Distillation based recovery of solvents used for tyre solubility

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Abstract

About 1.4 billion tyres for vehicles are manufactured annually all over the world. Every year an almost equal number of tyres are generated as waste. Knowing the composition of tyres, material recovery is a possible option for further utilization and can be realized with several techniques.

Beside the common constituents of tyres different solvents can be used for enhancing the rubber adhesivity and possible extracting of useful materials. In order to find the soluble components, solubility tests were carried out. Passenger car tyres were selected and eight different solvents. Shredded tyres with an average diameter of 0.2 mm were used in solubility tests in order to increase the mass transfer surface and decreasing the contact time. Temperature was varied from ambient to the value of boiling point of each solvent. Solvent was transported into the inner part of rubber by diffusion resulting in partial dissolution of the non-space polymer. The swelling of space polymer constituents could be observed at the same time. Swelling measured by mass by volumetric increase as well, and it was in correspondence with weight measurements and bulk densities. Extracts were analysed to define the dissolved components with X-ray fluorescence (XRF) spectrometer and GC-MS.

Solvents were recovered by common distillation. Volatile compounds extracted from the tyre were present in the distillate phase. GC-MS analysis proved the efficiency of the different solvents. 1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl was determined in the distillates. The possible source of this amine was isocyanates as binding components of textiles to polymer. Another distillation step of the solvents proved that further purified solvents met the quality standards. Therefore it could be concluded that the proper recovery of the solvents needs the application of rectification so that, they could be reused again or for other industrial tasks.

Keywords

Shredded tyres, swelling, extraction, solvent recovery, distillation

1. Introduction

While refuel cars, sometimes petrol or any other organic solvents' droplets fall accidentally on the tyre from the charging pipe. At this point the question presents itself: does the petrol react with the tyre material? Can it damage the tyre, or just extract some of its components? Does this shorten the tyre's lifetime? To answer these questions several solvents were selected to our experiments. Examination extended to basic solvents which are main products of the chemical industry. Besides the everyday situation of petrol droplets, treatment of tyre material with solvents can contribute to enhanced separation of metal and rubber parts of tyre by swelling, which is a key factor in material recycling.

Swelling depends on the solvent itself and the rubber matrix and the network density. Denser the network less the swelling factor [1,2]. Besides swelling, extraction and chemical reaction can take place, as well, but the dominant phenomenon is swelling that can be measured either by mass or volume [3].

Based on these considerations different solvents can be used for enhancing the rubber adhesivity and possible extracting of useful materials. In order to find the soluble components, solubility tests were carried out. Passenger car tyres were selected and eight different solvent such as cyclohexane, dichloro-methane, acetone, normal-hexane, normal-heptane, gasoline, ethyl-acetate, and gamma-valerolactone were applied. Solvent selection was based on relevant literatures [4-9] and environmental concerns were taken into account.

Shredded tyres with an average diameter of 0.2 mm were used in solubility tests in order to increase the mass transfer surface and therefore decrease the contact time. Temperature was varied from ambient to the value of boiling point of each solvent. Solvent was transported into the inner part of rubber by diffusion resulting in partial dissolution of the non-space polymer. The swelling of space polymer constituents could be observed at the same time. Swelling, extraction and the opportunity of chemical reactions were tested. Experiments were scheduled as follows:

- preparation of shredded tyres by washing with distilled water,
- vacuum drying of shredded tyres,
- weight of shredded tyres,
- dipping of samples into solvent, saturation with solvents,
- measure of mass and bulk volume of shredded tyres after 1 h, 2 h, 4h, 24h, 48h.

After the experiments, the recycling of solvents with distillation was carried out aiming for a complete recycling. By fractionate distillation each 10 ml of distillate was analyzed by GC-MS to make sure of the distillate is pure solvent and determine the rate of recycling. In order to determine the extracted components of shredded tires the bottom product was analyzed by X-ray fluorescence (XRF) emission technique.

2. Results and discussion

Table 1 summarizes the results of swelling tests including increase in mass and volume at different temperatures for each selected solvents.

Table 1 summary of increase in mass and volume relating to the selected solvents at different temperatures

solvent	Boiling point of solvent [°C]	Density of solvent [g/cm^3]	Increase in mass %			Increase in volume %			Extrac-tion
			20°C	**30°C**	**50°C**	**20°C**	**30°C**	**50°C**	
dichloro-methane	40	1.325	181.08	181.95	-	105.53	103.75	-	yes
cyclohexane	81	0.779	121.13	126.90	121.86	139.17	133.33	134.43	yes
n-hexane	69	0.659	44.46	52.11	48.80	52.78	66.53	65.69	yes
acetone	56	0.791	5.32	5.17	-	11.25	11.69	-	yes
ethyl-acetate	77	0.901	27.93	21.79	30.62	23.80	15.13	18.33	yes
n-heptane	98.4	0.684	-	61.16	-	-	82.33	-	yes
gamma-valerolactone	208	1.050	-	17.35	-	-	37.78	-	no
Petrol (95)	54-186	0.72-0.77	112.62	110.69	108.63	130.74	125.63	126.05	yes

Swelling was spectacular in the case of dichloro-methane: the transparent solvent turned to black and enormous increase was measured in mass: the final mass was 2.8-times the initial, i.e. about 180% increase could be reached. Due to relatively high density of dichloro-methane the increase in mass was higher than that of in volume. Dividing the final mass measure after 48 h of dipping by final volume of samples it equals to the solvent density (281.08/205.53=1.3). Regarding the effect of temperature no significant effect on increase in mass or volume could be detected, opposite to our expectations. Molecular diffusion can be enhanced with increasing temperature, but the back diffusion from solid to liquid phase is enhanced, too resulting in an occasional deviation between the measured values.

Acetone caused insignificant change in the samples in mass (5%) but noticeable in volume (11%). The degree of solvents' effect on mass from smallest to the greatest is as follows: acetone, gamma-valerolactone, ethyl-acetate, n-hexane, n-heptane, petrol, cyclohexane and dichloro-methane. Due to the different relative densities, ranking of effects on volume differs: most significant volumetric change could be achieved when dipping the tyre samples into cyclohexane or petrol. Considering petrol's effect it can be stated that with increasing contact time the swelling is more intensive, but the significant increase takes place in the first 15 minutes. Noteworthy to emphasize that in our experiments shredded tyre samples were dipped into the solvent, and the effect of contact surface was out of scope of our study. When one parks a car in a bog pool of petrol or a sump, the deformation of tyres should be taken into account.

GC-MS analysis of solvents proved that not only swelling but extraction and reaction took place inside the rubber matrix. 1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl was detected in samples of all tested solvents except gamma-valerolactone. Amine compounds are usually used in a form of isocyanates as binding components between textile and rubber in tyres.

After the distillation of used solvents, the remaining black gel-like bottom products were analysed by XRF. Elemental composition of bottom product verified that chemical reaction took place between the solvents and the rubber matrix. The bottom products contained 3.42-7.12 wt% (related to the total mass of bottom product) of sulfur. The detection of sulfur clearly indicates the breaking up of sulfur-hydrogen and disulfide bonds i.e. the cross bindings of rubber polymers. Considering the effect of temperature on sulfur extraction, a reversed ranking could be observed which was inconsistent to our expectations. Diffusion was enhanced by temperature, however extracted sulfur content decreased, consequently we assume that the solvent reacted with the polymer chains while breaking up the cross bindings at lower temperatures. Among other traces of elements zinc was in remarkable amount (5.4 wt%) in the bottom product of experiments with cyclohexane at 50°C.

Recycling of solvents

Taking into account the small quantity of solvent recycling experiments were carried out in batch mode. Due to the low boiling points of solvents (except gamma-valerolactone) atmospheric distillation was carried out. Distillates were collected in 10 ml fractions, and each fraction was analysed. When extraction occurred during the dipping and volatile compounds were extracted, they could be detected in the distillate phase. In the cases of n-hexane, cyclohexane and ethyl-acetate a distillate/feed ratio of 0.66 could be reached. Until this point he temperature was constant i.e. the boiling point of the solvent. After the recovery of 66.7% of solvents as distillate the temperature increased which points to the fact that the rest of feed contained solvent modified state and the extracted compounds. In all cases the 1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl amine component was detected in the 7^{th} fraction but it was in traces. The low concentration of amine in the solvent is in ppm range. When these solvents would be recycled to the process for the same aim, the ppm concentration of amine is allowable and an increased recycling rate of 77.8% could be reached.

3. Conclusions

1. As a conclusion it can be stated that out of the eight tested solvents seven do have effect on shredded tyres. Greatest swelling by volume was reached by using cyclohexane, but deviation between the different temperatures was 5% and could be neglected.
2. Similar swelling could be reached in the case of dichloromethane, but the increase in mass was more significant than that of in volume due to the relatively high density of the solvent.
3. Considering the extracted inorganic compounds, sulfur showed a remarkable part, and highest quantity was 7.90wt% of bottom product. (Dipping in ethyl-acetate at 30°C).
4. GC-MS analysis verified the reaction of solvents with rubber matrix. 1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl was detected in samples of all tested solvents except gamma-valerolactone. This amine could be formed from isocyanates (used as binding components between textile and rubber in tyres).