ENHANCEMENT OF ELECTRICAL CONDUCTIVITY OF COMPOSITE STRUCTURES BY INTEGRATION OF CNTS VIA BULK RESIN AND/OR BUCKYPAPER FILMS

I. Gaztelumendi[a*], M. Chapartegui[a], R. Seddon[a], S. Flórez[a], F. Pons[b], J. Cinquin[c], A. Korzhenko[d]

[a]*TECNALIA, Paseo Mikeletegi, 2 San Sebastián 20009, Spain*
[b]*AIRBUS FRANCE, 316 Route de Bayonne, 31060 Toulouse, Cedex 09, France*
[c]*AIRBUS GROUP INNOVATION, 12 Rue Pasteur 92152 Suresnes, Cedex, France*
[d]*ARKEMA, Groupe de Recherche de Lacq, RN117-BP34, 64170 Lacq, France*
**idoia.gaztelumendi@tecnalia.com*

Keywords: carbon nanotube, doped resin, buckypaper, electrical conductivity

Abstract
This work describes two approaches for the incorporation of Carbon Nanotubes (CNTs) in CFRP composites by infusion processing methods: firstly through the addition of the CNTs in the bulk resin to improve the electrical properties of the epoxy matrix prior to infusion [1], and secondly by the addition of CNT-based buckypaper (BP) in the CFRP structure for enhanced electrical properties [2]. Several laminates were manufactured with different formulations. A cross check of EC testing was carried out among different laboratories in order to compare different surface preparations and test methods. This characterization was completed with Scanning Electron Microscopy (SEM) analyses, in order to assess the presence of the filtering effect. In addition, ILSS tests were performed, comparing the results of the different formulations.

1. Introduction

In recent years, the implementation of non-metallic materials in aircraft structures has been increasing in order to meet new requirements and ecological policies, which enables the manufacturing of environmentally friendly and light-weight components. Nevertheless, the main drawback exhibited by composite materials relates to the lack of the necessary electrical conductivity required to cover different electrical functions such as edge glow, lightning strike, direct effect protection, short-circuits and electrical bonding [3]. Testing methodology is also an important parameter to master for electrical conductivity measurement [4]. These functions can be met by the use of nanotechnologies, by incorporating carbon nanotubes (CNTs) in the common composite manufacturing processes, which can then contribute to the development of improved materials with combined electrical, mechanical and thermal properties [5]. In the last two decades, the use of CNTs has become widely studied as a polymer reinforcement, due to its unique combination of superior properties [6]. In particular, the discovery of electrically conductive behavior dominated by percolation at low filler loadings has led to wide interest in the interplay between the processing and the electrical response of CNT based nanocomposites [7-10]. However, critical issues still need to be overcome especially when it comes to being processed by conventional CFPR composite

manufacturing methods, such as liquid injection technologies (infusion, RTM). The incorporation of CNTs in the resin creates an increase of the viscosity, which in turn can affect the impregnation of the fibre. On the other hand, CNTs can also be trapped in the carbon fibre during the infusion process causing a filtration effect. Furthermore, the increase in temperature during the processing and curing steps reduces the viscosity of the doped resin, which can cause the re-agglomeration of the CNTs. The main current activity in polymer-based CNT composites is in the field related to 'bulk' composites or CNTs dispersed in a polymer matrix, however, much less investigated are CNT-buckypaper based composites which can be used to overcome part of the critical issues that limit ultimate 'bulk' composite properties, such as: high CNT content, CNT orientation, and use of longer CNTs. A buckypaper (BP) consists of a highly dense network structure of carbon nanotubes compacted together to create a film like sheet [11]. The BP can be infiltrated by a resin that is subsequently cured to give composites with high CNT content, leading to superior electrical conductivities. In this way, BPs could be envisaged to replace or reduce the weight of the current metallic mesh used to disperse lightning strikes at the surface of the composite structure of the aircraft, while also providing an important reduction in global weight. However, the results on CNT-buckypaper based composites reported in literature have shown that some additional issues, such as infiltration difficulties, determine their properties [12]. Within this study, both, doped resin and BPs have been developed and optimized to be further incorporated in CFRP laminates manufacturing process, in order to improve the electrical behavior of the laminate in the through thickness direction.

2. Experimental

2.1. Materials

Nanocomposites were manufactured using an aeronautical grade epoxy resin (MVR444) provided by CYTEC. Due to transport safety issues, this resin was received in two parts (MVR444R-Part A + MVR444H-Part B). A CNT based MVR444R PART A masterbatch was developed by ARKEMA, containing 25% GRAPHISTRENGTH C100 CNT, which was supplied in pellet format, fulfilling health and safety regulations. This masterbatch was used for the doping of the epoxy resin. The same GRAPHISTRENGTH C100 CNTs in powder format were used for the BP manufacturing. Finally, for the manufacturing of the laminates via infusion process, a carbon fibre was used as reinforcement, in particular the 274 gsm UD fabric (V104505) from SAERTEX.

2.2. Manufacturing of doped resin and BPs

A two-step dispersion method was applied to reach a good quality dispersion and nanocomposites with 0,1%wt CNT were manufactured. The first step consisted of the dilution of the masterbatch down to 3%wt of CNT, adding MVR444R Part A by the calandering process, using a three roll mill EXAKT80E. This step was made according to a protocol consisting of a progressive reduction of the gaps between the rolls. Then, a second dilution down to 0,1%wt was carried out in a shear mixer DISPERMAT CA-60 by adding MVR444R part A. The MVR444H hardener was then preheated at 80ºC and mixed with the dispersion by mechanical stirring under vacuum. Finally, the mixture was cast in a metallic mould, degassed in a vacuum chamber to eliminate the air trapped in the mixture and cured (75min@160ºC + 2h@180ºC). The manufacturing process of BPs consisted of two main steps. In the first one, CNTs were ultrasonically dispersed in water, using sodium dodecyl sulphate (SDS) as a surfactant. This system was needed to provide suitably stable dispersions for later filtration.

The dispersion was then filtrated over a fine mesh polymeric filter. The thickness of the BP was controlled by the volume of dispersion filtrated under vacuum. The sheets were then perforated (to allow resin infiltration in the infusion process) using a multiple pinned roll.

2.3. Characterization of doped resin and BPs

Electrical conductivity measurements were carried out at room temperature with the two probe method using a source/meter Keithley 2410 and a resistivity chamber Keithley 8009, according to ASTM D257 standard test. Sample dimensions were 90x70x2 mm. Rheological analyses were also performed on the doped resin: Continuous flow and small amplitude oscillatory flow measurements were carried out in a Haake Rheostress 6000 rheometer using plate-plate geometry with 20 and 60mm diameter and 0.5-1 mm gap. In particular, viscosity profiles were analyzed at room temperature, and the gel time of the samples were obtained assessing crossing of storage (G') and loss (G'') moduli. Dimensions, thickness, weight and porosity of BPs were measured. BPs were also visually inspected and it was noticed that the appearance of the surface that was in contact with the filter during filtration was matt in comparison with the opposite surface. Therefore, both surfaces were studied by Scanning Electron Microscopy (SEM), JEOL JSM 5910 LV equipment, in order to gain insight on this phenomenon. Porosity values of the neat BPs were obtained by mercury intrusion porosimetry, using an AutoPore IV-9500 (MICROMEDITICS) porosimeter on 10x30mm samples. The manufactured BPs were also electrically characterized using the four probe Van der Pauw method [13] at room temperature using the Keithley 2410 sourcemeter. A current intensity of 10 mA was applied.

2.4. Manufacturing of carbon fibre based laminates

The composite laminates were manufactured via a lateral resin infusion process, with the following stacking sequence $[(+45/0/-45/90)_2]_s$. Four panels were manufactured based on the following formulations:

1. Panel 1: Undoped resin + carbon fabric (Reference panel)
2. Panel 2: Doped resin (0,1%wt CNT) + carbon fabric
3. Panel 3: Undoped resin + carbon fabric + buckypaper on the top surface
4. Panel 4: Doped resin (0,1%wt CNT)+ carbon fabric + buckypaper on the top surface

Resin and mould temperatures were adjusted according to the rheological analyses: resin temperature was increased from 70 ºC to 77ºC and the mould temperature from 80 ºC to 88ºC. Curing cycle was 75 min @160ºC followed by a postcuring cycle of 2h@180ºC.

2.5.- Characterization of carbon fibre based laminates

The possible filtering effect suffered by the doped resin during the infusion process was assessed by analyzing the presence of the CNTs in the outlet area of the laminates by SEM. The samples were fractured in liquid nitrogen and were sputtered with gold before imaging. ILSS tests according to the UNE EN 2563 were performed on samples of the four formulations, in an INSTRON 5500 universal testing machine in order to assess the influence of the CNTs in the laminate and also any possible filtering effect. Therefore samples were taken from each laminate at different zones from inlet area to outlet area (see Figure 1).

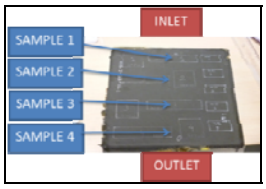


Figure 1: Characterization zones

Electrical conductivity was measured through the thickness of the laminates on 40x40mm samples from the four different zones. A four wire methodology was used in order to eliminate the effect of the electrical resistance of the wires. The contact resistance between the electrode and the sample, as well as ensuring a full contact between the electrodes and the sample are important parameters to take into account. Therefore correct sample preparation (metallization) prior to testing is a key aspect. In order to assess the influence of the optimum metallization type and the different testing methods, a cross-check was performed between different laboratories (EADS-IW-FRANCE- now AIRBUS GROUP INNOVATION-; AIRBUS FRANCE and TECNALIA): Silver paint based metallization (reference laminates, BP based laminates), silver paste based metallization (doped resin based laminates), and Ni electrodeposition (all) were compared. The Ni metallization of the surface was performed by CVD metallization of a nickel layer as the first step and the electrodeposition of a nickel layer as a second step. Each laboratory applied the following testing procedure: EADS-IW-FRANCE (Multimeter Agilent 34 420A) applying a pressure of 50 MPa during the measurement to minimize the contact resistance. Both AIRBUS FRANCE (Burster Resistomat 2316 series) and TECNALIA (Keithley 2410) carried out the test according to the AITM2-0065 standard [14].

3. Results and discussion

3.1. Doped resin

CNT doped resin shows a conductivity of 1.10^{-6} S/m, five orders of magnitude higher than that of the neat resin. The generation of the electrical path by the CNT is then confirmed. Regarding the rheological analyses, the evolution of viscosity with temperature was analysed (see Figure 2). Initially, the viscosity decreases when temperature is increased up to approximately 200ºC, at which point the resin viscosity increases due to crosslinking phenomena becomes preponderent. As expected, the viscosity of the 0.1 wt.% CNT dispersion is higher than that of neat epoxy, especially at high temperatures. This requires new resin and moulding temperatures for infusion, 77 º C and 88 º C respectively. In order to calculate the gel time of the doped resin, the evolution of storage and loss moduli was also studied (Figure 3).

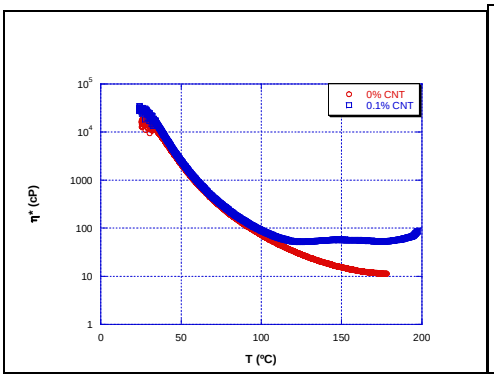


Figure 2: Evolution of viscosity with temperature

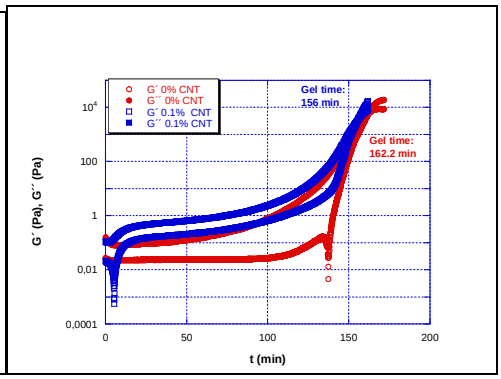


Figure 3: Evolution of storage and loss moduli

Considering the gel time as the time at which G´=G´´ crossing is observed [15-18], with 0.1 wt.% CNT the gel time decreased by 6 minutes with respect to the neat resin (from 162min to 156min). This accelerating effect could be attributed to the catalyst impurities of the carbon nanotubes [19].

3.2. BP characterization

The BPs have an areal weight range of 40-80g/m^2 with a thickness in the range of 130 - 230 µm. In Figure 4, SEM photographs corresponding to the upper and lower surfaces of the BPs are shown. The BPs consist of randomly interconnected CNTs, forming a network structure. In the matt surface (Fig. 4a) pores of different size can be observed, whereas in the glossy surface (Fig. 4b) the CNTs are very densely packed.

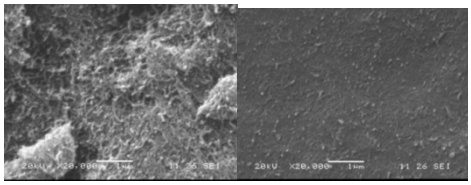
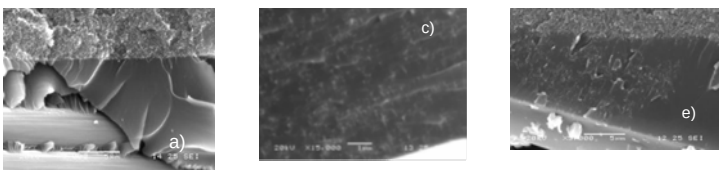


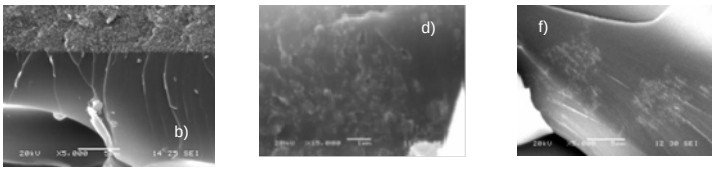
Figure 4: SEM photographs of the buckypaper: a) matt surface, b) glossy surface

A possible explanation for this phenomenon could be that, during filtration, the first surface that is constituted (the matt surface) copies the roughness of the filter but, as filtration progresses, new surfaces are continuously forming and carbon nanotubes are placed on these surfaces, acting as a filter for the suspension that is not yet filtered. As a consequence, the pore size of the consecutive surfaces becomes smaller, giving rise to a glossy surface at the end of the filtration process. To our knowledge, this feature has not been previously reported in the literature. Therefore, more studies would be required to understand the detailed mechanics of the individual nanotube layer formation during filtration. EC values in the range of 3000-5000 S/m, nine orders of magnitude higher than the doped resin were measured. This can be related to the electron transport mechanisms that are taking place in each case. In the case of doped resin, the CNTs are surrounded by the insulating resin, so the electrons transport is based on the tunneling effect; Tunneling has to be taken into account for the electrical conductive behavior of CNT-filled composites. When nanotubes reach the electrical percolation threshold in a polymeric matrix, they need not always physically touch each other, as long as they are just close enough to allow the hopping/tunneling process [20]. In the case of BPs, this effect is not needed since the CNTs are in contact. The porosity of the BP was determined to be 65% with a mean pore diameter of approximately 60 nm.

3.3. Laminates characterization

BP based laminates were analyzed by SEM. A good impregnation of the resin in both surfaces on the top and on the bottom of the BP can be seen in Figures 5a and 5b, for both the inlet and the outlet parts of the laminates (according to the scheme shown in Figure 1).





Figures 5: a) BP + undoped resin based laminate- Inlet zone, b)Outlet zone; Doped resin based laminate- c) Inlet zone d) Outlet zone; BP+ doped resin based laminate- e) Inlet zone f) Outlet zone

Figure 5c and 5d show the SEM images of resin analyzed from the inlet and the outlet part, in the central area of the doped resin based laminate. In general a good dispersion of CNT in the resin can be observed. The presence of CNTs in both the central and outlet parts of the laminate, rules out a total filtering effect. Regarding the doped resin + BP based laminate, the BP was also well impregnated. Well dispersed CNTs were found in the central area of the laminate, as well as the central outlet part (Figures 5e -5f). Regarding the ILSS tests, the doped laminate presents slightly higher values with respect to the neat resin laminate (Fig. 6).

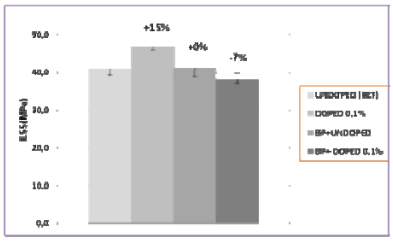


Figure 6: ILSS test results

The BP does not affect the mechanical properties, but the doped resin and BP based laminate shows a slightly decrease with respect to the neat resin. These small differences can be due to the variability usually found in the infusion process. For the EC test reference panel samples, the metallization methods using silver paint and the Ni electrodeposition were compared. Figure 7 shows that the metallization does not affect the final EC results. In the same way, these results were not influenced by the different testing methods. Regarding the different testing zones, a high dispersion of results was noticed between the different tested samples. The undoped resin + BP samples were metallized by AIR-F, after previously being silver painted by TECNALIA. The results are not strongly affected by the metallization or by the testing method (Figure 8).

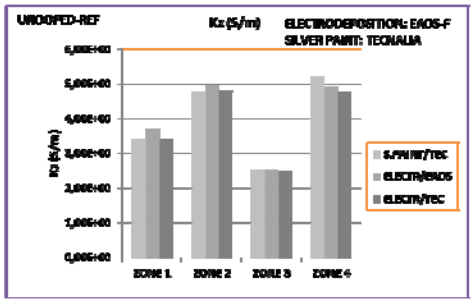


Figure 7: EC for undoped resin based laminates

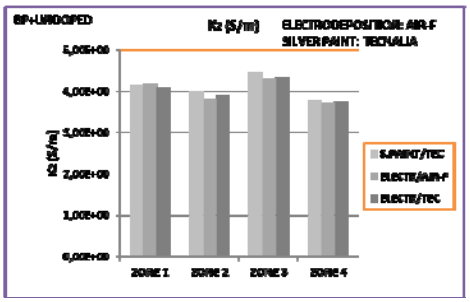
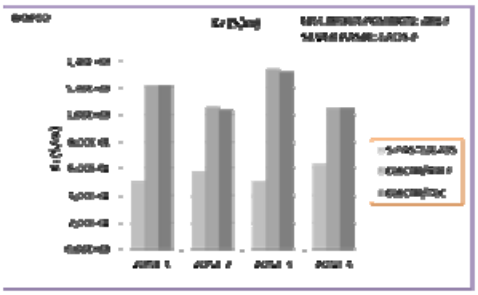
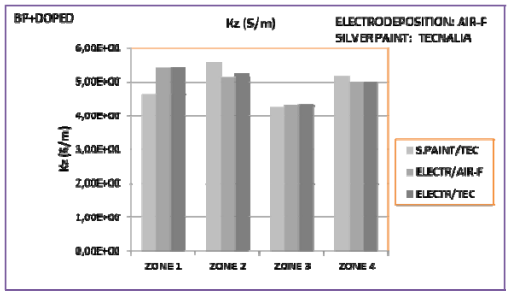


Figure 8: EC for BP+undoped resin based laminates

A comparison between silver paste and Ni electrodeposition was made on the doped resin based samples. The electrodeposited samples presented the same results using both testing methods (AITM and compression based methods). However, the compression method did not show a stabilization of the measured resistance when using the silver paste, which led to a higher contact resistance compared with Ni electrodeposition (Figure 9). In BP+doped resin

samples, silver paint and Ni electrodeposition were studied. Figure 10 shows similar results for the different metallization and testing methods.





Figures 9: EC for doped resin based laminates

Figures 10: EC for BP+doped resin based laminates

Figure 11 summarizes all of the previous EC test results: It is important to highlight the decrease in values for the doped resin based laminate which can be attributed to the presence of pores Attention has to be paid to the high dispersion of results, especially in the reference panel which can be attributed to the contact between the fibres in the Z direction. The highest EC values were found in the BP+doped resin based laminates, where a 30% increase with respect to the reference laminate was measured.

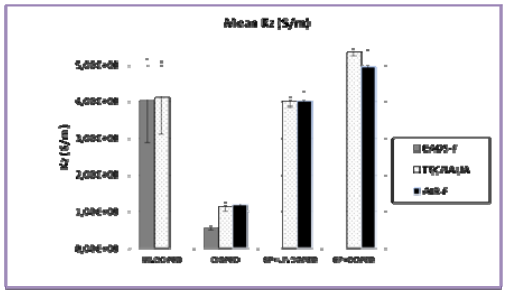


Figure 11: EC results summary

4. Conclusions

A combination of CNT doped resin and BP layered nanomaterialss have been successfully manufactured into CFRP composites using an infusion process. The original composite mechanical properties were maintained. Good dispersions of CNTs have been achieved, as confirmed by rheological analysis, which revealed an accelerating effect of the CNTs in the epoxy resin. CNT doped resin shows a significant improvement in electrical conductivity, compared to undoped resin, reaching values up to 1.10^{-6} S/m. The BP manufacturing has been optimized to improve the resin infiltration during the infusion process. The doped CFRP laminates exhibit good dispersion of CNTs and the SEM analysis confirms that a complete filtering effect did not occur in the laminate. The total impregnation of BP with the resin was also observed and confirmed in the demoulding step. The peel ply layer was easily removed, avoiding any damage to the BP structure. The presence of CNTs reduced the EC values in the through thickness direction. A possible reason for this is the presence of porosity and which is currently under further investigation or the number of carbon fibre contact in the samples thickness direction that could change from a sample to another. These values are significantly improved with the presence of the BP in the doped laminates, where an increase of 30% is observed with respect to the reference samples. It is important to pay attention to the high

dispersion of results in the reference panel, which reveals the low repeatability of the infused laminates, even in the undoped samples. The cross check performed on EC sample preparation and testing methods has confirmed that using silver paste as a metallization material produces lower results in the through thickness direction, due to the high contact resistance, than the other methods based on silver paint and Ni electrodeposition. The AITM based testing methods, applied in different laboratories, and the test under pressure based method, produced similar values when using either the electrodeposition or silver paint metallization methods.

5. Acknowledgments

We gratefully acknowledge the financial support from FP-7 EU project ELECTRICAL (Novel Aeronautical Multifunctional Composite Structures with Bulk Electrical Conductivity and Self-Sensing Capabilities ACP8-GA-2010-265593).

References

[1] Chapartegui M, Markaide N, Flórez S, Elizetxea C, Fernandez M, Santamaría A. *Composites Science and Technology* 70 (2010) 879-884.
[2] Chapartegui M, Barcena J, Irastorza X, Elizetxea C, Fernández M, Santamaria A.: *Composites Science and Technology* 72 (2012) 489–497
[3] M.T. Blanco; F. Pons, P.C. Woelcken *08th International Technical Conference & Forum SETEC 13* Wuppertal, Germany (2013)
[4] J.Cinquin, C.Heinrich, E.Balland, F.Pons, I.Gaztelumendi, A.Vavouliotis, C.Kostagiannakopoulou. "*08th International Technical Conference & Forum SETEC 13* Wuppertal, Germany (2013)
[5] Gojny F H., Wichmann M. H. G., Fiedler B., Bauhofer W., Schulte K., 2005, *Composites Part A*, 36 (2005) 1525-1535
[6] M. Moniruzzaman, K.I. Winey, *Macromolecules*, 39, 5194-5205 (2006)
[7] A. Battisti, A.A.Skordos, I.K. Partridge, *Composites Science and Technology*,70, 633-637(2010).
[8] J.K.W. Sandler, J.E. Kirk, I.A. Kinloch, M.S.P. Shaffer, A.H. Windle, *Polymer*,44,5893-5899 (2003).
[9] E.T. Thostenson, T.W. Chou, *Carbon*, 44,3022–3029 (2006).
[10] J.Z. Kovacs, B.S. Velagala, K. Schulte, W. Bauhofer, *Composites Science and Technology*, 67(5), 922–928 (2007)
[11] M. M. Zimmer, Florida State University, *PhD Dissertation* (2009)
[12] P.E. Lopes, F. van Hattum, C.M.C. Pereira, P.J.R.O. Nóvoa, S. Forero, F. Hepp, L. Pambaguian, *Composite Structures*, 92, 1291–1298 (2010)
[13] Rabin Bissessur a,Wade White a, Douglas C. Dahn *Materials Letters* 60 (2006) 248– 251
[14] AITM 2-0065: *Airbus Test Method.*
[15] M. Abdalla, D. Dean, P. Robinson, E. Nyairo, *Polymer*, 49, 3310–3317 (2008)
[16] D. Dean, A.M. Obore, S. Richmond, E. Nyairo, *Composites Science and Technology*, 66, 2135–2142 (2006).
[17] S. Ganguli, D. Dean, K. Jordan, G. Price, R. Vaia, *Polymer*, 44, 6901–6911 (2003)
[18] M. Ehsani, A.A. Yousefi, S.S. Yeganeh, *e-Polymers*, 140 (2009)
[19] A. Allaoui, N. El Bounia, *eXPRESS Polymer Letters*, 3(9), 588-594 (2009).
[20] W. Bauhofer, J. Z. Kovacs, *Composites Science and Technology*, 69(10), 1486-1498 (2009)