Rubber Science, **29**(2): 207-214, 2016 *SHORT SCIENTIFIC COMMUNICATION*

FEASIBILITY OF MODIFIED STARCH AS BIO-FILLER IN NATURAL RUBBER COMPOUNDS

Joy Joseph and Rosamma Alex
Rubber Research Institute of India, Kottayam - 686009, Kerala, India

Received: 08 February 2016 Accepted: 20 July 2016

Joseph, J. and Alex, R. (2016). Feasibility of modified starch as bio-filler in natural rubber compounds. *Rubber Science*, 29(2): 207-214.

In order to impart strength and reduce cost natural rubber (NR) is compounded with fillers of different types. In this work we have attempted to study the feasibility of using starch as a bio-filler in NR. Starch was incorporated into NR by directly mixing on a two roll mixing mill and also in the presence of a plasticizer to reduce the softening point of starch. Starch was also modified with resorcinol- formaldehyde resin and incorporated into NR in the latex stage which was then coagulated and dried to obtain a modified starch incorporated NR. The study showed that when NR was compounded with starch directly on a two roll mixing mill the properties were not improved. Natural rubber when compounded with starch in the presence of a plasticizer like ethylene glycol, the properties were slightly improved. Starch was modified with resorcinol-formaldehyde resin and was incorporated to NR in the latex stage, the properties were improved significantly. The compound containing 10 phr starch showed much better properties than the control. The study showed that starch can be used as a filler in NR to enhance its properties. Though carbon black cannot be fully replaced with starch, partial substitution is possible.

Keywords: Bio-filler, Carbon black, Filler, Latex, Natural rubber, Starch

In natural rubber, crosslinking introduced by vulcanization prevents the polymer chains from moving independently. As a result, when stress is applied, the vulcanized rubber deforms, but upon release of the stress it reverts to its original shape. Vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials via the addition of sulphur or other equivalent curatives in thepresence of accelerators. These additives modify the polymer by forming crosslinks (bridges) between individual polymer chains preventing the chains from free movement. Vulcanized materials are less sticky and have superior mechanical properties (Lewis *et al.*, 1937)

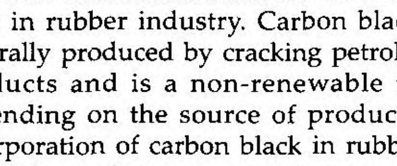
In order to impart strength and reduce cost in rubber products, natural rubber is compounded with fillers of different types. Some fillers are reinforcing while some others are inert fillers. Inert fillers are used to reduce the cost of the compound. The most commonly used filler in natural rubber is carbon black. Non-black fillers like silica, clay *etc.* are also used with natural rubber (Kaushik *et al.*, 2010).

Carbon black is an indispensable filler for making tyre and most of the automobile

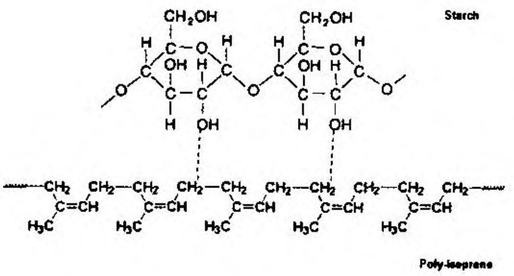
---

Correspondence: Joy Joseph (Email: joyjoseph@rubberboard.org.in)

rubber components. Similarly carbon black is used as the filler in many non-tyre products. Non-black fillers are generally used in non-tyre sector for specific applications; otherwise carbon black remains the dominant filler in rubber industry. Carbon black is generally produced by cracking petroleum products and is a non-renewable item depending on the source of production. Incorporation of carbon black in rubber is difficult and is a troublesome job. Considering the declining source of petroleum, exploration of novel renewable fillers for rubber reinforcement is necessary. Starch is an abundantly available renewable biomaterial which is already being used in many areas like paper, textile industries (Sirimaporn *et al.*, 2012). The structure of simple starch is given below.



The –OH group may form hydrogen bonds with the isoprene units of natural rubber and hence starch can act as a filler in natural rubber (Lee and Rashid, 2013; Miren *et al.*, 2011).



There are reports that starch rubber composites are suitable in some medical applications (Altpeter *et al.*, 2003). Starch filled rubber composites are more biodegradable than normal rubber composites (Gomes *et al.*, 2001). In this context it is worthwhile to study the effect of starch as a bio-filler in natural rubber which can partially or fully replace the carbon black. The present work is an attempt in this line.

Latex used for this study was the field latex collected from the research farm of Rubber Research Institute of India, Kottayam, Kerala. Compounding ingredients such as zinc oxide (ZnO), stearic acid, 2,2,4-trimethyl-1,2-dihydroquinoline (TDQ), N-cyclohexyl-2-benzothiazole sulphenamide (CBS), and sulphur (insoluble) used were supplied by Bayer (India) Ltd. Laboratory grade soluble starch was supplied by Micro Fine Chemicals, Chennai.

Modified starch was prepared by treating starch with resorcinol and formaldehyde (RF). Starch solution was prepared by making 30g starch into a paste with water and adding it to water at 90^{0}C with stirring so that the final volume of the solution becomes one litre. Then 4.4 g of resorcinol and 1.8 g of formaldehyde was dissolved in 10 ml water at a pH of 9. This resorcinol formaldehyde solution was added to starch solution slowly with stirring and heated to 90^{0}C for further 30 minutes to get modified starch solution. The modified starch solution was added to ammoniated latex containing a dry rubber content of 30 per cent with stirring and coagulated by adding 5 per cent formic acid. The coagulum was pressed and dried at 70^{0}C to get starch modified NR. Quantity of starch solution added to the latex was so adjusted to get a loading of 2, 5 and 10 parts per hundred rubber (phr).

The thermal decomposition behavior was studied by using Thermo Gravimetric Analyzer (TGA-50, Shimadzu, Japan).

The dry rubber used for the study was obtained by coagulation of fresh field latex.

Table 1. **Formulation of mixes**

Ingredients	Mix identification		
	Dry mix with starch	Dry mix with starch and plasticizer	RF modified starch incorporated in latex stage
Natural rubber	100	100	100
Zinc oxide	4	4	4
Stearic acid	2	2	2
TDQ	1	1	1
CBS	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5
Starch	Variable (2,5,10 phr)	Variable (2,5, 10 phr)	Variable (2, 5, 10 phr)
Ethylene glycol	-	3	-

Mixes containing starch and starch with plasticizer (ethylene glycol) was compounded on a two roll mixing mill as per the formulation given in Table 1. Rubber composites containing modified starch at different loading were further compounded with other ingredients as given in Table 1 on the mixing mill. The resulting compound was kept for maturation for 24 hours and the cure characteristics were determined using a Rubber Process Analyzer (RPA, Alpha Technologies, USA) as per ASTM D 5289. Die swell properties were also studied using RPA. Test samples were moulded as per the respective standard using a hydraulic press from the matured compounds for various tests and the technological properties were evaluated. Tensile properties, tear strength, heat build-up, compression set and hardness were tested as per the respective ASTM standards D 412, D 624, D 623, D 395 B, and D 792 / 2240.

Technological properties of the NR-Starch mix (NRS) made by direct mixing of starch on the mixing mill is shown in Table 2. By direct incorporation of starch into NR in the mixing mill no significant improvement in technological properties could be observed. This is in tune with earlier reports (Carvalho *et al.*, 2003; Khalaf *et al.*, *2012*). This is probably due to the fact that the softening point of starch is above 200^{0}C and it cannot get softened by mixing in a two roll mill

Table 2. **Technological properties of the NR-starch mix directly compounded on the mill**

Property	Compound identification			
	Control	Starch (2 phr)	Starch (5phr)	Starch (10 phr)
Tear strength (kNm^{-1})	35	31	31	28
Tensile strength (MPa)	31	29	30	30
EB (%)	1070	988	990	993
M_{100} (MPa)	0.96	0.90	0.91	0.91
M_{300}(MPa)	2.19	2.09	2.11	2.13
Heat build-up, ΔT(^{0}C)	2	2	3	3
Compression set (%)	44	40	38	37
Hardness (Shore A)	44	40	44	45

Table 3.**Technological properties of the NR-starch composites with plasticizer**

Property	Compound identification			
	Control	Starch 2 phr	Starch 5 phr	Starch10 phr
Tear strength (kNm^{-1})	31.51	30.69	30.46	30.47
Tensile strength (MPa)	23.57	26.34	29.39	29.41
Elongation at break (%)	985	1111	1079	1084
M_{100} (MPa)	0.89	0.88	0.92	0.92
M_{300} (MPa)	2.03	1.99	2.06	2.08
Heat build up ΔT (^0C)	3	6	6	6
Compression set (%)	42	50	54	52
Hardness (Shore A)	40	42	42	42

where the temperature does not reach up to the softening point of starch (Jitlada *et al.*, 2011). In a second set of NR-starch compounds which was also prepared in the mixing mill, ethylene glycol was added as a plasticizer to reduce the softening point of starch. Technological properties of the vulcanizates made from these composites are given in Table 3.

From the results it can be seen that when starch was incorporated into NR in the presence of a plasticizer, only a slight improvement in tensile strength, elongation at break and hardness was noticed. In a third

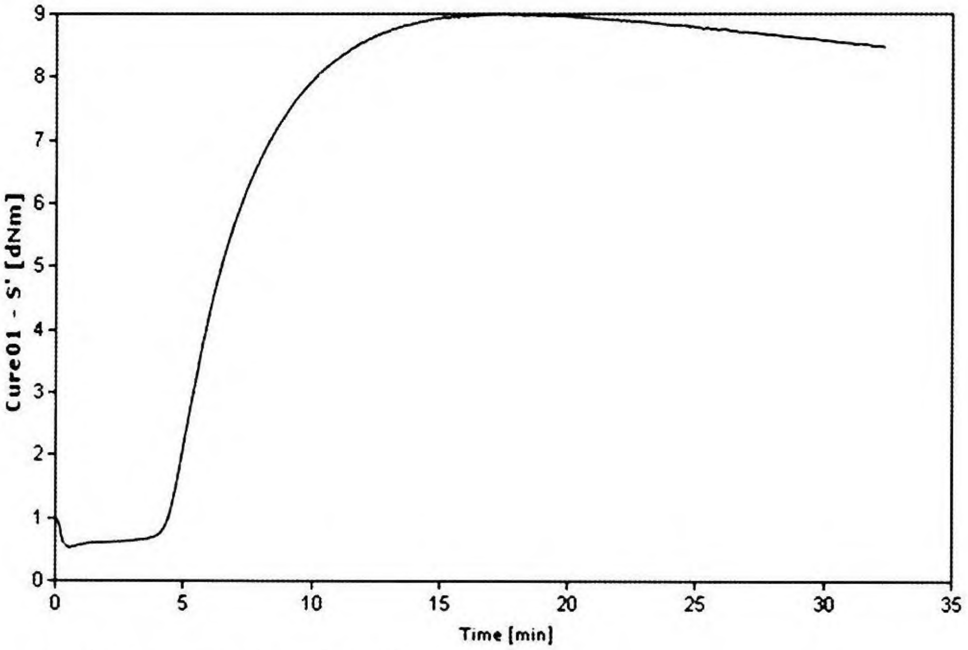


Fig.1. Rheogram of RF starch modified NR composite

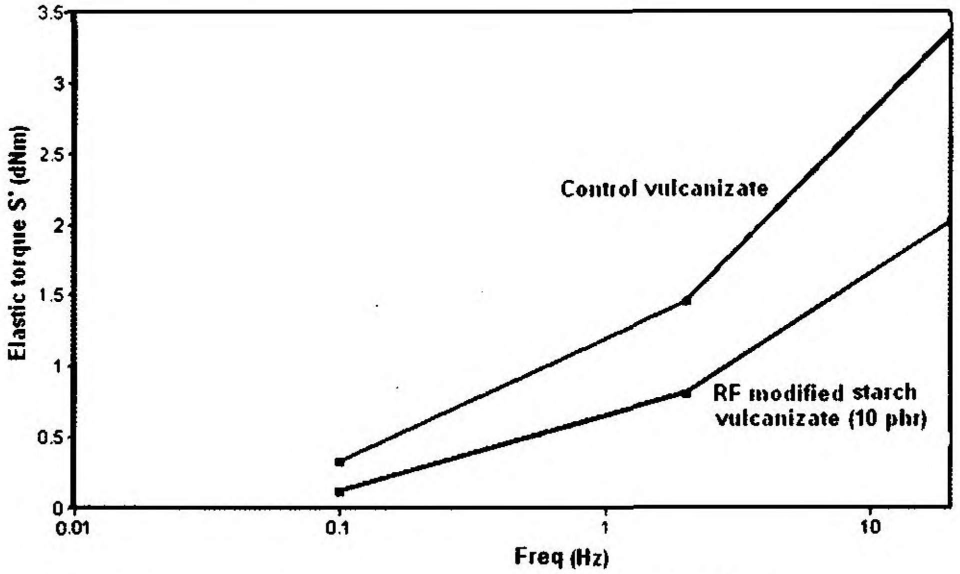


Fig. 2. Plot of elastic torque S′ vs frequency of RF starch modified NR composite

set of compounds, starch was modified with resorcinol-formaldehyde resin as explained earlier and the modified starch was incorporated into NR in the latex stage. Modified starch incorporated latex was coagulated and dried. The dry rubber thus obtained was compounded as per the formulations given in Table 1. The cure characteristics are given in Table 4. From the data it can be seen that when NR was modified with RF starch, minimum torque was less compared to the control. However, maximum torque has increased from 7.37 dNm to 9 dNm. Similarly Tan D and cure time are also increased.The rheogram of the above compound is shown in Fig. 1.

Samples of the RF modified starch-NR compound were tested for its technological properties. The results are given in Table 5. From the results, it can be observed that when RF modified starch was incorporated into NR, most of the technological properties were improved. Tear strength was enhanced from 31.55kNm^{-1}(for the control without starch) to 32.01kNm^{-1}; 33.64kNm^{-1} and 35.14 kNm^{-1} on incorporation of 2, 5 and 10 phr of RF modified starch, respectively. Corresponding improvement of tensile strength was from 23.51 MPa to 24.48 MPa, 26.51 MPa and 28.69 MPa. Modulus at 100 per cent elongation was improved from 0.88 MPa to 1.08 MPa, 1.11 MPa and 1.17 MPa and the Modulus at 300

Table 4. **Cure characteristics of RF modified starch-NR composite**

Particulars	S'ML (dNm)	S'MH (dNm)	Tan D ML	Tan D MH	T90 (min.)
RF modified starch NR composite	0.53	9.00	0.94	0.02	10.56
Control	0.78	7.37	0.65	0.004	6.98

Table 5. **Technological properties of RF modified starch-NR composite**

Property	Compound identification			
	Control	2 phr	5 phr	10 phr
Tear strength (KNm^{-1})	31.55	32.01	33.64	35.14
Tensile strength (MPa)	23.51	24.48	26.51	28.69
Elongation at break (%)	982	980	989	992
M_{100} (MPa)	0.88	1.08	1.11	1.17
M_{300} (MPa)	2.04	2.27	2.35	2.91
Heat buildup ΔT (°C)	3	3	3	3
Compression set (%)	46	47	47	46
Hardness (Shore A)	40	45	46	49

per cent elongation was enhanced from 2.04 MPa to 2.27 MPa, 2.35 MPa and 2.91 MPa, respectively. Heat build-up and compression set were almost at par with the control. Hardness increased from 40 to 45, 46 and 49 Shore A for 2,5 and 10 phr of modified starch, respectively. There was no noticeable change in the compression set of compounds when RF modified starch was incorporated.

The probable reason for the enhancement of properties is that when a phenolic compound (resorcinol) with an aldehyde (formaldehyde), react under alkaline conditions in the presence of pasted

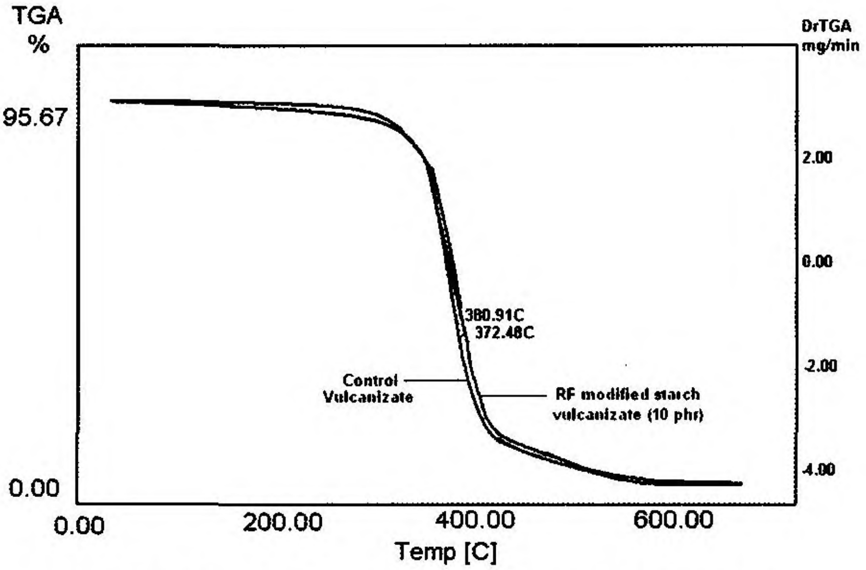


Fig. 3. Thermogram comparing the decomposition behavior of NR and NR- starch composite

starch so as to form an in situ phenolic-aldehyde resin-starch reaction product which forms hydrogen bonding with isoprene units of natural rubber and thereby reinforce the rubber.

Die swell properties of RF modified starch (10 phr) are shown in Fig 2. It can be seen from the figure that when elastic torque S' was plotted against frequency, the starch modified compound exhibited less torque values compared to the control. Since die swell is directly proportional to S' it can be observed that the starch modified compounds exhibited lower die swell compared to the control. Low die swell properties are required for extruded products where exact dimensions are to be maintained (You-Ping *et al.*, 2006).

Control and RF modified starch (10 phr) incorporated samples were subjected to Thermogravimetric analysis and the thermogram is given in Fig.3. Thermogravimetric analysis gives the thermal decomposition behavior of materials. From the thermogram it can be seen that the thermal decomposition pattern of starch incorporated sample almost coincides with that of the control. This shows that presence of starch does not affect the thermal decomposition pattern of NR.

The study showed that when natural rubber (NR) was compounded with starch on a two roll mixing mill, at the loading mentioned in this work, the technological properties are not improved. Starch when incorporated into NR along with a plasticizer like ethylene glycol the properties are only slightly improved. When RF modified starch was incorporated into NR in the latex stage, most of the technological properties got improved. Though conventional reinforcing fillers may not be fully replaced with starch, partial substitution is a possibility in rubber products, and it also contributes to biodegradability of rubber.

REFERENCES

Altpeter H, Bevis, M. J., Gomes, M. E., Cunha,A. M. and Reis, R. L. (2003). Shear controlled orientation in injection moulding of starch based blends intended for medical applications. *Plastics, Rubber and Composites,* **32**(4): 173-181.

Carvalho, A.J.F.,Job, A.E., Alves, N., Curvelo, A.A.S., .S1, A.A, and Gandini A. (2003). Thermoplastic starch/natural rubber blends. *Carbohydrate Polymers,* **53**(1): 95-99.

Pal, K., Rajasekar, R., Kang, D.J., Zhang, Z.X., Pal, S.K., Das, C.K.and Kim, J.K.(2010). Effect of fillers on natural rubber/high styrene rubber blends with nano silica: Morphology and wear. *Materials & Design,* **31**(2): 677-686.

Sansatsadeekul, J., Sakdapipanich, J. and Rojrutai, P. (2011). Characterization of associated proteins and phospholipids in natural rubber latex.*Journal of Bioscience and Bioengineering,* **111**(6): 628-634.

Khalaf, A.I. and Sadek, E.M. (2012). Compatibility study in natural rubber and maize starch blends. *Applied Polymer Science,* **125**(2): .959-967.

Lee Xing Min, A. Rashid Azura (2013). Effect of modified tapioca starch on mechanical properties of styrene-grafted natural-rubber/ starch composites.*International Journal of Materials Engineering Innovation,* **4** (3&4).

Gomes, M.E., Ribeiro, A.S., Malafaya, P.B., Reis, R.L. and Cunha, A.M. (2001). A new approach based on injection moulding to produce biodegradable starch-based polymeric scaffolds: morphology, mechanical and degradation behaviour. *Biomaterial,* **22**: 883-889.

Ichazo, M.N., Albano, C., Hernández, M, González, J. and Peña, J. (2011).Characterization of Natural Rubber/Cassava Starch/Maleated Natural Rubber Formulations. *Rev. Latin Am. Metal. Mater,* **31**(1): 1-104.

Watcharakul, S.,Umsakul, K., Hodgson, B., Chumeka, W. and Tanrattanakul,V. (2012). Biodegradation of a blended starch/natural rubber foam biopolymer and rubber gloves by

Streptomyces coelicolor ch.13. *Electronic Journal of Biotechnology,* **15**(1): 1-14.

You-Ping Wu a, Qing Qi a ,Gui-Hua Liang a , Li-Qun Zhang. (2006). A strategy to prepare high performance starch/rubber composites: In situ modification during latex compounding process. *Carbohydrate Polymers,* **65**(1): 109-113.

Lewis, W. K., Squires, L. and Nutting, R.D. (1937). Mechanism of Rubber Vulcanization with Sulfur. *Industrial and Engineering Chemistry Research,* **29** (10): 1135–1144.