

Effect of N,N-Dimethylacetamide/lithium chloride modified microcrystalline cellulose (MCC) on the processing behaviour and properties of cellulose-rubber (NBR and EPDM) composites

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ABSTRACT

Rubber composites of nitrile (NBR) and Ethylene-Propylene-Diene (EPDM) containing unmodified and modified microcrystalline cellulose (MCC) are evaluated for their processing behaviour. The used modified MCC (T-MCC) was treated by N,N-dimethylacetamide/lithium chloride (DMAc/LiCl). ATR-FTIR spectra of NBR-MCC composites have indicated N-H stretching and bending vibrations and confirmed interactions between nitrile rubber and MCC. AFM studies have indicated that the average roughness of NBR-T-MCC was significantly reduced when compared to that of NBR-untreated MCC. Important processing parameters such as scorch time and cure time are found to decrease significantly for both NBR and EPDM composites with T-MCC. Mechanical properties of these composites are found to be low irrespective of cellulose. While swelling of NBR-T-MCC composites was found to be higher in ethylmethyl ketone and DMAc/LiCl solvent systems. The composites with EPDM rubber do not indicate any swelling in DMAc/LiCl and in toluene.

KEYWORDS: Cellulose-rubber composites, Microcrystalline cellulose, N,N'-dimethylacetamide/lithium chloride (DMAc/LiCl).

INTRODUCTION

The necessity for reinforcing fillers from renewable biomass for making composite materials is on the rise now-a-days because of their sustainable nature, low cost, low density and biodegradability^[1-3]. Fibrous fillers such as cellulose^[4-6] and starch^[7-9] are used in elastomer compositions with enhanced mechanical properties while providing scope for biodegradation of such composites. Cellulose contains both amorphous and crystalline regions and the latter confer high strength and stiffness to cellulose fibers^[10]. It is known that the reinforcing potential of any particulate filler depends primarily on the filler surface characteristics, particle size and its distribution. If short fibers are used as fillers for the reinforcement of elastomers, mechanical properties are predominantly in the direction of orientation of the fibers during processing and therefore exhibit anisotropic behaviour.

To improve the compatibility and miscibility, numerous surface modifications have been carried out in order to improve the bonding between the hydrophilic cellulose and hydrophobic rubber matrix. Many authors have studied surface modification of cellulose fibers using sodium hydroxide (NaOH) treatment and acetylation for improving interfacial adhesion with rubber matrix and found that such composites performed better with chemically treated fibers.^[11-14] During acetylation, hydroxyl groups in cellulose chains are substituted by acetyl groups which increase the adhesion of the filler to the matrix.^[15-16] Coupling agents such as silanes and maleic anhydride grafted polypropylene (MA-g-PP) copolymers are used in wood-plastic composites in order to

improve the interfacial adhesion between cellulose and the matrix for better mechanical properties^[17]. Grafting of allyl acrylate and allyl methacrylate on to cellulose fibres are found result in better wetting and improved adhesion with the matrix.^[18]

Microstructures of nanocrystalline cellulose (NCC) and reinforcement in Nitrile Butadiene Rubber (NBR) composites have^[19] found to form agglomeration due to different properties. Vulcanized thermoplastic elastomer based on EPDM rubber /Polypropylene(PP) with cellulose short fibre was^[20] found that 5% of cellulose fibre has no appreciable changes in tensile behaviour. But 20% cellulose fibre with EPDM/PP has shown toughened plastic type behaviour.

Surface modification using reactive difunctional reagents such as diisocyanate grafted cellulose fibres are reported with better mechanical properties in rubber composites^[21]. When surface modified with acryloyl chloride or alkenyl ketene dimer, cellulose provides functional groups to form covalent linkages with rubber matrix during vulcanization^[22]. N-N'carbonyldiimidazole is found to be an effective activator for functionalizing cellulose surface with a carboxylic porphyrin acid^[23]. N,N-dimethylacetamide/ lithium chloride (DMAc/ LiCl) is an effective solvent system for making cellulose solution^[24-30]. N,N Dimethylacetamide/ lithium chloride (DMAc/LiCl) treated silica is used as a reinforcing filler in nitrile rubber (NBR)^[31].

The present work is focussed on the modification of microcrystalline cellulose (MCC) in its solid state by treating it with DMAc/ LiCl. The effects of modified cellulose on

incorporation in NBR and EPDM rubbers on the cure characteristics and mechanical properties are studied. A small quantity of 9% DMAc/LiCl has been used to treat MCC in solid state and the treated samples have been compounded with NBR and EPDM elastomers for making rubber composites. Effects of treated MCC (T-MCC) on the structure, morphology, processing behaviour, mechanical properties and swelling behaviour of the rubber composites are reported in this work.

EXPERIMENTAL

Materials

Nitrile rubber (NBR-KNB35L, 34% Acrylonitrile content) and EPDM rubber (A terpolymer of ethylene-propylene-diene monomer with an ethylidene norbornene content of 4.5%) were supplied by R.K Polymers, India and used as received. Microcrystalline cellulose (MCC, CAS No-9004-34-6) was purchased from sigma Aldrich-India and used after drying at 120°C for 1h. Laboratory grades of N, N'-Dimethylacetamide (DMAc), Lithium chloride (LiCl), ethyl methyl ketone (MEK) and toluene were obtained from Sisco Research Laboratories Pvt. Ltd., India and used as received. Industry grade rubber chemicals such as sulphur, zinc oxide, stearic acid, tetramethylthiuram disulphide (TMTD), 2-mercaptobenzothiazole disulfide (MBTS) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) were used as received.

Preparation of 9 % (W/V) DMAc/LiCl solution and Modification of MCC

A solution was prepared by dissolving 9 gm anhydrous LiCl in 100 ml of N, N'-Dimethylacetamide (DMAc) solvent to form 9% (W/V) solution. 2ml, 4 ml and 6ml of this solution were added to 50 gm of MCC powder and tumble mixed for 30 minutes in a flask and the contents were kept for 24 h so that the DMAc/LiCl solution was absorbed by MCC. Thus treated MCC (T-MCC) was obtained. This T-MCC was used for making rubber composites.

Preparation of Rubber-cellulose Master-batch

Compounding of nitrile and EPDM rubbers along with MCC and T-MCC was carried out using a laboratory two roll mill maintained at room temperature. The rubber was first made into a smooth sheet on the mill and modified and unmodified MCC were slowly added into the rubber on the mixing mill either with NBR or EPDM rubber to form the respective rubber-MCC and Rubber-T-MCC master-batches. From the master-batch sheets were obtained and samples were taken for ATR, AFM and SEM analysis.

Characterization

Fourier transform infrared spectra ATR-FTIR (Model-Spectrum one: Perkin Elmer Spectrometer) of rubber-MCC sheets were performed with the resolution of 1cm⁻¹. Topographic and phase imaging of the rubber-MCC master-batches were performed using atomic force microscopy (AFM model Park XE100) in non-contact mode to study the effect of DMAc/LiCl treatment of MCC on its dispersion in the rubber matrix. Morphological nature of MCC and T-MCC samples, were analyzed using a Carl-Zeiss MA15/EVO 18 model Scanning Electron Microscope (SEM) after they were sputter coated with gold. The MCC samples were separated from nitrile rubber using MEK and from EPDM using toluene. As the rubbers dissolved in these solvents, cellulose particles settle down, separated, washed repeatedly with the respective solvents and dried samples were used in the analysis.

Compounding of NBR-MCC and EPDM-MCC master-batches

The master-batches were converted into rubber compounds with the addition of rubber ingredients on a two-roll mill. Table 1 shows the formulations of NBR-MCC, NBR-T-MCC, EPDM-MCC and EPDM-T-MCC compounds used in this work.

After conditioning for 24 h, the compounds were characterized using a Mooney viscometer (Model-EKTRON Mooney viscometer EK7-2001m) operated at 135°C in order to understand their processing behaviour according to the procedure described in ASTM D1646. The rubber-MCC compounds were then compression moulded into composites in an electrically heated

TABLE 1. Formulations for NBR-MCC and EPDM-MCC composites

Ingredients	phr	
	NBR (100phr)	EPDM (100 phr)
MCC/T-MCC	50	50
Sulphur	1.0	0.8
TMQ	0.5	0.5
ZnO	5.0	5.0
Stearic acid	2.0	2.0
TMTD	1.5	1.5
MBTS	1.0	1.5

* parts per hundred rubber

hydraulic press maintained at 165°C for 15 and 20 minutes respectively for NBR and EPDM rubbers.

Measurement

The tensile tests were performed using a universal testing machine (Model Shimadzu AGS-2000G) according to ASTM D412. The test specimens were cut from the compression moulded rubber composites and tested at a rate of 500mm/min. Tear strength specimens were cut from the rubber composites according to ASTM D624. Hardness (Shore A) of the samples was also measured.

A Known amount of composite specimens were immersed separately in MEK, toluene and DMAc/LiCl solvent system for 48h at room temperature for swelling. After 48h, weight of the specimens was determined and percentage swelling was calculated using the following equation:

$$\% \text{ of Swelling} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 is the mass of sample before swelling and W_2 is the mass of sample after swelling.

RESULTS AND DISCUSSION

The following results correspond to composite materials before compounding.

ATR-FTIR Spectroscopy

The interaction of DMAc/LiCl system with cellulose is shown in Fig. 1 and Fig. 2 using ATR-FTIR analysis. This interaction reduces intermolecular hydrogen bonding in cellulose. This further reduces the dipoles on the cellulose and makes cellulose as lipophilic rather than hydrophilic. The hydrophilicity is reduced with the addition of DMAc/LiCl system. The smaller Li^{++} cation has stronger interaction with cellulose hydroxyl group oxygen atoms. The OH group interacts with the ketone group of acetamide through hydrogen bonding. This breaks the macro molecular network of hydrogen bonding in cellulose and thereby enhancing the dispersion of the cellulose in the rubber matrix.

The ATR spectrum indicated the presence of a broad band around 3450 cm^{-1} in Fig. 1b and 1c. In Fig. 1c the new OH band is prominent and sharper due to the presence of LiCl and DMAc. But the interactions of T-MCC with nitrile rubber also have been inferred. On the basis of comparison of the ATR spectrum of Fig. 2c

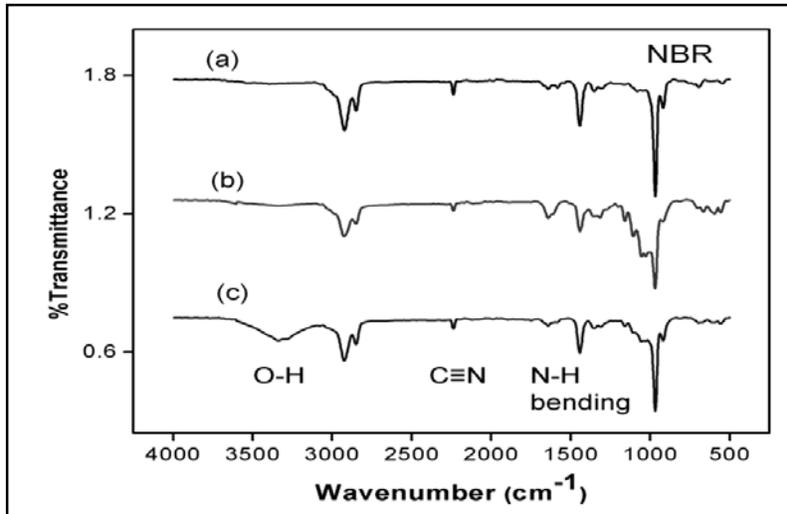


Fig. 1. ATR-FTIR spectra of MCC and T-MCC using NBR rubber system: a) NBR rubber; b) NBR-MCC master batch; c) NBR-T-MCC master batch.

which involves the EPDM rubber which cannot have the hydrogen bonding interaction.

The ATR spectra of the Fig. 2b and 2c showed a broad and sharp because there is no interaction of T-MCC with EPDM. Further the EPDM matrix coming in between cellulose

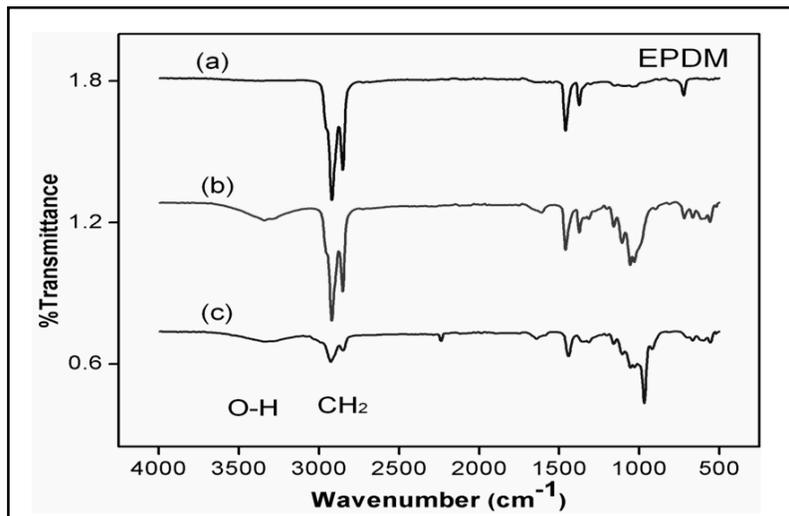


Fig. 2. ATR-FTIR spectra of MCC and T-MCC using EPDM rubber system: a) EPDM rubber; b) EPDM-MCC master batch; c) EPDM-T-MCC master batch.

structure will dilute the composite. This dilution enhances long range hydrogen bonding with increased distances and therefore the OH peak is broader and diffused.

Atomic Force Microscopy

Atomic force microscopic observations have been carried out on rubber-MCC masterbatches in non-contact mode in order to observe the dispersion of MCC in the rubber matrix. NBR and EPDM matrices containing

MCC and T-MCC samples are examined and the results are shown in Figure 3.

For the NBR rubber-MCC system, a relatively rough surface morphology with an average roughness value of 57 nm is observed in Figure 3a. However, this value is decreased significantly to 15 nm when T-MCC is used in NBR indicating better distribution of the MCC as shown in Figure 3b. Polar interactions among the three constituents namely, DMAc/

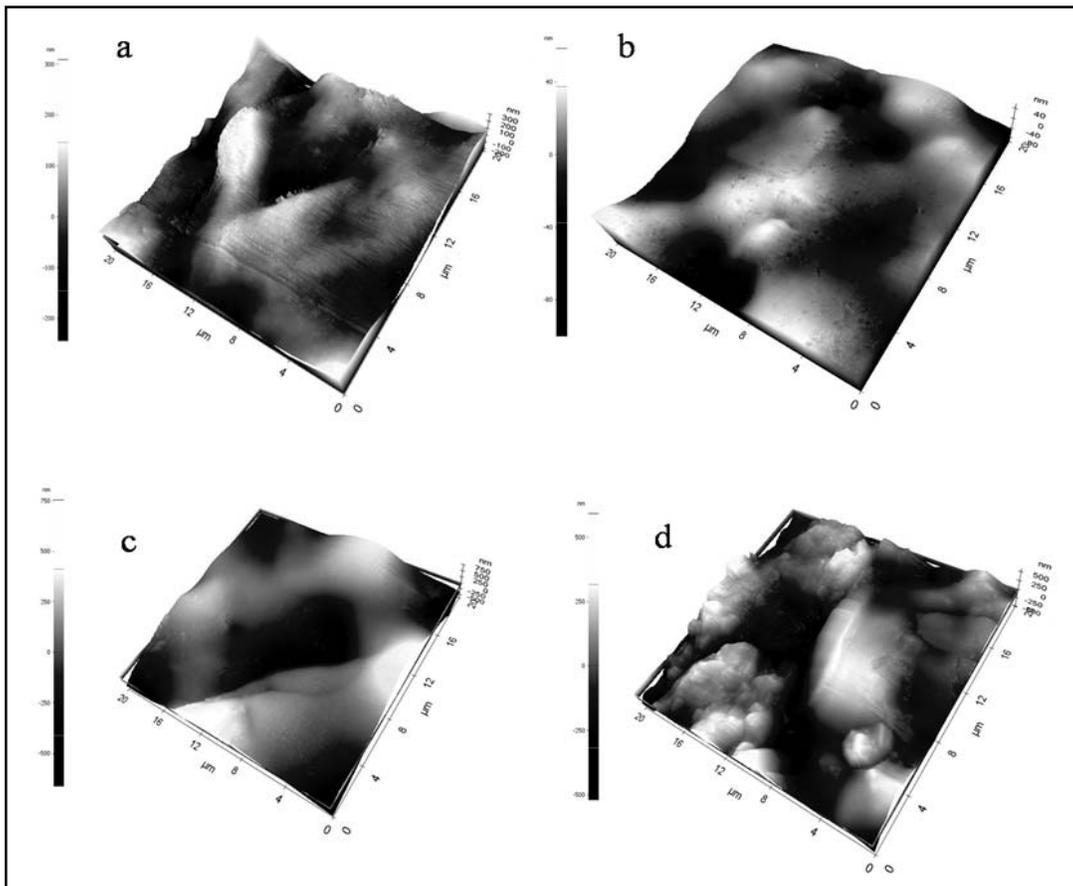


Fig. 3. AFM images of MCC and T-MCC system with NBR and EPDM rubber: a) NBR-MCC; b) NBR-T-MCC; c) EPDM-MCC; d) EPDM-T-MCC system.

LiCl, MCC and NBR could be attributed for reduced self-association between cellulose molecules and enhanced inter-association between cellulose and NBR resulting in reduced surface roughness in this system.

However, in the non-polar EPDM matrix, when T-MCC is added, interactions can happen only between DMAc/LiCl and MCC. In this case, therefore, EPDM with the untreated MCC samples has shown higher average roughness values of 162 nm as shown in Figure 3c as

against the 131 nm shown in Figure 3d for the sample having T-MCC. In the latter system, a polar interaction between DMAc/LiCl and MCC enhances the dispersion of MCC into EPDM rubber could be the reason for relatively lower surface roughness when compared to EPDM containing MCC. The T-MCC has become less polar and therefore its dispersion in EPDM would be enhanced. Therefore, a smooth surface results in this (Fig. 3d) composite.

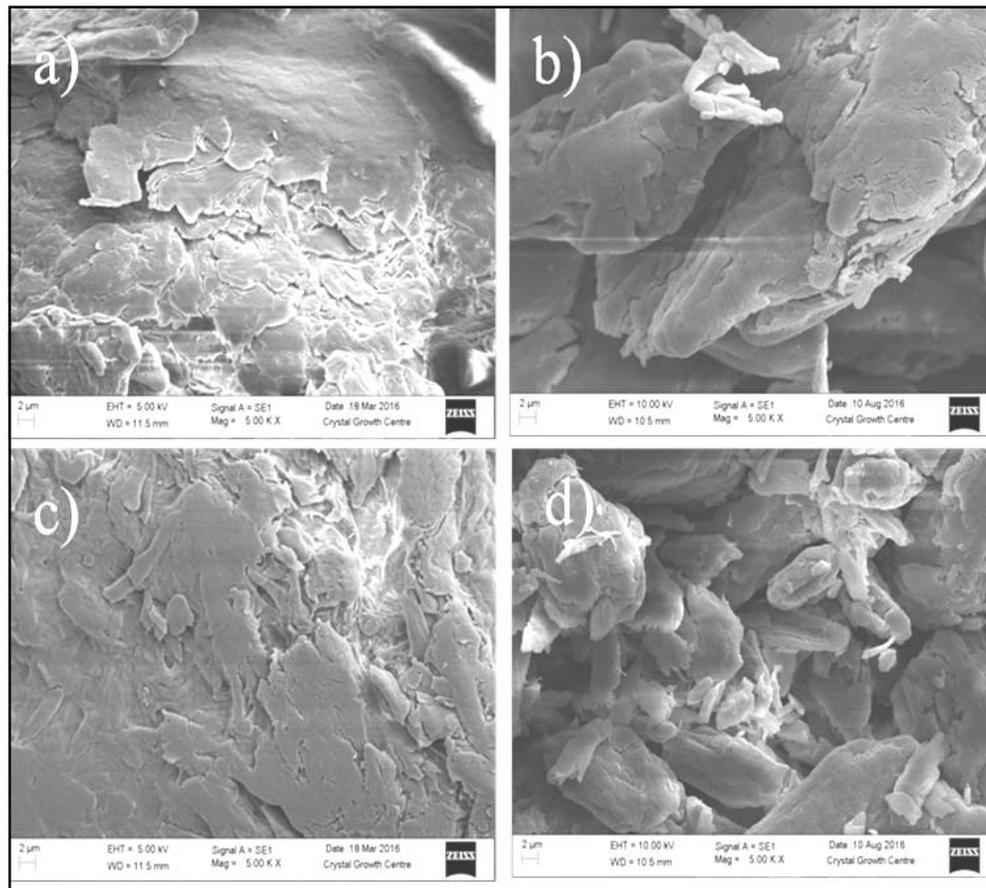


Fig. 4. SEM micrographs of MCC and T-MCC samples separated from NBR and EPDM rubber: a) NBR-MCC; b) NBR-T-MCC; c) EPDM-MCC; d) EPDM-T-MCC.

Scanning Electron Microscopy

The untreated MCC samples separated from the rubbers to show a continuous plate like morphology and with the larger particulate or crystallite size (Fig. 4a and 4c).

When the NBR-T-MCC was treated with MEK, it can remove DMAc as it is soluble. The SEM picture showed a discontinuous leaf like structure indicating the cellulose particle dispersion in the rubber matrix (Fig. 4b). Fig. 4d indicated a finer dispersion of cellulose

particles which present as clusters. In EPDM-T-MCC composite was treated with toluene which cannot remove either LiCl or DMAc and therefore the representing a realistic picture of cellulose moiety that could have dispersed in EPDM rubber.

Curing Characteristics

The physical composite MCC and NBR itself had shown a drastic decrease in curing time indicating good dispersibility, stronger interaction between T-MCC and NBR probably

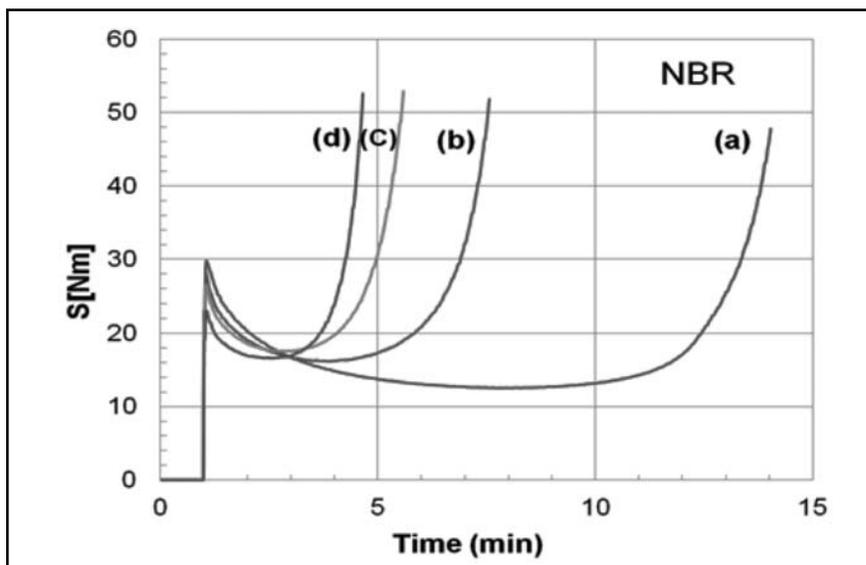


Fig. 5. Mooney viscosity of MCC and T-MCC using NBR rubber composites: a) NBR rubber; b) NBR-MCC composites; c) NBR- T-MCC (2ml); d) NBR-T- MCC (6ml).

through the inter molecular hydrogen bonding. The treated MCC with DMAc/LiCl has shortened the curing time as observed in Fig. 5 (c & d). As the concentration of DMAc/LiCl increased the curing time decreases almost a decrease of 10 min in the curing time. The addition of DMAc/LiCl would

have enhanced the interaction between micro cellulose and NBR. As the numbers of interactions are stronger and greater the curing time is expected to decrease.

In EPDM rubber composites addition of untreated MCC did not show a change in curing characteristics (Fig. 6a & 6b). The probable

reason is that the interaction between MCC having OH groups with EPDM having saturated alkyl groups will be negligible. When T-MCC is mixed with EPDM rubber showed comparatively a lesser curing time as in Fig. (6c & 6d). The reason is that the treated MCC has lesser dipolar structure and therefore its interaction or dispersibility in EPDM increases

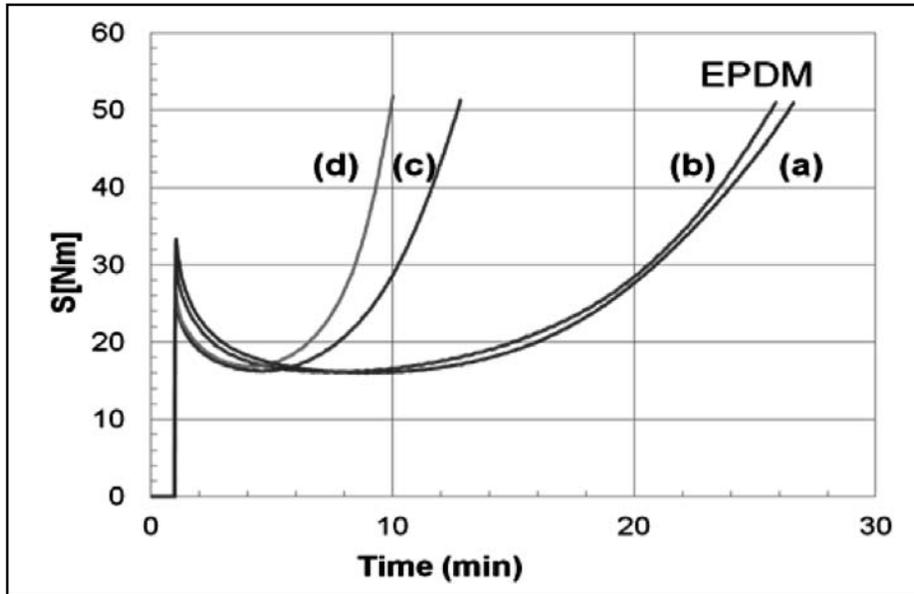


Fig. 6. Mooney viscosity of MCC and T-MCC using EPDM rubber composites: a) EPDM rubber; b) EPDM-MCC composites; c) EPDM-T-MCC (2ml); d) EPDM-T-MCC (6ml).

TABLE 2. Effect of T-MCC on the scorch and cure time of nitrile rubber and EPDM rubber

Composition	Minimum Torque [N-m]	Maximum Torque [N-m]	Scorch time [min]	Cure time [min]
NBR	12.5	47.77	12.05	14.02
NBR-MCC	16.14	51.83	6.03	7.34
NBR-T-MCC [2ml]	16.52	52.9	4.25	5.35
NBR-T-MCC [6ml]	17.58	52.61	3.51	4.39
EPDM	15.97	51.01	16.40	26.36
EPDM-MCC	16.00	51.00	15.52	25.52
EPDM-T-MCC [2ml]	16.17	51.34	8.13	12.49
EPDM-T-MCC [6ml]	16.77	51.9	7.03	10.02

and therefore reduces the curing time. From the present investigation we conclude the DMAc/LiCl is a good structural modifying agent for cellulose and cellulose derivatives for the effective dispersion into rubber compounding and composites.

Mechanical properties

Mechanical properties have been studied for the compounded rubber prepared (Table 1).

NBR showed greater tensile strength, elongation, tear strength and hardness compared to EPDM. This is due to greater dipolar interactions present in NBR due to nitrile groups. In EPDM there are greater van der waals type of interaction which are comparatively weaker than in NBR. Addition of T-MCC has decreased the tensile strength, elongation, tear strength and hardness. This is because addition of T-MCC will decrease the

TABLE 3: Mechanical properties of compounded NBR and EPDM containing untreated and T-MCC

Rubber	Amount of DMAc/LiCl for Treatment MCC [ml]	Tensile strength [MPa]	Elongation at break [%]	Tear Strength [Kg/min]	Hardness [Shore A]
NBR	0	2.55	259	1.70	67
	2	2.38	226	1.40	64
	4	2.21	217	1.40	62
	6	1.91	211	1.40	61
EPDM	0	1.24	165	.070	52
	2	1.21	171	0.64	51
	4	1.20	176	0.59	51
	6	1.30	178	0.57	50

interactions in NBR and therefore these mechanical properties showed a decrease.

NBR and EPDM are elastomers but intervened by modified MCC, the interactions decreases

TABLE 4: Swelling behaviour of NBR and EPDM composites containing untreated and treated MCC (T-MCC)

Amount of DMAc/LiCl used for treating MCC [ml]	% Swelling of		
	NBR-MCC composites in MEK	NBR-MCC composites in DMAc/LiCl	EPDM-MCC composites in toluene
0	58	11	51
2	60	15	51
4	64	22	47
6	65	27	47

for the elongation purpose and thereby affected the mechanical properties.

Swelling behaviour of vulcanized rubbers

In NBR-MCC composites, methyl-ethyl-ketone (MEK) can interact with cellulose and as well as with NBR causing swelling of the composites. But NBR-MCC when dipped in DMAc/LiCl, the excess of Li⁺ can interact with cellulose and thereby decreased the swelling. In case of EPDM-MCC composites when dissolved in toluene, the treated MCC reduces the penetration of the aromatic hydrocarbon toluene and therefore the swelling decreased as DMAc/LiCl concentration was increased.

CONCLUSION

This present studies indicated that DMAc/LiCl is a good chemical modifying reagent for microcrystalline cellulose in order to achieve miscibility and good dispersibility in rubber matrixes like NBR or EPDM. If the rubber has dipoles or polar functional groups this particular reagent is superior in bringing out uniformly distributed rubber composites with cellulose and cellulose derivatives. Cellulose interactions with such a rubber are appreciable. But for rubber made up of hydrocarbon like isoprene or EPDM, DMAc/LiCl will be a best modifying agent to make rubber composites using cellulose.

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