Preliminary Studies on the Synthesis and Characterization of Cellulose – Maleic Anhydride – Dicyclopentadiene Composites

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Cellulose composites with maleic anhydride – dicyclopentadiene copolymer matrix were obtained by "in situ" free-radical polymerization. The syntheses were carried out in two different solvents: toluene and dioxane, aiming at determining their influence upon both the polymerization process and properties of the resulting materials. The composite materials obtained were characterized both structurally by FT-IR, XRD and SEM, and from the thermal behavior point of view by TGA-DSC-MS analyses.

Keywords: cellulose composites, maleic anhydride – dicyclopentadiene copolymer, in situ polymerization

Cellulose is the most abundant natural polymer, which can be found in the cellular wall of the large majority of plants and has a special importance due to its biodegradability and regenerability [1,2]. However, cellulose displays some deficiencies as a material: it is hydrophilic, and its processing temperature is low, around 200°C as the cellulosic materials start decomposing at about 230°C. The hydrophilic character is due to the presence of anhydro-d-glucose (it contains 3 hydroxy groups) in the elementary unit of the cellulose macromolecule [3]. One of the most employed methods to reduce the hydrophilic character of cellulose is its esterification [4-7] with various compounds like: maleic and acetic anhydrides, fatty acids, vinyl acetate, etc.

As it is well known, maleic anhydride (MA) does not homopolymerize radically. That is why, to introduce the anhydride and corresponding acid (obtained after mild hydrolysis) groups into polymers, MA copolymerization with various comonomers like propylene, styrene, ethylene, etc. is employed [8-11].

Dicyclopentadiene (DCPD), one of the most available cycloolefin, is a free radically non-homopolymerizable monomer. One of the most used method of valorization of DCPD is copolymerization. Within the last period of time, a special interest was devoted to elucidating the reaction mechanism and process features of the homogeneous copolymerization of DCPD and MA [12,13]. Thus, the influence of various solvents (dioxane and toluene) upon the copolymerization process was investigated. During these studies, it was demonstrated that dioxane is a very good solvent, the polymerization process being a homogeneous one, whereas toluene is a bad solvent, and therefore the process is quasi-heterogeneous this time, more precisely a precipitating one.

On the basis of the above considerations, the present work aims at preparing cellulose composites employing MA and DCPD as the monomers. One should mention that, to the best of our knowledge, there are no studies in literature concerning the preparation of such materials up to now. Both the characteristics of the cellulose-AM-DCPD copolymer composite synthesis process in two different solvents, i.e. a precipitating one (toluene) and a non-precipitating one (dioxane), and the influence of these ones upon the copolymerization process were investigated.

Experimental part

Materials

Maleic anhydride (MA), Fluka, was purified by recrystallization from chloroform.

Dicyclopentadiene (Merck, DCPD), and 1,4-dioxane (Fluka), were used as received.

Toluene (Chimopar S.A.), was washed with H_2SO_4 d=1.84, K_2SO_4 10% aqueous solution, then twice with distilled water and finally rectified on a column at atmospheric pressure.

The initiator was 2,2'-azo-bis-isobutyronitrile (AIBN), purified by recrystallization from chloroform/methanol mixture.

Cellulose D (Riedel-de Haen) with DPn=400–500, dried overnight at 1÷2 torr and 40°C, was used as filler.

Characterizations

All composites were characterized in solid state by FT-IR spectroscopy, using a Bruker VERTEX 70 instrument, equipped with a Harrick MVP2 diamond ATR device.

The thermal analyses were performed on a NETZSCH STA 449C Jupiter simultaneous TGA-DSC system at 5K/min, under He atmosphere coupled with Aeolos 2 mass spectrometer.

X-ray diffraction (XRD) spectra of cellulose and obtained composites were collected on a Siemens XRD 6000 instrument at room temperature.

Textural investigation was realized by scanning electron microscopy (SEM) on a HITACHI S-2600N apparatus.

Polymerization

Polymerizations were carried out in microreactors with magnetic stirring under nitrogen. In all cases the monomer concentration was 3 mol/L, while the ratio between MA and DCPD was modified. The cellulose content was either 5 or 10 wt.%. The AIBN concentration was $5 \cdot 10^{-3}$ mol/L.

Cellulose was dispersed first in the solvent at room temperature, under magnetic stirring. The monomers, MA and DCPD, were added in the system under continuous

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Table 1
EXPERIMENTAL CONDITIONS EMPLOYED IN THE SYNTHESIS OF THE COMPOSITES

Code[1]	Code[2]	MA[3] mole fraction	Cellulose[4] weight %
DD1	DT1	0.10	5
DD2	DT2	0.25	5
DD3	DT3	0.50	5
DD4	DT4	0.75	5
DD5	DT5	0.90	5
DD6	DT6	0.10	10
DD7	DT7	0.25	10
DD8	DT8	0.50	10
DD9	DT9	0.75	10
DD10	DT10	0.90	10

[1] solvent dioxane
[2] solvent toluene
[3] in the monomer mixture
[4] based on the total amount of monomers

stirring, until a perfect mixing of the system components was achieved. Then the initiator was added and the polymerization was started at 80°C. The reaction time was two hours. After this time interval the reactor was cooled down, while two phases separated: a solid one and a liquid one. When dioxane was the solvent, the liquid phase was transparent, whereas for toluene it was translucent. The two phases were separated and individually washed with diethyl ether. The obtained composites were dried at 1 torr and 60°C for 24 h.

In order to remove the copolymer which is not grafted onto cellulose, the samples thus synthesized were extracted with dioxane in a Soxhlet apparatus for 10 h.

Results and discussion

In order to prepare cellulose hybrids with MA-DCPD copolymer matrix, the two comonomers were free-radically copolymerized in the presence of cellulose. Two different solvents were employed, i.e. dioxane and toluene, which differ each other from their ability to dissolve the forming copolymer point of view. Previous studies, carried out in the absence of the organic support, showed that dioxane is a good solvent for the MA-DCPD copolymer and therefore the polymerization mixture is homogeneous throughout the polymerization process, while the polymerization in toluene is of precipitating type [12,13]. Besides the influence of the solvent nature, we studied also the effect of the organic support upon the composite synthesis process by varying the cellulose weight percentage in the feed. Table 1 shows the amount of reactants employed to synthesize the composites in the presence of either toluene or dioxane as solvent.

A first parameter investigated was monomer conversion, which was calculated based on the total amount of material isolated from both the liquid phase and the solid one. Figure 1 displays the evolution of overall monomer conversion as a function of the MA mole fraction in the monomer feed for all the composite materials synthesized.

It can be seen that, regardless of the solvent employed, the dependence of the conversion on the MA mole fraction passes through a maximum at $x_{MA}=0.5$. This behavior can be explained by the different monomer composition of the feed, the obtained data suggesting an alternating – type copolymerization.

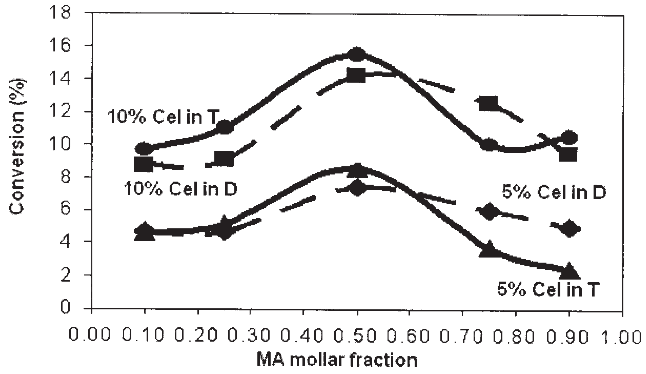
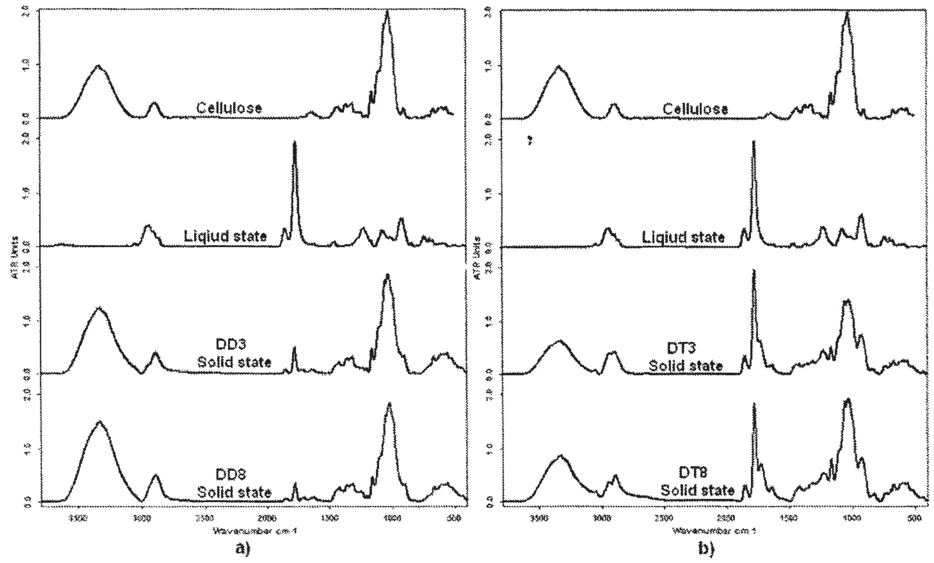


Fig. 1. Dependence of overall monomer conversion on the MA mole fraction for the samples synthesized in both dioxane and toluene

It can be noticed that irrespective of the reaction medium, for the same MA content, the conversion is higher when the cellulose amount is 10%. It is very likely that cellulose favours the copolymerization process, the number of active centers within the system increasing as the amount of the organic support enhances.

Also, irrespective of the cellulose percentage in the feed, the conversion is a little higher in toluene than in dioxane when the mole ratio of the two comonomers equals unity. A possible explanation consists in the polymer precipitation during the polymerization process in toluene, leading to the formation of trapped radicals which determines the autoacceleration of the process. However, regardless of the reaction medium employed or cellulose amount in the substrate, the conversions obtained after 120 min are less that 20%. This is in agreement with the results of the MA-DCPD copolymerization in both dioxane and toluene, in the absence of cellulose [12,13]. Conversion values higher than 20% were attained in homogeneous medium in the case of reaction times equal or higher than 180 min.

All composite materials synthesized were characterized qualitatively by IR spectroscopy. As an example, Fig. 2 shows the FT-IR spectra of the composites synthesized in both dioxane and toluene at 5 and 10% cellulose in the initial substrate at equimolar monomer ratio. All spectra are presented in comparison to the unmodified cellulose spectrum.



a) b)

Fig. 2. FT-IR spectra of the composites obtained in dioxane (a) and toluene (b)

In the case of toluene as the solvent, for both samples isolated from the solid phase (5 and 10% cellulose, respectively), the characteristic peaks of the cellulose OH (3336 cm^{-1}) and ether (C-O-C) groups (1160 cm^{-1}), as well as for the cellulose skeleton at 1020 cm^{-1} can be seen. One can also remark in the case of the solid phase, the presence of the carbonyl peak of cellulose – MA ester at 1700 – 1715 cm^{-1}, which qualitatively supports the formation of some MA-DCPD-cellulose hybrids with chemical insertion.

Both solid and liquid phase IR spectra display the peaks characteristic for the MA-DCPD copolymer at 1630 - 1640 cm^{-1} (the dicyclopentene cycle of DCPD) and 1849 - 1850 cm^{-1} and 1777-1778 cm^{-1} (anhydride cycle of MA). The polymerization system employing toluene as the solvent being a precipitating one favors the formation of the cellulose - poly(AM-DCPD) composite.

The FT-IR spectra of the composites synthesized in the presence of dioxane display the same characteristics as those obtained in toluene. However, as compared to the IR spectra of the composite materials obtained in toluene in the solid phase, a decrease of the intensity of the peaks characteristic to the MA-DCPD copolymer is observed. Also, a slight rounding off of the peaks characteristic to the cellulose skeleton at 1000-1050 cm^{-1} can be observed in the case of the products synthesized in toluene, very likely because of a higher degree of cellulose esterification as compared with the composite prepared in dioxane.

The higher amount of copolymer in the solid phase in the case of toluene can be explained through the lower solubility of poly(MA-DCPD) in this solvent leading to copolymer precipitation and as a consequence to an increase of the probability of its grafting onto cellulose.

To demonstrate that cellulose composites are indeed obtained, the samples prepared were extracted with dioxane. Figure 3 displays the FT-IR spectra of the extracted samples in the case of equimolar monomer mole ratio and 10% cellulose. To better observe the differences between the extracted and non-extracted samples, the FT-IR of the original samples are presented as well. The FT-IR analysis shows that the extracted samples preserve the characteristic peaks of the MA-DCPD copolymer alongside the cellulose skeleton peak at 1000-1050 cm^{-1} The decrease, but not the disappearance, of the AM characteristic peaks at 1778 cm^{-1} and 1853 cm^{-1}, as well as of the dicyclopentene ring peak of DCPD at 1630-1640 cm^{-1} demonstrates both the grafting of the copolymer onto the cellulose support and the formation of non-grafted copolymer.

After the extraction with dioxane, the peaks of the graft copolymer obtained in toluene have larger intensity that in the case of dioxane as the solvent. Thus, we can conclude that in the case of toluene the extracted material contains more graft copolymer than in the case of dioxane. Therefore, the precipitating process favours grafting because of the polymerization occurring in solid phase, practically on the cellulose surface. Alongside with grafting by esterification, a free-radically grafting process through the extraction of a hydrogen atom from the carbon atom of the cellulose CH$_2$OH groups followed by polymerization reinitiation is also possible to take place.

Further, all the materials synthesized and isolated from the solid phase were characterized from the thermal behaviour point of view, the results of the analyses being shown in figure 4 together with that of original cellulose.

One can see that the organic support employed displays two main stages of mass loss, and the residue at 700°C is 11.84%. The first stage (2.54 % mass loss) ranges between 40 and 180° and represents water removal. The second stage, which is the most important (85.18% mass loss) extends between 180 and 600°C and represents the thermal degradation of cellulose.

In the case of composites prepared in dioxane the TGA-DSC-MS (fig.4 and 5a) analysis reveals the presence of four mass loss stages. The first stage is between 40 - 135°C (mass loss ~2%). According to the MS analysis, this step can be ascribed to the loss of non-bound water, the mass fragment with z = 18 being the only one showing a maximum within this temperature interval. The second mass loss stage, ranging from 135°C to 185°C (mass loss ~1.6%) is not very well evidenced. The MS analysis shows a small variation of CO$_2$ behaviour on this interval. The third stage, which is the most important, ranges between 185°C and 390°C (mass loss 75-77%) and according to the MS analysis it represents the thermal degradation of the synthesized material. One can observe within this interval the variation of all mass fragments followed. The last stage, within the interval 390 - 620°C (5.5-6.5% mass loss), corresponds to the thermal degradation of the dicyclopentadiene units, as can be seen from the variation

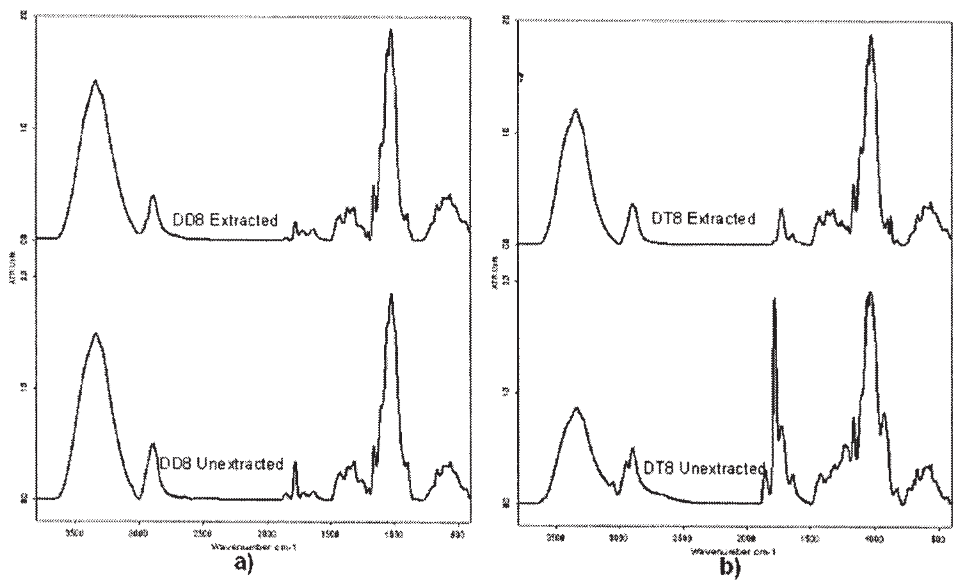


Fig. 3. FT-IR spectra of the composites with 10% cellulose, x_{MA} = 0.5, prepared in dioxane (a) and toluene (b)

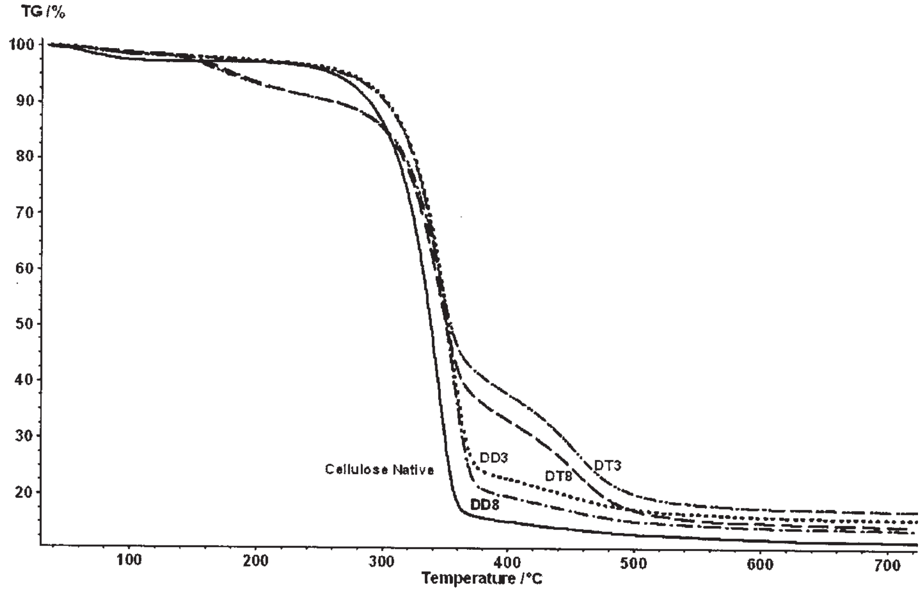


Fig. 4. TGA analysis of the synthesized composite materials, in comparison with the original cellulose

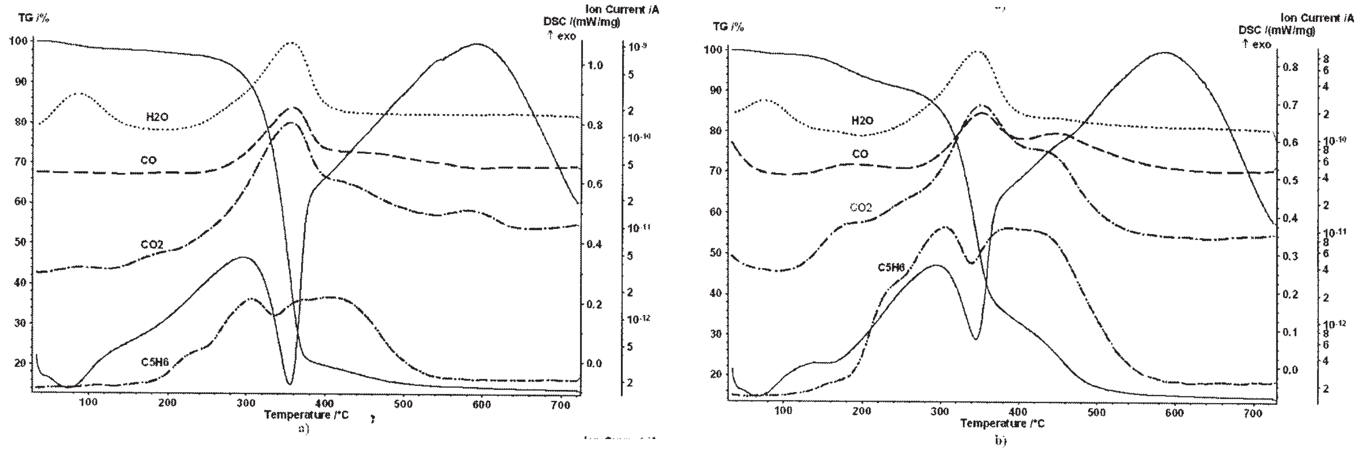


Fig.5. TGA-DSC-MS analysis for a)DD8 and b) DT8

of the CO_2 and C_5H_6 (cyclopentadiene) fragments behavior in the MS analysis.

For the composites obtained in toluene, five thermal degradation stages can be seen (fig.4 and 5b). The first stage extending from 40 to 120°C (1.2-1.4% mass loss) corresponds to the loss of non-bound water according to the MS analysis, the z = 18 mass fragment being the only one that displays a maximum within this interval. The second stage, ranging between 120 and 264°C (8.4-8.7% mass loss) is due to many simultaneously occurring processes: the reaction between maleic anhydride and the OH groups in cellulose; the reaction between the resulting carboxyl groups and the OH groups of cellulose which takes place with water removal, and decarboxylation followed by elimination of DCPD fragments. One can notice that the behavior of the CO_2 and C_5H_6 fragments varies within this interval. This stage can be seen in the case of dioxane as well, but it is not very

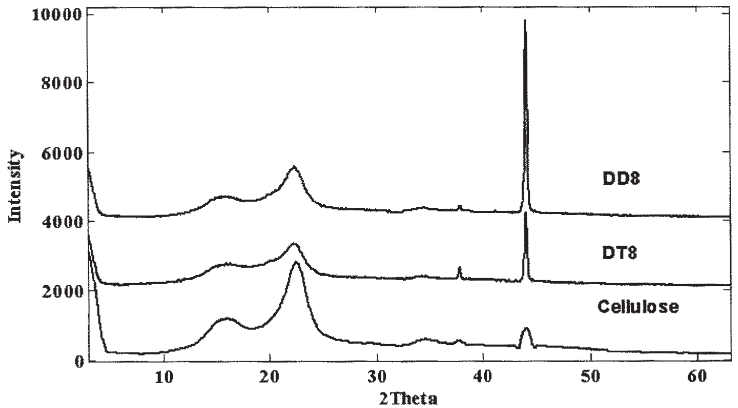


Fig. 6. XRD analysis of both the composites with 10% cellulose and original cellulose

well exposed because of the small amount of copolymer, and therefore it can not be assigned separately. The third stage of thermal degradation at 264 – 385 °C (50-55% mass loss) corresponds to the first degradation step of the synthesized material. One can see from the MS analysis the variation of all the mass fragments followed, as in the case of the materials synthesized in dioxane. The thermal degradation stage of the material synthesized in toluene is split, being continued in the fourth stage as well, which extends within the thermal interval 382 - 500°C (17-18 % mass loss). One can notice in this interval as well the variation of the behavior of all mass fragments followed, as evidenced by the MS analysis.

Irrespective of the solvent employed, the materials prepared display a residue at 700°C ranging within 14 and 16% (fig.4).

The XRD analysis of the materials synthesized, carried out comparatively with that of the original cellulose, reveals the structural modification of cellulose as a consequence of MA-DCPD copolymer grafting. Regardless of the solvent used, one can notice a reorganization of the cellulose structure by both the decrease of the peak at $2\theta=22.6°$ and increase of the peaks at $2\theta=38°$ and $2\theta=45°$, respectively. These modifications of the cellulose structures are a consequence of the chemical interaction between cellulose and the MA-DCPD copolymer.

The SEM analysis (fig. 7) of the composites obtained in both dioxane and toluene proves the uniformity of the samples prepared.

Conclusions

Composites cellulose – MA-DCPD copolymer were synthesized through “in situ” radical polymerization, by employing 1,4-dioxane and toluene as solvents. Irrespective of the solvent employed, the dependence of conversion on the MA mole fraction in the monomer feed displays a maximum at $x_{MA}=0.5$, like in the case of alternating radical polymerizations. In the case of syntheses performed in toluene, the FT-IR analysis of the samples isolated from the solid phase shows the amplification of the peaks characteristic to the MA-DCPD copolymer as compared to those isolated from the polymerization in dioxane, which can be explained through the precipitating character of the process in the former case. Also, a slight rounding off of the peaks characteristic to the cellulose skeleton at 1000-1050 cm^{-1} can be observed in the case of the products synthesized in toluene, very likely because of a higher degree of cellulose esterification as compared with the composite prepared in dioxane. After extraction with dioxane, the FT-IR peaks characteristic to the MA-DCPD copolymer are preserved, which proves its grafting onto cellulose. The XRD analysis proves the chemical interaction among the components of the composite material, especially through the decrease of the characteristic peak of cellulose from $2\theta=22.6°$. The SEM micrographs of the composites obtained in both dioxane and toluene prove the homogeneity of the synthesized samples.

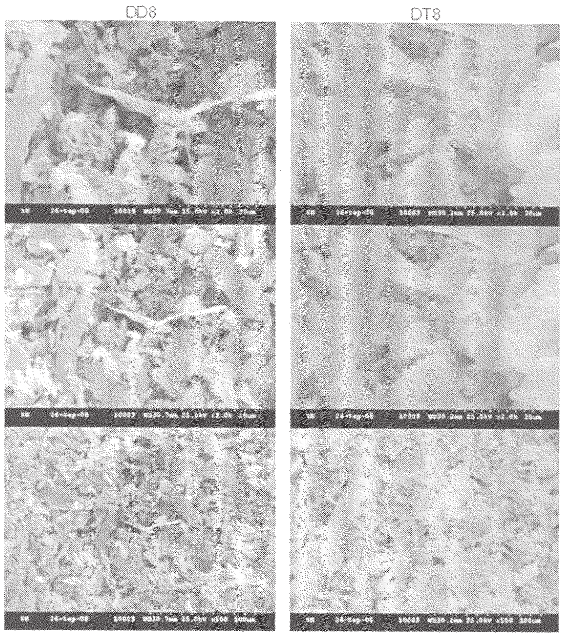


Fig. 7. SEM analysis of the composites with 10% cellulose

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