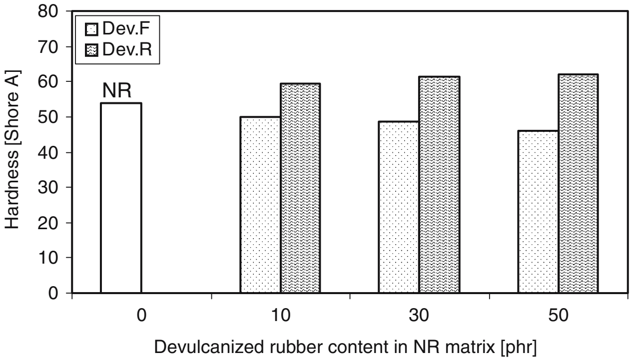

Fig. 10 Hardness versus devulcanized rubber content in NR matrix

The plot of hardness versus waste rubber content is shown in Fig. 10. Hardness drops slightly with an increase in Dev.F loading and rises with an increase in Dev.R loading. The shortest fragments, lack of sulphur and low crosslink density are reasons for the decrease in hardness in the Dev.F compounds. In comparison, the Dev.R systems with sufficient sulphur and higher crosslink density have better hardness.

Morphology

SEM photomicrographs of the tensile fractured surface of compounds with 10 phr devulcanized rubber are shown in Figs. 11 and 12. It can be seen that quite good adhesion exists between the devulcanized rubber and the NR matrix in the Dev.R system and that a crosslink reaction has actually occured between devulcanized rubber and the virgin matrix. However, clear phase

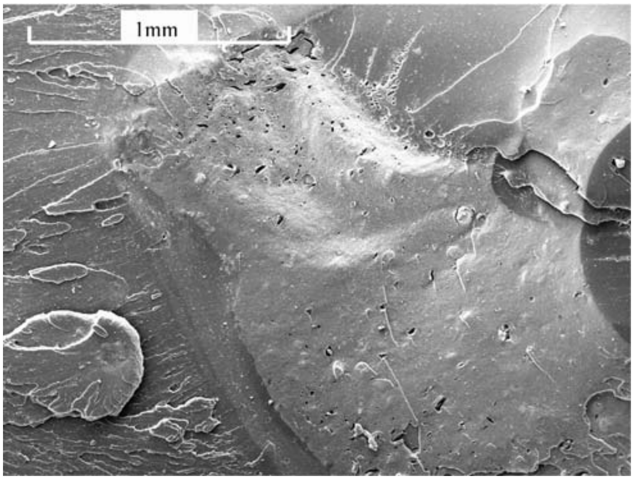

Fig. 11 SEM of Dev.R 10 phr tensile fractured surface

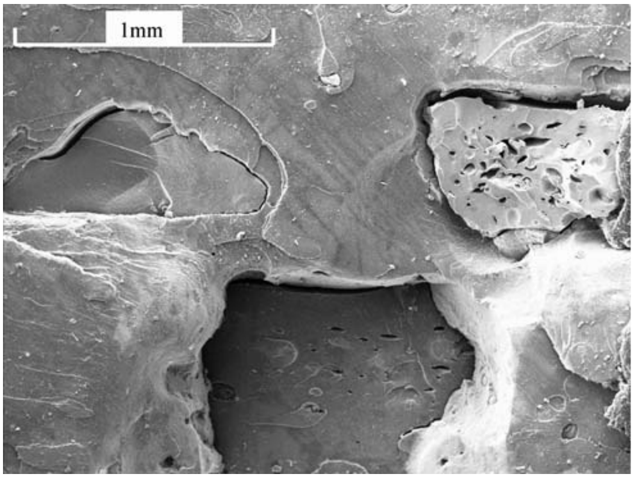

Fig. 12 SEM of Dev.F 10 phr tensile fractured surface

separation can be observed for the Dev.F compound. The weak adhesion causes impairment of the mechanical properties, which is in agreement with the former conclusions.

Conclusions

Devulcanized rubber waste produced with continuous shear flow reaction technology incorporated in virgin NR matrix compounds as both inactive filler and part of rubber. Results show that cure time and scorch time remain quite stable with both systems with an increase in devulcanized rubber content in the NR matrix. It was evident that the processability of the systems did not change significantly with the devulcanized rubber loadings. When Dev.F was introduced in virgin rubber, an increase in swelling degree and a decrease in crosslink density could be observed. Dev.R compounds behaved in quite the opposite way. Tensile strength, elongation at break, hardness and abrasion resistance deteriorate with an increase in waste rubber loading in Dev.F compounds. At 10 phr waste rubber loading in Dev.R compounds, tensile strength and elongation at break are improved compared to the case with virgin rubber. At higher concentration of waste rubber these properties are impaired. Tear strength was improved in the Dev.R system with all waste rubber loadings applied in the tests. Also the abrasion resistance and hardness are still better at 50 phr waste rubber loading in Dev.R compounds than in virgin natural rubber. Based on the achieved results, an incorporation level up to 15 phr of Dev.F and up to even 50 phr of Dev.R is realistic in virgin natural rubber. At these levels there is no significant deterioration in performance.

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