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Ethylene Vinyl Acetate Blends with Cellulosic Fillers and Reinforcements

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Abstract

Polymeric blends based on ethylene vinyl acetate (EVA) rubbers filled with high mol. wt. carboxymethyl cellulose were investigated in view of possible employment as biodegradable materials. The effect of vinyl acetate content and of addition of transesterification agent to increase interaction between EVA and cellulosic components was considered. Blends reinforced with cellulose microfibrils in different amounts were also characterized in their mechanical, rheological and thermal behavior.

Keywords: poly(ethylene-co-vinyl acetate); carboxy methyl cellulose; cellulose microfibrils; polymeric bio-blends; reactive compatibilization.

Introduction

Polymeric materials enter various areas of our everyday life and, therefore, management of polymer wastes is one of the primary problems that industrially advanced nations, but not only, are required to cope with. Considering such issue, all polymeric materials that undergo complete or partial degradation after their application life become preferable. Environmentally degradable polymers and their blends with natural reinforcements are thus important for modern technology since they can often be considered as ecologically safe materials. New materials based on starch or cellulose derivatives and a number of synthetic polymers find a number of interesting applications in different industrial sectors, as for example in packaging, products for agriculture, vehicle components but also in personal hygiene and medical items. In the automobile industry and civil constructions, for instance, starch derivatives and biofibers are extensively employed as additives or reinforcements in plastics, elastomers, insulating materials. In agriculture and gardening, the continuously growing use of biodegradable objects ranges from flexible mulching films, to rigid containers for plants and fertilizers [1-3].

Blends of starch or cellulose derivatives and certain synthetic polymers hold the lead among some new materials that have found successful applications. In these materials, the presence of synthetic polymers is often needed to impart the necessary physical or mechanical properties to the blends. As a matter of facts, many of the candidates for biodegradable polymers have some limitations in their mechanical performances, processability or cost; such aspects represent serious drawbacks for their extensive use. Blending of starch or cellulose based materials with non-biodegradable commodity polymers can overcome such limitations, yet with a reduction of the total amount of plastic wastes, even though it should not be assumed as the ultimate solution to environmental problems caused by plastic wastes disposal.

A further mean to improve mechanical performances without affecting biodegradability is represented by the addition of reinforcing cellulosic natural fibers. High quality fibers, suitable as

plastic reinforcements, can be extracted from a large variety of plants and crops through processes able separate fibers with micro and even sub-micron dimensions [1,4].

In this research, blends based on poly(ethylene-co-vinyl acetate) (EVA) and carboxy-methyl cellulose (CMC) with different compositions were produced by reactive blending; their physical-chemical properties as well as thermal, mechanical and rheological behaviour were investigated. These blends represent a new type of flexible material with performances promising for the substitution of traditional polymers in a number of industrial and agricultural applications. Blends reinforced with cellulose microfibers were also produced and tested. In this way, the stiffness and hardness of the resulting flexible blends may be increased and tuned in accordance to the requirements entailed by the expected applications.

CMC is a natural organic polymer that is non-toxic and fully biodegradable. It is a polysaccharide whose properties make it ideal for some industrial uses and one of the most promising materials for biodegradable plastics. It is extensively employed as viscosity modifier and emulsion stabilizer in many industrial sectors including food, textiles, paper, adhesives, paints, pharmaceuticals, cosmetics and mineral processing. However, direct employment of CMC to produce items has some limitations related to its poor mechanical properties and processability, which make it little appealing for a number of convenient uses.

Polymer blending of selected components is one of the easiest and most cost-efficient ways to produce new materials with desired characteristics. Polymers are usually thermodynamically immiscible in blends because of the low entropy of mixing. On the other hand, in many instances immiscible blends possess remarkable characteristics, which are useful for a number of practical applications. Moreover, polymer modifications or compatibilizing additives are often employed to modify components affinity and to improve blends performances [5- 7].

A further way to get improved interactions is through reactive compatibilization of immiscible polymers. Reactive compatibilization is used to overcome agglomeration problems and weak interactions between immiscible phases; it is often more efficient in stabilizing blends of immiscible polymers and has a number advantages over the use of compatibilizers, deriving from the formation of chemical bonds directly at the interface. Reactive compatibilization can be activated either through the use of specific reactants and by proper selection of processing conditions [8-11].

The polyester family has the possibility to create chemical reactions thanks to formation of ester bonds and transesterification is a primary reaction in polyesters. Researches about the exchange reaction in polyesters usually refer to polymer blends in which ester bonds exist in their polymer backbones. Less common are the investigations about polymers in which reactive groups are located in branching chains, such as EVA. EVA, is a modification of polyethylene (PE) with vinyl-acetate as comonomer; the presence of vinyl-acetate in the chain reduces crystallinity and modifies melting behavior, compared to pure PE [12]. Thus, it has many characteristics of thermoplastic elastomers, depending on the percentage of vinyl acetate content. EVA addition to a biodegradable polymers in blends may provide improved mechanical properties, better ozone resistance, good weather resistance and lower material cost. Moreover, EVA is a non-biodegradable polymer; on the other hand it can experience biodegradation under particular conditions and specially when a high percentage of vinyl acetate is present in the copolymer [2, 13].

The preparation of CMC/EVA blends and CMC/EVA reinforced with cellulose microfibers by melt reactive mixing in presence of a transesterification agent is here described. The addition of a

transesterification agent to improve compatibility between EVA and CMC is investigated. Thermal, rheological and mechanical properties of the new materials obtained are described and discussed in relation to their composition and morphology.

Experimental

Carboxymethyl cellulose sodium salt (CMC), average MW ca. 250,000, was obtained in form of solid powder from Sigma-Aldrich, Saint Louis, MO 63103 USA.

Ethylene-vinyl acetate random copolymers with vinyl acetate (VA) contents of 38-41 % (EVA 40) and 17-19 % (EVA 18) were received from Arkema, Legnago, Italy (EVATANE®).

Cellulose microfibrils (WS) extracted from cotton, with a fiber length of 300-500 μm , were supplied by West System, Bay City, Michigan, USA.

Tin 2-ethylhexanoate was purchased by Sigma Aldrich and used as transesterification agent (TA).

CMC-EVA blends with different compositions were prepared by melt reaction of CMC and EVA in the presence of transesterification agents (TA) in a Brabender mixer. CMC-EVA 40 blends (50% CMC), added with 10 and 30 % wt of cellulose microfibrils were also prepared. All materials were dried at 50 °C in vacuum for 12 hrs before blending. Torque-time curves were recorded to get information on the compounding effectiveness and shear stability of the blends. Compounding was performed at 150 °C and 50 rpm for about 6 min. All the blend samples were then compression molded by hot pressing at 150 °C to make plates with 1 or 2 mm thickness; specimens for mechanical and DMTA measurements were die cut from molded plates.

Glass transition of blends with EVA 40 was determined by DSC (TA Instruments mod. Q100) at 10 °C/min heating rate. Blends composition and corresponding glass transition temperatures are reported in Table 1.

Table 1 - Composition and thermal properties of blends

Sample	CMC (wt%)	EVA (wt%)	Cellulose Fibers (wt%)	TA (%)	Tg (°C)
EVA 40 (1)	-	100	-	-	-32.2
CMC35-EVA 40	35	65	-	-	-31.8
CMC35-EVA 40 TA	34.5	64.5	-	1	-31.8
CMC50-EVA 40 TA	49.5	49.5	-	1	-31.5
CMC70-EVA 40 TA	69	30	-	1	-31.1
CMC35-EVA 18 (2) TA	35.4	63.6	-	1	nd
CMC50-EVA 18 TA	49.7	49.3	-	1	nd
CMC70- EVA 18 TA	69	29.96	-	1	nd
CMC50-EVA 40 TA - F10	44.2	44.3	10.5	1	nd
CMC50-EVA 40 TA - F30	34.5	34.5	30	1	nd

(1) EVA 40 = 40 % vinyl acetate content

(2) EVA 18 = 18 % vinyl acetate content

Tensile tests according to ASTM Standard D882 were performed by an Instron Model 3366 Universal Testing Machine. Strength, elongation at break, elastic modulus were determined with 1 mm thick specimens.

Torsional dynamic-mechanical tests (DMTA) were performed with 2 mm thick specimens by a Rheometrics RDAII rheometer. Temperature sweep tests (-100 °C/+100 °C) at 1 Hz frequency were carried out; curves of complex viscosity vs. frequency at 150 °C were also determined.

TGA analysis (T.A. Instrument Model Q500) was used to investigate thermal degradation effects in the blends.

Morphological analysis of blends after rupture was done by SEM (Hitachi TA3000) in order to estimate phase distribution. Specimens were observed after gold metallization at 100X to 3000X magnifications.

Results and Discussion

The recording of torque vs. time during blend production allowed to follow the viscosity evolution during mixing and to reach blends stability at the end of mixing. It was observed that after an initial reduction of torque, the viscosity of blends increased to a fairly stable situation after about two minutes. The presence of transesterification agent reduces the time to reach stability improving processability. After blending, the resulting material appeared visually homogeneous and the components well dispersed. DSC analysis of the blends (Table 1) indicates that no appreciable modification of EVA phase glass transition results from the addition of CMC phase either with or without transesterification agent. On the other hand, mechanical properties are markedly modified by addition of CMC and, to some extent, of TA (fig. 1-2).

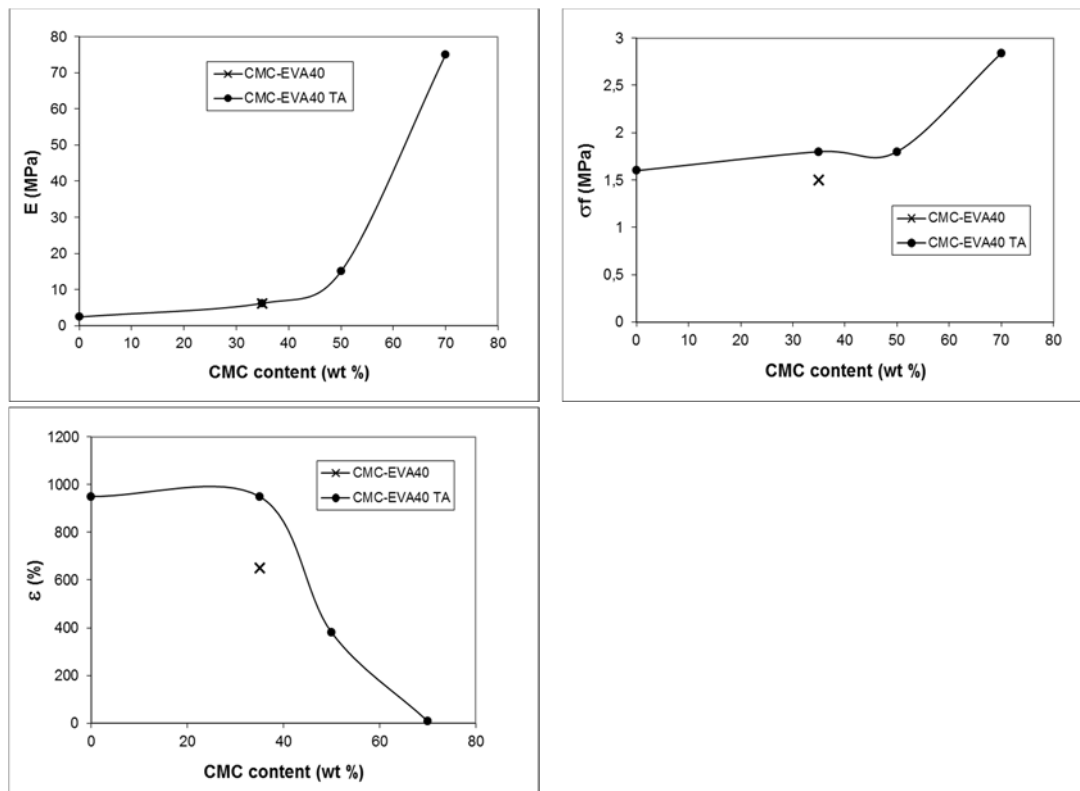


Figure. 1 – Mechanical properties of CMC-EVA40 blends as function of CMC content

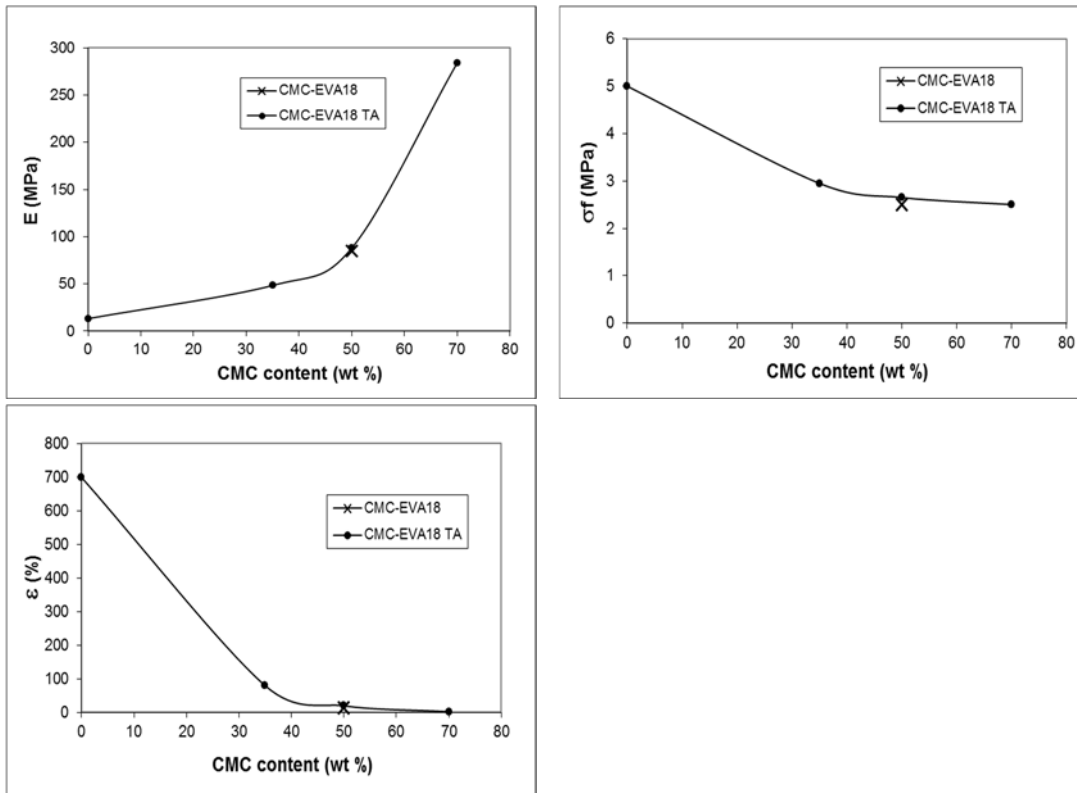


Figure. 2 – Mechanical properties of CMC-EVA18 blends as function of CMC content.

The blending of EVA 40 with CMC leads to an increase of both stiffness and strength, which, however, remain relatively limited up to CMC content of 35-50 %. It is interesting to notice that up to such content, also elongation remains fairly high and the resulting material maintains good flexibility and extensibility. If no TA is employed, somewhat lower strength and elongation is observed. At higher CMC contents, the evident stiffening and strengthening effect of CMC is accompanied by a remarkable drop of elongation at break.

In case of stiffer EVA 18, the addition of CMC remarkably reduces elongation already at contents lower than 35 %; a reduction of strength is also observed possibly due to a higher sensitivity to stress concentrations and brittleness introduced by CMC particles.

A further relevant effect over mechanical properties of the blends of EVA with CMC is that, consistently with the DSC results, loss of flexibility is observed practically unvaried for all blends at about the same temperature, lower than about $-20\text{ }^{\circ}\text{C}$, i.e. approaching T_g . Conversely, on increasing CMC content, stiffness is maintained over extended temperature ranges, i.e. up to above $50\text{-}60\text{ }^{\circ}\text{C}$ (figure 3).

Measurements of complex viscosity vs. frequency of CMC-EVA 40 blends (fig. 4) show that melt viscosity remarkably increases with increasing CMC content. Moreover, the presence of TA leads to a somewhat higher viscosity compared to the similar blend with no TA; this may suggest an effective compatibilizing action of TA, i.e. increasing transesterification, leading to modification of interactions of CMC particles with EVA matrix although a definite relationship between viscosity and compatibilization is not clear [8,9].

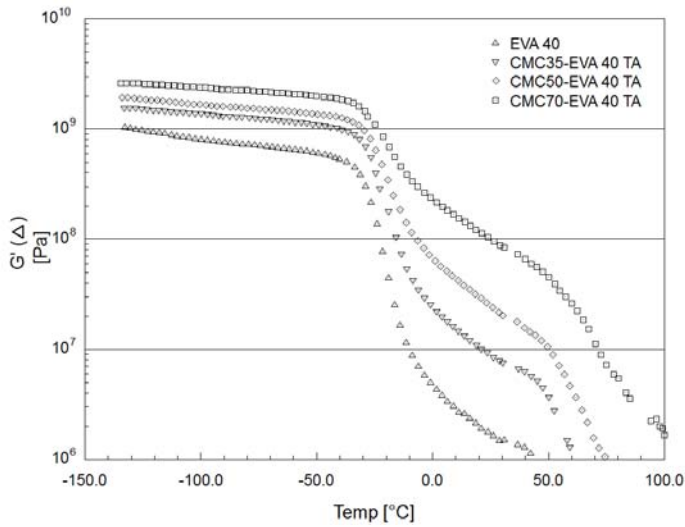


Figure 3 – Dynamic mechanical modulus (G') as function of temperature of different CMC-EVA40 blends.

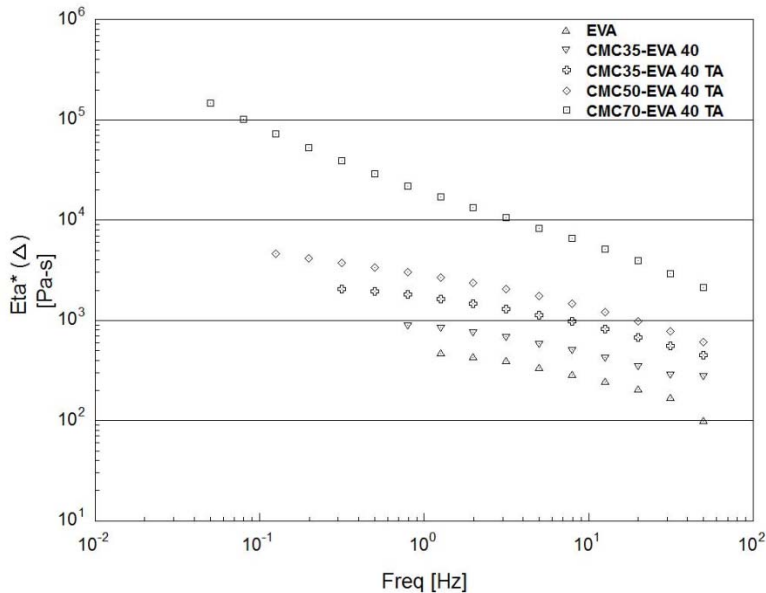


Figure. 4 – Complex viscosity curves of EVA and EVA-CMC blends with different CMC content ($T = 150\text{ }^{\circ}\text{C}$)

The dispersion of cellulosic microfibers in CMC-EVA blends introduces further remarkable modifications in rheological and mechanical characteristics. Considering the affine chemical nature of cellulosic microfibers with CMC it is not surprising that easy fiber dispersion is obtained by melt mixing. Fig. 5 shows SEM micrographs of CMC-EVA 40 with 50% CMC (Fig. 5a) and its blends with 10 % wt of microfibers (Fig. 5b). At the magnification level employed, a fairly homogeneous dispersion of particles and fibers was observed. Interestingly, CMC particles often appear quite elongated, probably as result of the intensive mixing procedure, so that they bear resemblance to a sort of fibers. Fracture surfaces always show extensive deformation of the rubbery EVA matrix; due to the full straining and eventual detachment of CMC particles, no evident information about possible effects of transesterification agent on interface interactions could be drawn from micrographs.

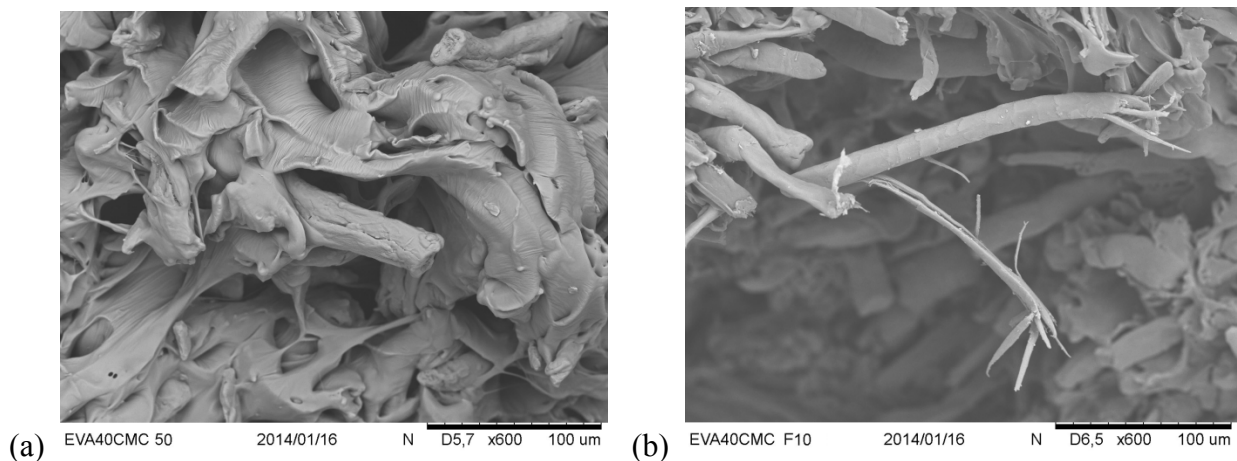


Figure 5 - SEM micrographs of CMC-EVA 40 blend (a) and the same blend with cellulose microfibrils (b)

As expected, the addition of microfibrils consistently enhances blend viscosity, thus affecting processing. In figure 6, the viscosity of CMC-EVA 40 blends with different microfibril contents is reported. It can also be observed that the presence of TA leads to an increase of viscosity, although to a limited extent; this is certainly related to the higher viscosity of the blend matrix, but may also suggest better interaction between matrix and cellulosic fibers.

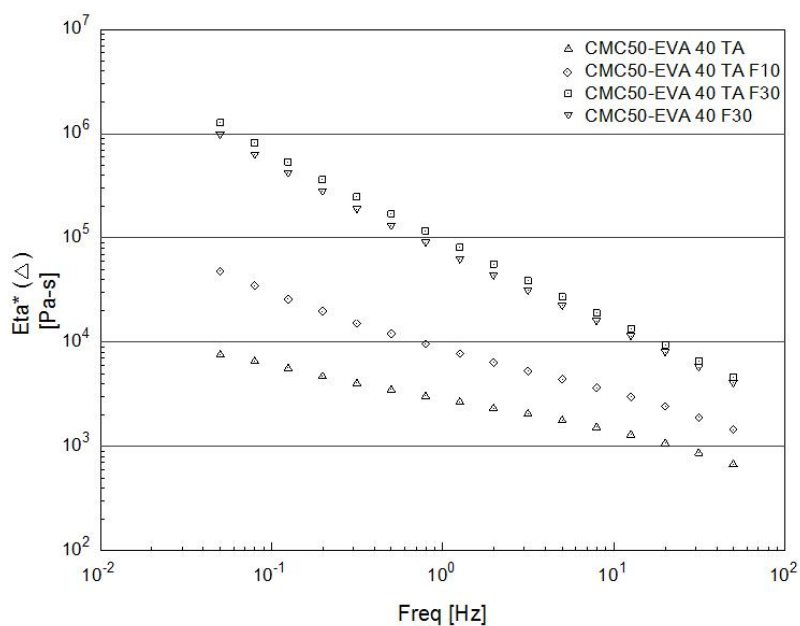


Figure 6 - Complex viscosity curves of EVA-CMC blends with different cellulosic microfibrils content ($T = 150 \text{ }^\circ\text{C}$).

Dynamic-mechanical and mechanical tests of the blends with microfibrils show that a consistent reinforcement is obtained with addition of 10 and 30 % fibers (figure 7 and 8). It is observed that the stiffening effect of microfibrils allows to further increase the possible application temperature range compared to the polymer blend alone. Increase of modulus and strength is however accompanied by a remarkable reduction of elongation at break, which may prevent the use of such

material for flexible or extensible films. As for viscosity, the presence of TA leads also to a minor increase of mechanical strength, which, again, can be a possible consequence of better interaction between matrix and fibers.

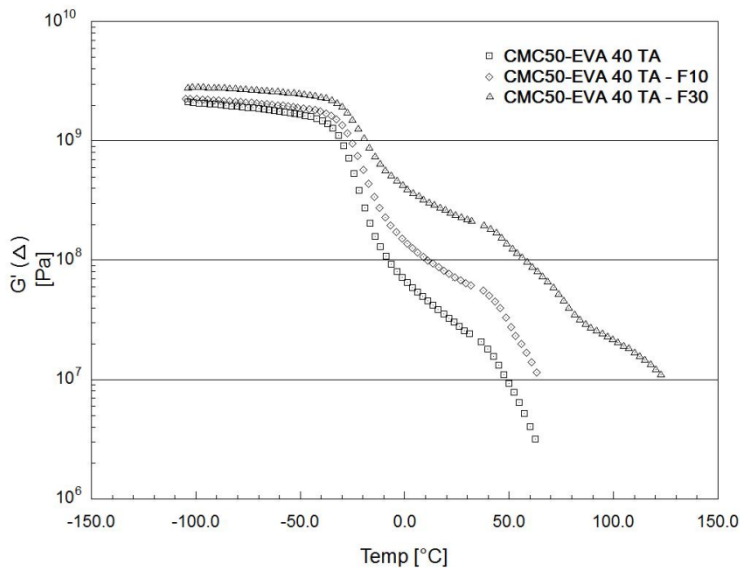


Figure 7 - Dynamic mechanical modulus (G') as function of temperature of CMC 50-EVA40 blends with different fibers content.

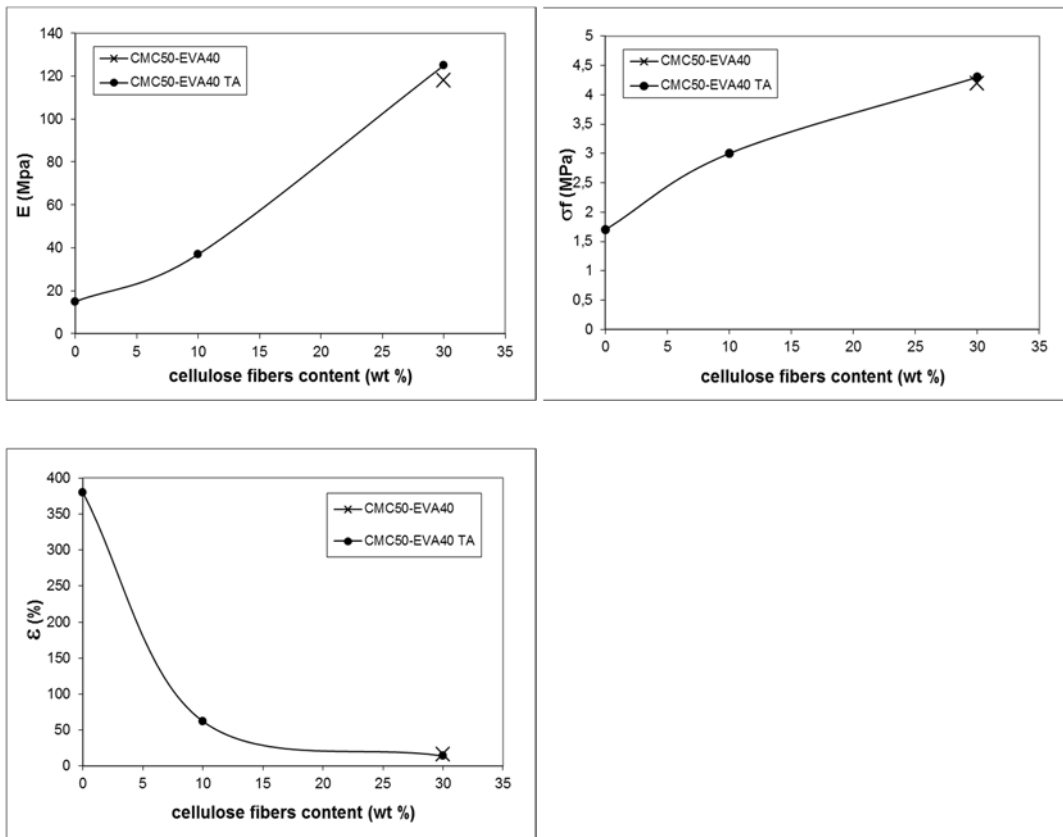


Figure 8 - Mechanical properties of CMC50-EVA40 blends with different fibers content.

Thermogravimetric analysis of CMC-EVA and CMC-EVA added with cellulose microfibrers (figure 9) shows a significant loss of about 5%, at temperatures ranging from 100 °C to 150 °C, due to the absorbed water. Thermal degradation appears to be relevant only at temperatures above 270 °C, indicating that processing at lower temperature can consistently limit degradation effects.

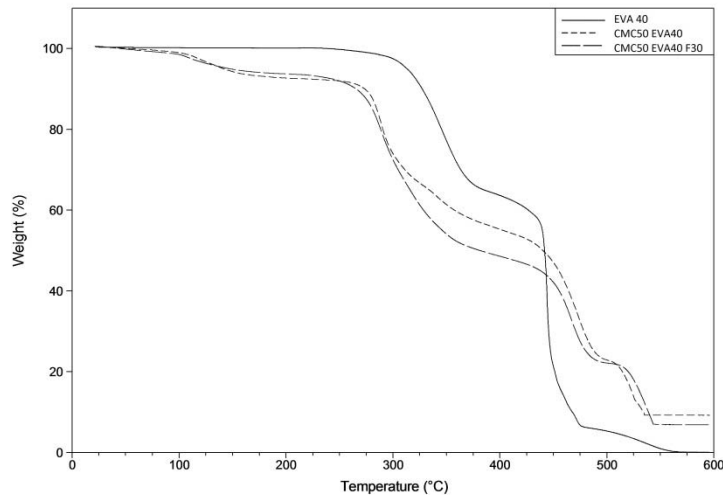


Figure 9 – Thermogravimetric analysis of EVA40, CMC50-EVA40 and CMC50-EVA40 with 30% cellulosic microfibrers

Conclusions

Reactive blending of cellulose based biodegradable polymers with EVA in different relative amounts leads to flexible or rigid materials, which may be processed to obtain stretchy films or stiff plastic components suitable for a number of applications. The addition of a transesterification agent increases possible interactions between EVA matrix and CMC particles with positive effects over dispersion and mechanical properties. The introduction of cellulose microfibrers can be used as a further tool to tune the processability and mechanical performances of the material, still maintaining the biodegradation characteristics. As expected, thermal degradation effects pose constraints to the maximum materials processing temperature; good mixing and molding can however be carried out at relatively low temperatures, well compatible with degradation limits.

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