

Development of Modified Soybean Oil Based Crosslinker For Starch/Caco₃ Biocomposites

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Abstract: A thin flexible (tensile strength 17.216 N/mm²) biocomposite of starch/ CaCO₃ crosslinked by succinic acid modified soybean oil crosslinker (SOS). The as prepared crosslinker was determined by FT-IR spectroscopy while the biocomposite fabricated was ascertained by XRD and SEM studies. The result shows synthesis of SOS crosslinker and all the components were coalesced. The outcomes infer that soybean oil based crosslinker can be efficiently developed and can be employed actively as a key ingredient in the processing and development of biodegradable films. These results demonstrate the SOS crosslinked starch/CaCO₃ biofilms can be developed as efficient substitute for non-biodegradable material due to its reasonable plasticity.

Keywords: Soybean oil, crosslinker, biocomposite, polymers, matrix, filler

1. Introduction: Plastics (synthetic polymers) since first synthesized are the one of the most important, versatile, used and under scrutiny discovery of man-kind which had not only made our life easy but under threat also. Due to its versatile applicability and dependence on these man-created (artificial and synthetic) polymers today our existence without them is unimaginable [1-4]. Synthetic materials (polymer) are being engendered and used in excess all over the globe owing to their versatile and adaptable properties. These varieties of polymer had efficaciously substituted many of the basic components used throughout the human life, except some of the material used in construction and allied sectors. According to a report 320 million tons of polymers (fibers not included) were generated in year 2015 all across the earth [5], according to studies of Geyer et al. 2017, out of 6.3×10^3 metric tons of plastic waste generated, 12% was destroyed through incineration, only 9% was recovered by recycling while the rest 79% was found to be accumulated in landfills or was scattered as such in natural ecosystem [1]. These synthetic and non-biodegradable polymers not only pose a significant threat on the existence of

microbes and other floras and faunas but also brought up certain undesired malformations/problem to human (health hazards) and its environ [6].

To cope up with the problems bred with these assisting yet hazardous synthetic polymers profuse investigations are being conducted over the globe, one of the way is generation of biocomposites (bioplastics), which can be brought into existence via enforcement of bio-filler (natural material) in a matrix. The bio-filler added generally include, materials like starch, pectin, cellulose, plant and animal fibers etc. which are biodegradable in their usual form and are extracted from the source simply and in profusion [7-8]. Starch due to its easy extraction, moldability, gelatinization and diverse applicability is employed as a most preferred matrix for fabrication of biocomposites [9-10]. These various characteristics of starch provide mankind an alternative competitor for petroleum based polymers. However starch is set backed with the property that it is fragile at adverse condition of temperature and stress also it is not highly moisture resistant thus have a short shelf life. Thus to modify and enhance the properties certain filler (metal oxides, animal and plant fibers etc.) are incorporated in certain ration as to maintain the biodegradability, while increasing strength and shelf life of such starch based composites. Another component which determine the application of these biomaterial in our different commodities is crosslinker which helps in reducing the stress of the individual components in the polymer through its numerous dendrite type structures, these dendrites like structure are actually the functional groups through which they linkup the polymer chains to provide high degree of linkage and strength, thus elevating the various required properties for a biopolymer composite [11-12].

In this work the authors had attempted to development a crosslinker by modifying Soybean oil for starch/CaCO₃ biocomposites. This investigation includes the studies of preparation and characteristic behavior of resulted crosslinker and biocomposite.

2. Experimental:

2.1. Chemical and materials used: Soybean oil, HCl, methanol, succinic acid, starch, CaCO₃

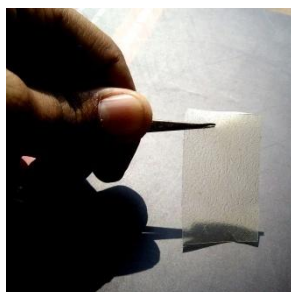
2.2. Modification of Soybean oil: Soybean was modified to obtain as an effective crosslinker for Starch and Starch/CaCO₃ composites by pursuing the following route:



Picture 1: Soybean oil/Succinic acid (SOS) solution

Soybean oil (1g) was taken in a double-neck round bottom flask, to this HCl (30%, w/w, 0.450 g) was added dropwise at maintained temperature of $0\pm 1^{\circ}\text{C}$, with constant stirring (6 hrs), this enables to reduce unsaturation and incorporation of H and Cl species in the molecule. The obtained material was further treated with succinic acid (0.450 g) dissolved in methanol, to result in the desired modified material (scheme 1), which was further refluxed for $\sim 2\frac{1}{2}$ hrs to obtained pale yellowish coloured gel, miscible in water and other polar solvents (picture 1).

2.3. Development of Starch Composite: Starch (5 g) was previously gelatinized in deionised water (100 ml), for $\sim \frac{1}{2}$ hr, at $95\pm 5^{\circ}\text{C}$ to this was added modified Soybean oil crosslinker (SOS) in varying concentration (1:0.25, 1:0.5, 1:0.75, 1:1, 1:1.25 and 1:1.50). It was observed that composite with starch: SOS 1:0.75, and 1:1 results in flexible and strong film (picture 2). While below this composition the composite remain fragile and above these the material becomes much sticky. This obtained ratio (starch: SOS 1:0.75, and 1:1) of the two suggest crosslinker.

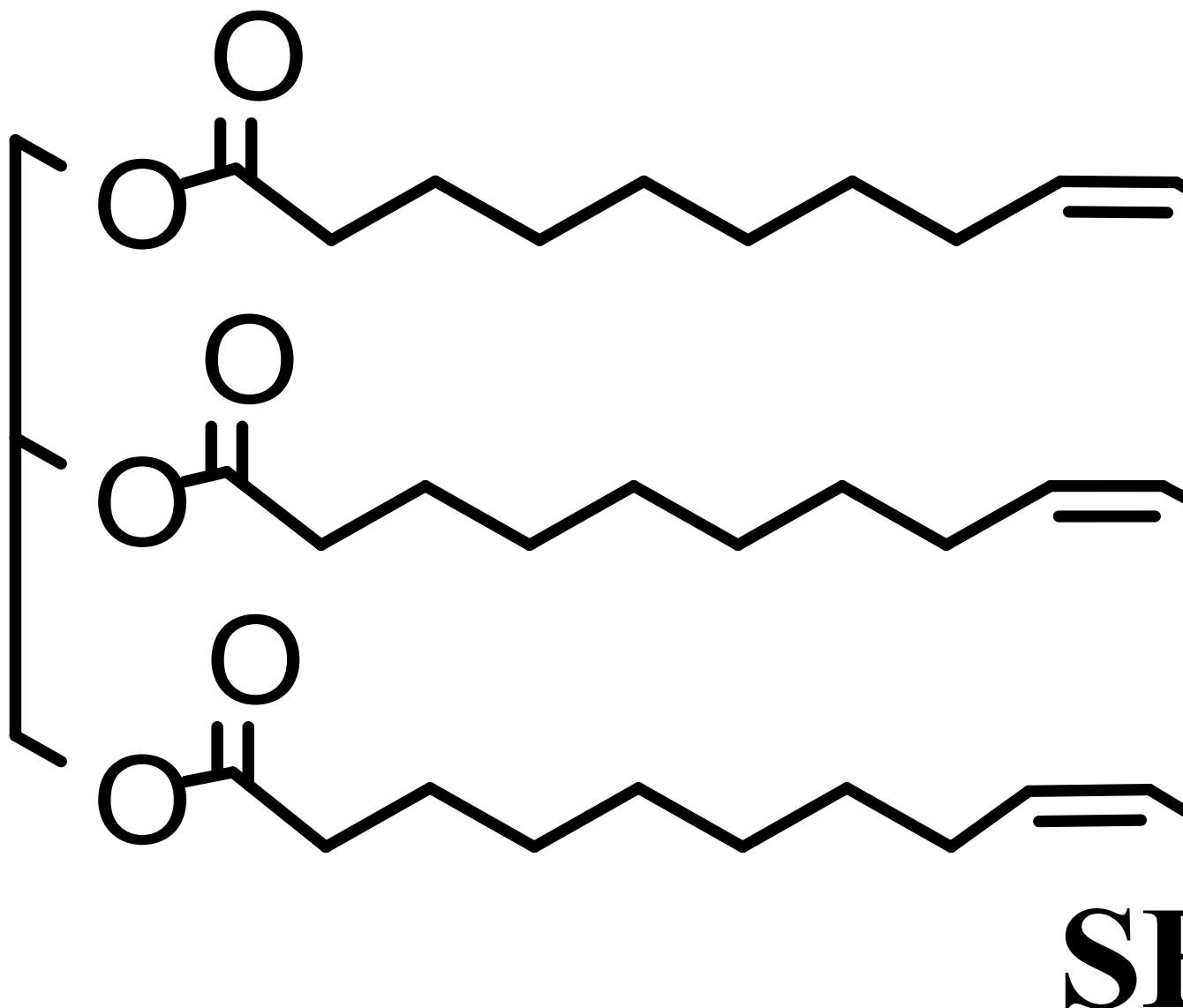


**Soybean: Succinic acid
(1: 0.75)**



**Soybean: Succinic acid
(1:1)**

Picture 2: Starch/SOS composite film in desired ratio



Scheme 1: Scheme for the preparation of modified crosslinker (SOS) from soybean oil.

2.4. Development of SOS crosslinked Starch/CaCO₃ Composites: Previously gelatinized Starch (5g) in deionised water (100 ml), for ~ ½ hr, at 95±5°C to this was added modified Soybean oil crosslinker (SOS, 5g), the mixture was vigorously stirred with the help of mechanical stirrer @ 2000 rpm. In the resultant matrix, varying concentration of filler (CaCO₃, table 1) was added.

Table 1. Composition of Starch/CaCO₃ composites:

Code	Starch (g)	Crosslinker [SOS] (g)	CaCO ₃ (% , w/w)
A	5	5	0
B	5	5	10
C	5	5	20
D	5	5	30
E	5	5	40
F	5	5	50

Physical appearance of the Starch/CaCO₃ Composites is depicted in Fig. 3. The composites containing 10 and 20 %, w/w CaCO₃ showed better stability improved plasticity.



A

B C

Picture 3. Starch/CaCO₃ Composites with 20% percentage of filler.

3. Result and discussion:

3.1. Characterization of Soybean oil/Succinic acid (SOS) by FT-IR: ATR-FTIR spectroscopy of SOS was studied for determining present functional group in the solution. Following data predicts the major functional groups present in the derived product (Figure 2, Table 1).

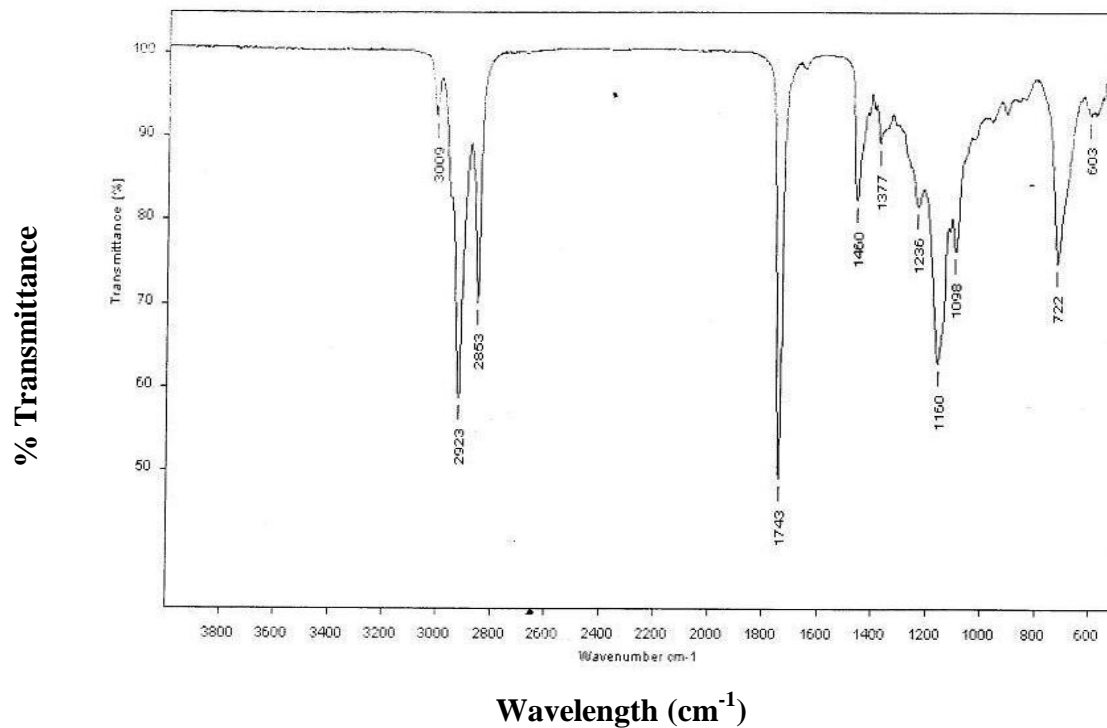
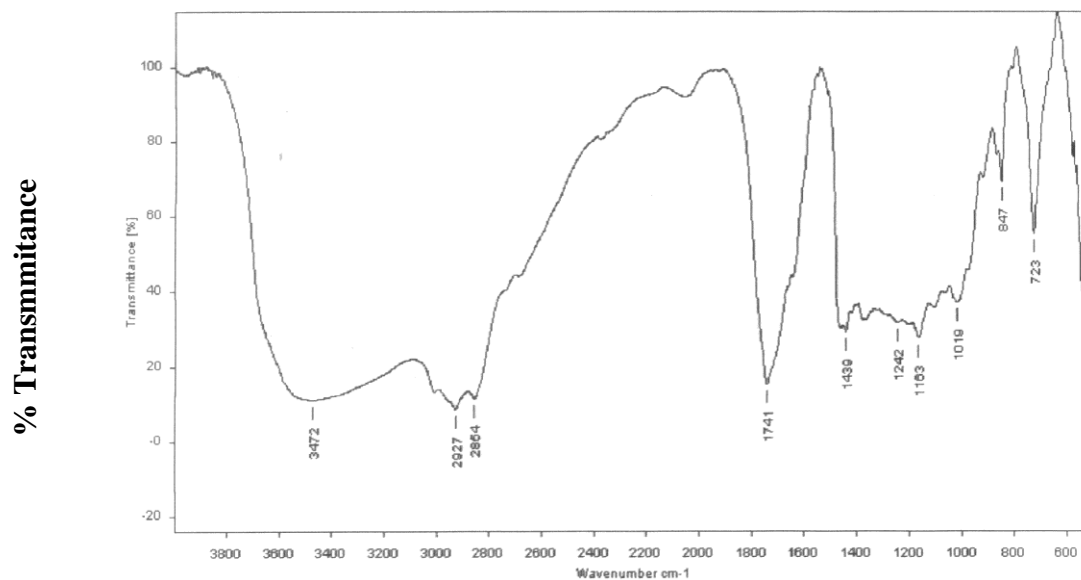


Figure 1. FTIR spectra of Soybean oil



HS1

Wavelength (cm⁻¹)

Figure 2. FTIR of SOS

Table 2: FT-IR of SOS

Functional group	Absorbance (cm ⁻¹)
C=C, Str (remaining)	2922, 2875 (w)
-OCO-	1743 (s)
C-H Str	~3300 (s)
C-Cl Str (remaining)	850-550

3.2. Characterization of Starch/CaCO₃ Composites:

X-Ray Diffraction (XRD):All the major peak of starch were observed at 2θ= 11.4, 14.8, 17.0, 23.06 and 26.6° also, characteristic peak at 28.8, 37.4, 47.3 and 48.5° indicates the presence of CaCO₃ in the Starch/SOS composite. Due to addition of CaCO₃ in the matrix the crystallinity of the composite was enhanced.

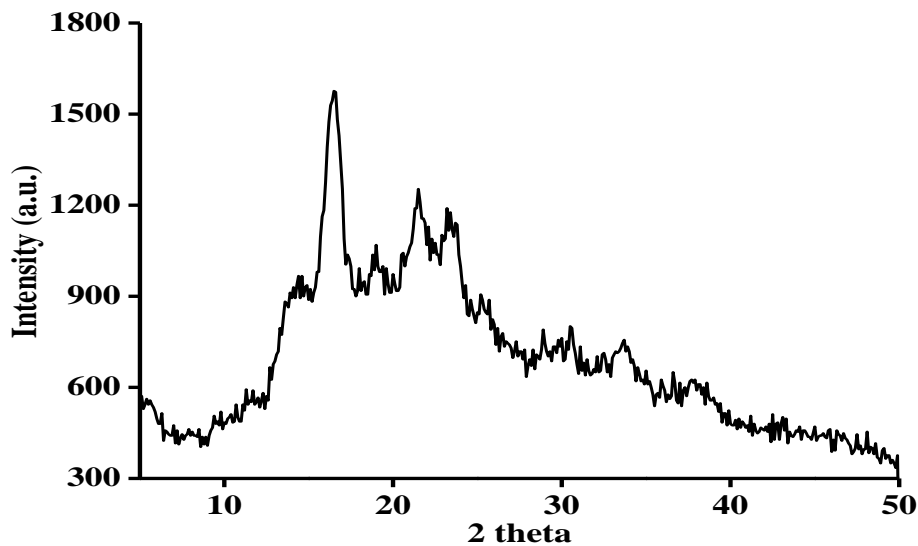


Figure 2. XRD of SOScomposite

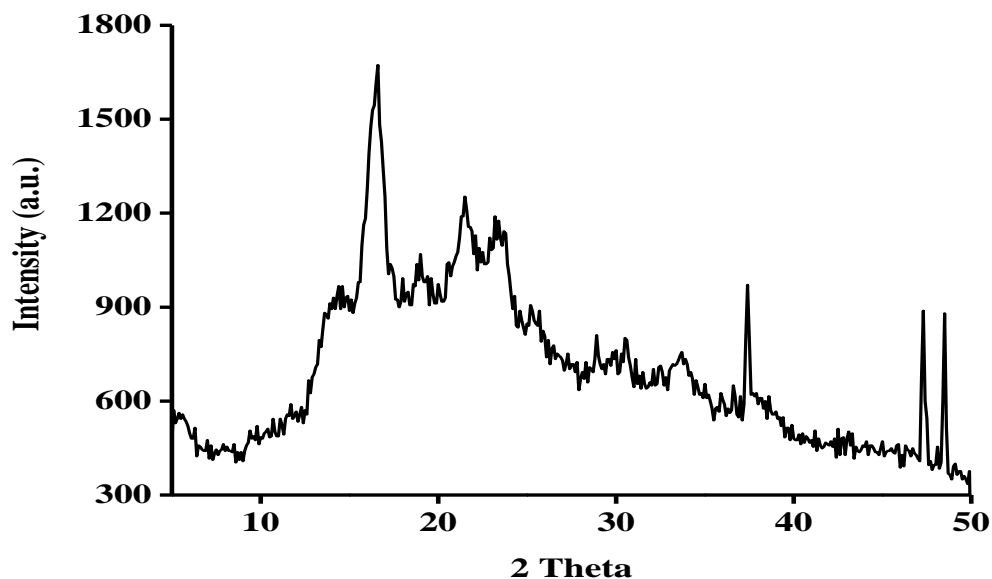


Figure 3. XRD of SOS/CaCO₃ composite

3.3. Scanning Electron Microscopy (SEM):

SEM of the material provided the information regarding the interaction between starch and succinic acid. The SEM data revealed that the material prepared with gelatinized starch alone showed fragility which was absent or overcome in the material/composite (SOS). Therefore, the present study concludes that the crosslinker prepared in laboratory may be explored to impart strength to the developed film.

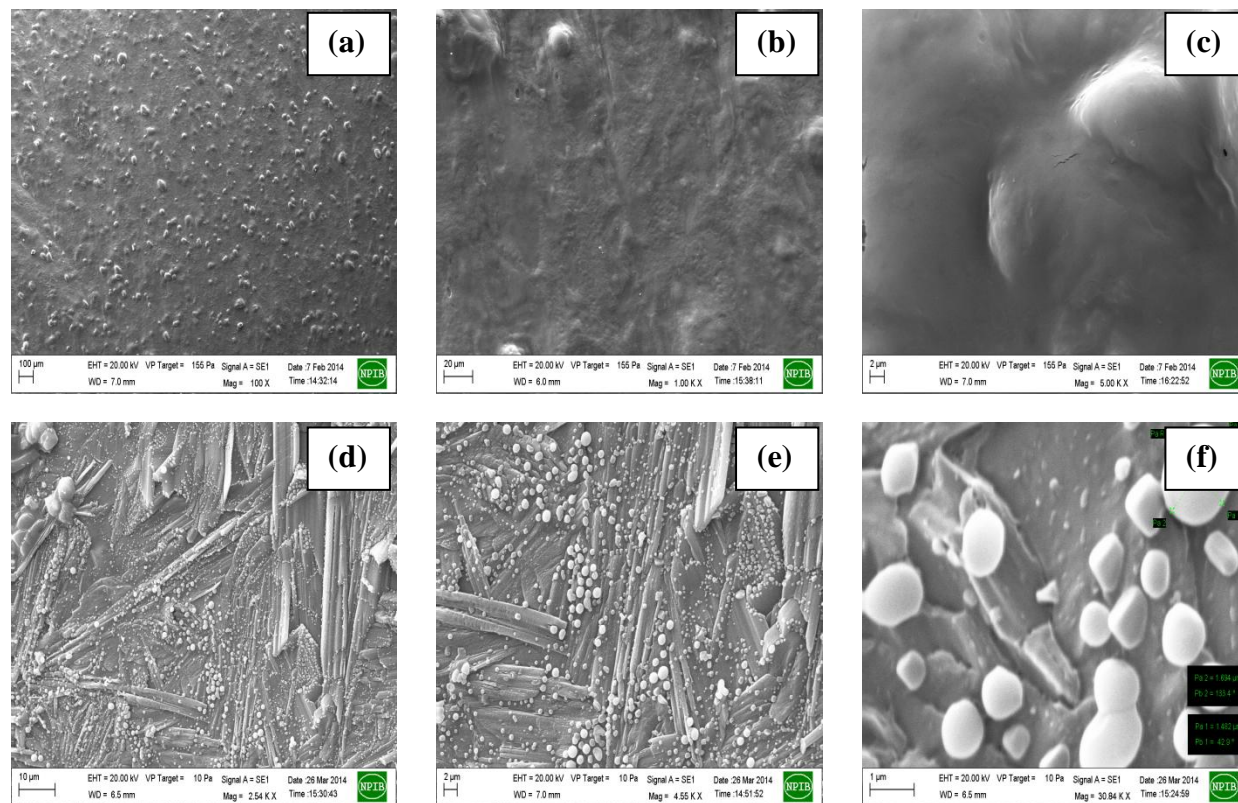


Fig 4. SEM Images of SOS (a-c) and SOS/CaCO₃ (d-f)

Fig 4(a-c) shows the SEM images of SOS at three different magnifications. The images show no distinct phase in the matrix suggesting complete intermingling and reaction of starch and the crosslinker. While fig 4(d-f) depicts the SEM images for SOS/CaCO₃ composites. Images clearly reveal the presence of grain of CaCO₃ in the matrix of starch. On increasing the magnifications the clear distinct grains of CaCO₃ are being observed further more due to the presence of CaCO₃ grains the uniformity of the starch matrix got disturb is found in form of flakes.

3.4. Tensile strength of SOS/CaCO₃ Composites: To study the tensile strength (TS), 5 samples of dimension 1.5 cm x 10 cm, were cut from each variant. The initial grip separation and crosshead speed were set at 50 mm and 20 mm/min, respectively. Tensile strength was calculated by dividing the maximum force by the initial specimen cross-sectional.

Table 3: Effects of Starch Type on Tensile Strength

Code	CaCO ₃ (%)	TS (N/mm ²)
A	0	3.39 ± 0.09
B	10	14.28 ± 0.18
C	20	17.22 ± 0.20
D	30	12.17 ± 0.18
E	40	9.54 ± 0.15
F	50	7.32 ± 0.12

The TS of the control films (unfilled starch nano crystals) was 3.39 N/mm². When the CaCO₃ nano powder was added to rice starch films, the TS of the resulting films increased linearly with the CaCO₃ nano powder content up to 30 % which is being used as filler material resulting TS of 17.22 N/mm² (Table 3 and Fig. 4).

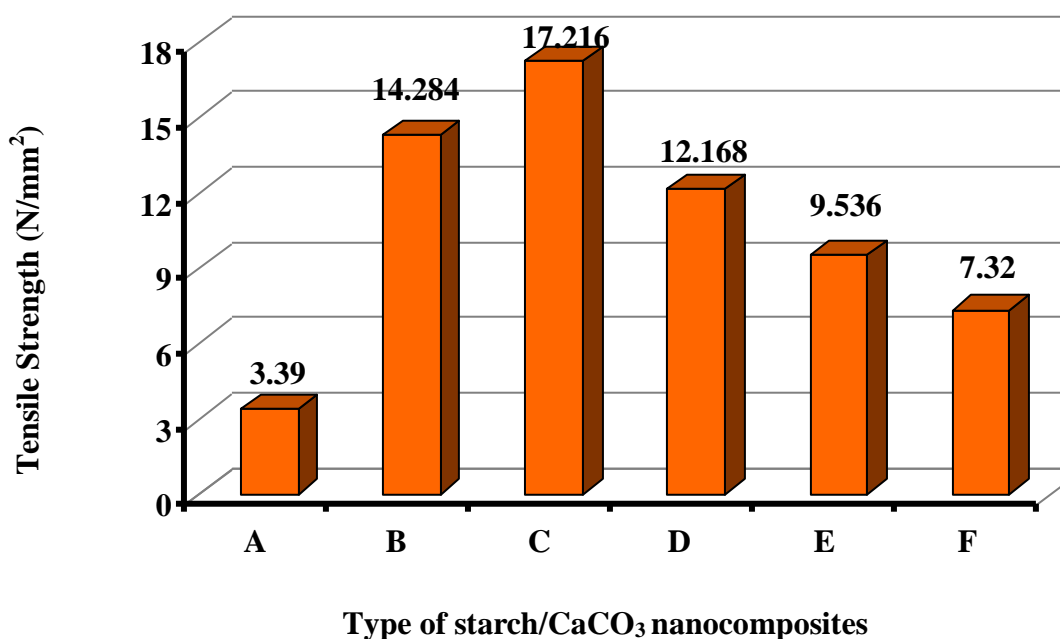


Figure 5: Effect of starch nano crystals content on tensile strength

Conclusion: Soybean oil was modified to crosslinker (SOS) with the introduction of succinic acid, which was used as to generate effective flexible (tensile strength 17.216 N/mm²) composite of starch/CaCO₃. The above results infer that soybean oil based crosslinker can be effectively developed and can be employed actively as a key ingredient in the processing and development

of biodegradable films. These results demonstrate the SOS crosslinked starch/CaCO₃ biofilms can be developed as efficient substitute for non-biodegradable material due to its fine plasticity.

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