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Investigation of the Possibilities of Regulating Boundary Processes in the Composite Material Made from Scrap Tires and Polymer Binder

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Abstract **– Investigation of the possibility to regulate the boundary processes in the composite material made from scrap tires and polymer binder must be considered as a perspective direction so that to regulate the essential properties of composite material. The modification of rubber crumb was performed by means of treatment with inorganic acid in order to improve adhesive interaction between rubber and polymer binder.**

The influence of rubber crumb modification on such parameters as Shore C hardness, tensile strength and elongation at break, impact strength, apparent density of composite material in correlation with its composition and adhesion between rubber and polymer binder were investigated.

Close correlation between composition, modification of rubber crumb and selected properties of the composite material was demonstrated.

Key words: **composite material, scrap tires, polymer binder, modification, adhesion, hardness.**

I. Introduction

One of the most perspective direction of used tire recycling is combination of scrap tires with polymer binder and production of composite materials /1,2,3/.

The present study is continuation of previous studies /4,5,6/ and is intended to investigate the possible regulation of the boundary processes in the composite material made from scrap tires and polymer binder. The modification of rubber crumb was performed by means of treatment with inorganic acid in order to improve adhesion between rubber and polymer binder /7,8/.

The compressive stress and compression modulus of elasticity at 10% deformation, Shore C hardness, tensile strength and elongation at break and impact strength, apparent density of composite material in correlation with its composition, as well as adhesion between rubber and polymer binder were investigated.

Modification of rubber crumb can be useful in the purposeful improvement of the investigated mechanical properties and production technology of the composite material.

II. Materials and Methods

Mechanically grinded, modified and non-modified rubber crumb, obtained from the used tires with particle size from 0.2 to 7.0 mm and polyurethane type binder with selected reactivity, were used to produce samples of the composite material. Different compositions of rubber crumb and polymer binder (from 8 to 23 wt.%) were used.

Samples of the composite material were prepared under constant and definite conditions: formation temperature (17–22^{0}C), moulding pressure (0.004 MPa), curing time (24 h) and relative air humidity (20–40%).

Chemical modification of rubber crumb with 96% sulphuric acid was used at the selected time points of treatment to estimate possible intensification of adhesive interaction between the polymer binder and rubber particles.

In order to determine changes in rubber surface energy before and after modification, wetting properties (contact wetting angle ϴ° of water droplet on a rubber surface) of solid rubber samples were examined. Special samples were prepared to investigate the strength of adhesive bonding between the polymer binder and modified rubber surface according to LVS EN 28510-1.

The apparent density AD (kg/m^3) of composite material was determined according to LVS EN 1602. Shore C hardness was investigated by using Shore durometer (Type C; ISO 7619, ISO 868). Mechanical properties of composite material (compressive stress at 10% deformation and compressive modulus of elasticity) were determined by using testing apparatus Zwick/Roell7020 according to LVS EN 826. In the tensile mode of loading, the ultimate tensile strength and elongation at break for specially prepared samples with definite dimensions were determined according to LVS EN ISO 527-3.

III. Results and Discussion

Modification of rubber crumb with 96% sulphuric acid was used at different reaction times in order to explore the possibilities to intensify adhesion between the polymer binder and rubber particles and thereby, probably, the mechanical properties of the investigated composite material /7,8,9/. Chemical modification of rubber crumb showed significant changes in apparent density compared to the samples of composite material prepared under the same conditions, where non-modified rubber crumb was used (Fig. 1). This can partially be explained by the essential changes in a particle size distribution of rubber crumb after chemical modification (Fig. 2).

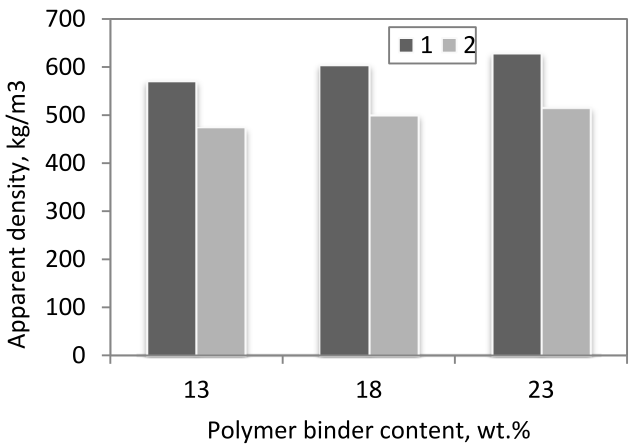

Fig. 1. Variation in the composite material apparent density AD (kg/m^3) with composition of material and modification of rubber crumb. 1 – non-modified rubber crumb; 2 – chemically modified rubber crumb.

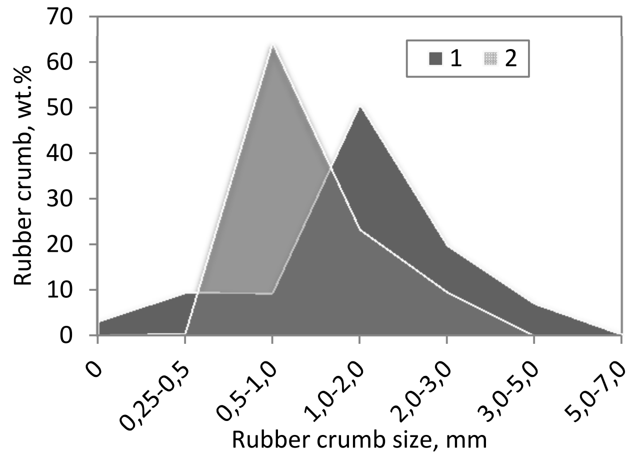

Fig. 2. Particle size distribution of scrap tires prior and after surface modification with sulphuric acid. 1 – non-modified rubber crumb; 2 – chemically modified rubber crumb.

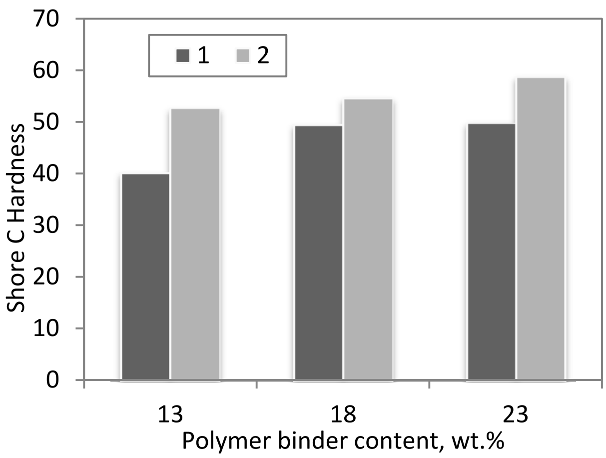

Fig. 3. Variation in the composite material Shore C hardness with composition of material. 1 – non-modified rubber crumb; 2 – chemically modified rubber crumb.

At the same time, the experiment showed that Shore C hardness increased up to 15%, when the modified rubber crumb was used, probably, due to destruction of double bonds on the rubber surface consequently leading to the loss of their elasticity (Fig. 3). The chemical modification of rubber surface with sulphuric acid was mainly carried out to investigate subsequent changes in adhesive interaction (bonding) between rubber and polymer binder. To improve interfacial compatibility in composite materials, surface oxidant treatment was also demonstrated in the systems containing polyolefins /9,10/. Experimental results of Peel Test showed that the chemical modification of rubber surface promoted adhesive bonding for the selected samples (Fig. 4). The results of Peel Test correlated with rubber surface wettability measurements – contact angle decreased after treatment with acid from 102^0 to 65^0.

A visual evaluation of failure character of adhesive joints after Peel Test mainly demonstrated the adhesive type of destruction.

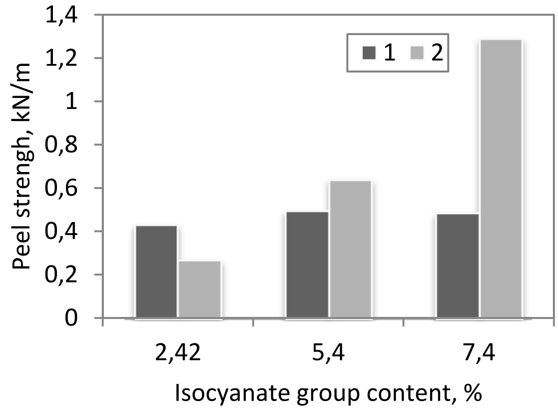

Fig. 4. Variation in Peel strength with polymer binder activity prior and after chemical modification of rubber surface. 1 – non-modified rubber crumb; 2 – chemically modified rubber crumb.

To investigate subsequent changes in mechanical properties, the ultimate tensile strength (σ_t) and elongation at break (ε_t) in the tensile mode of loading of composite material (polymer binder with 2.42% isocyanate group content) were determined (Table 1).

TABLE 1

ULTIMATE TENSILE STRENGTH (σ_T), ELONGATION AT BREAK (ε), COMPRESSIVE STRESS AT 10% DEFORMATION ($\sigma_{10\%}$) AND COMPRESSIVE MODULUS OF ELASTICITY (E) OF COMPOSITE MATERIAL

	Rubber crumb	Polymer binder content (wt.%)	y_t (MPa)	e (%)	$y_{10\%}$ (MPa	E (MPa)
1.	Non-modified	13	0.068	66	0.21	0.25
		18	0.152	57	0.28	0.36
		23	0.175	51	0.39	0.42
2.	Modified					
		13	0.064	67	0.80	1.50
		18	0.104	-	1.00	6.80
		23	0.106	62	1.38	7.00

Mechanical properties, such as modulus of elasticity and compressive stress at 10 % of deformation, were enhanced by improving adhesion between rubber and polymer binder. This is highly related to the improvement of wetting capability (hydrofility) of rubber crumb due to the processes arising from the influence of sulphuric acid on the chemical structure of rubber surface /7/. This was also proved by the experiment, where the adhesion between the preliminary treated rubber substrate and polymer binder was investigated (Fig. 4).

This fact establishes the importance of individual properties of constituent materials used in the production of composite material by means of variation of their individual properties.

IV. Conclusion

Remarkable influence of rubber crumb treatment with sulphuric acid on the selected properties (Shore C hardness, compressive stress and modulus of elasticity, peel strength) of the composite material was mainly observed due to the increase in rubber surface hydrofility and, thereby, improved adhesion with polymer binder.

Investigated method of the modification of rubber crumb can be useful in the purposeful improvement of mechanical properties and production technology of composite material.

References

[1] **J.E.Mark, B.Erman, R.Erich**. The Science and Technology of Rubber, 3 d. Ed.,Elsvier Inc., USA,2006, 763 pp.

[2] **H.F.Lund.** McGraw – Hill recycling handbook,R.R.Donelly & Sons Company,USA, 1993, 18.2-18.35 ch.

[3] **Adhikari B. ,Maiti S**., *Progress in Polymer Science*, 25,2000, p.909-948. http://dx.doi.org/10.1016/S0079-6700(00)00020-4

[4] **Malers L., Plesuma R., Locmele. L**., *Mech. Comp. Mat.*, 45**,** 2009, 1-6.

[5] **Malers L., Plesuma R., Locmele.**, *Scientific Journal of Riga Technical University: Material Science and Applied Chemistry*, 21**,** 2010, 35-38.

[6] **Malers L., Plesuma R., Locmele L.,Megne A.,Mateusa-Krukle I**.,*Polymer composites:Book of abstrcts,*Zapadočesks Univerzita v Pilzen, the Czech Republic,2011,p.135 – 136.

[7] **Cepeda-Jimenez CM.,Pastor– Blas MM, Ferrandiz-GomezTP.,Martin –Martinez JM.,** *J.Adhes*., 73, 2000,p.135-160.

[8] 8.**Goncharuk G.P., Knunyants M.I., Kruchkov A.N**., **Obolonkova E.S**., Vysokomolekularnye Soedineniya, 40, 1998, p.877.

[9] **Colom X.,Carrillo.F., Canavate J**.,*Composites,*38**,** 2007, p.44-50. http://dx.doi.org/10.1016/j.compositesa.2006.01.022

[10] *Pat.US* 6833396B2, 21.12.2004.

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Laimonis Mālers, Renāte Plesuma. Robežprocesu regulēšanas iespēju izpēte nolietotu riepu smalkni un polimēra saistvielu saturošā kompozītmateriālā.
Nolietotu riepu racionāla izmantošana joprojām ir būtiska, realizējot un pilnveidojot materiālu reciklēšanas tehnoloģiju un politiku. Starp dažādiem šī materiāla utilizācijas veidiem kā perspektīvs virziens ir jāmin sasmalcinātas riepas izmantošana kompozītmateriālu izveidē. Šī virziena perspektivitāte iegūst sevišķu nozīmi ņemot vērā to, ka nolietotu riepu dabiska sadalīšanās prasa ļoti ilgu laiku, un nepamatoti tiek noslogoti atkritumu deponēšanas poligoni. Šāda kompozītmateriāla praktiskas pielietošanas iespējas var saskatīt gan būvniecībā, gan citās tautsaimniecības nozarēs.
Šī darba mērķis ir noskaidrot , kā ,veicot gumijas smalknes ķīmisku modificēšanua ar neorganisku skābi (sērskābi,), iespējams iespaidot robežprocesus (adhezīvo mijiedarbi) kompozītmateriālā, kas satur nolietotu riepu gumijas smalkni un poimēra saistvielu, un tādejādi arī vienlaicīgi kompozītmateriāla mehāniskās īpašības.
Noskaidrots, ka gumijas smalknes ķīmiska modifikācija izmaina gumijas daļiņu granulometrisko sadalījumu un virsmas enerģiju (samazinās tās hidrofobitāte), kas ir par iemeslu intensīvākai gumijasun polimēra saistvielas adhezīvai mijiedarbei. Konstatēts, ka šāda gumijas apstršade būtiski iespaido kompozītmateriāla mehāniskās īpašības –palielinās materiāla Šora C cietība ,spiedes spriegums un elastības modulis .
Parādīts, ka izvēlētā gumijas smalknes ķīmiskās modificēšanas metode, apvienojot to ar mērķtiecīgu kompozītmateriāla sastāva un pielietotās polimēra saistvielas aktivitātes maiņu, ļauj mērķtiecīgi mainīt kompozītmateriāla īpašības un turpmāk pilnveidot tā iegūšanas tehnoloģiju.

Лаймонис Малерс, Ренате Плесума. Исследование в области возможностей регулирования граничных процессов в композиционном материале, содержащем крошку изношенных шин и полимерное связующее.
Рациональное использование изношенных шин является существенным фактором при реализации и совершенствовании технологии и политики рециклизации материалов. Среди прочих способов утилизации шин перспективным направлением следует признать использование измельченных шин для создания композиционного материала. Перспективность этого направления приобретает особую важность, учитывая то, что естественное разложение шин требует очень большого времени и необоснованного загружения полигонов размещения отходов. Практическое применение такого материала можно ожидать как в строительстве, так в других отраслях народного хозяйства. Целью настоящей работы является выяснение возможности влиять неорганической (серной) кислотой на граничные процессы (адгезионное взаимодействие) в композиционном материале, содержащем измельченные шины и полимерное связующее, и таким образом одновременно на механические свойства композиционного материала. Установлено, что химическая модификация резиновой крошки меняет гранулометрическое распределение частиц и их поверхностную энергию (понижается ее гидрофобность), что является причиной более интенсивного адгезионного взаимодействия резины и полимерного связующего. Показано, что такая обработка резины существенно влияет на механические свойства композиционного материала – повышается твердость по Шору С, напряжение и модуль упругости при сжатии.
Показано, что выбранный метод модификации резиновой крошки в сочетании с направленным изменением состава композиционного материала, а также активности полимерного связующего, позволяет целенаправленно менять свойства композиционного материала и в дальнейшем совершенствовать технологию его получения.