ΤΕΧΝΟΛΟΓΙΚΟ ΕΚΠΑΙΔΕΥΤΙΚΟ ΙΔΡΥΜΑ ΠΕΙΡΑΙΑ

ΤΜΗΜΑ ΚΛΩΣΤΟΫΦΑΝΤΟΥΡΓΩΝ ΜΗΧΑΝΙΚΩΝ Τ.Ε.

ΗΛΕΚΤΡΟΪΝΟΠΟΙΗΣΗ, ΧΡΩΜΙΚΑ ΥΛΙΚΑ, ΜΙΓΜΑ ΝΑΝΟΪΝΩΝ, ΥΛΙΚΑ ΕΠΙΘΕΜΑΤΑ ΤΡΑΥΜΑΤΩΝ

ELECTROSPINNING, CHROMIC MATERIALS, BLEND NANOFIBERS, WOUND DRESSING MATERIALS

ΚΩΝΣΤΑΝΤΙΝΑ ΠΑΡΙΤΣΗ

ΕΠΙΒΛΕΠΩΝ ΚΑΘΗΓΗΤΗΣ ΔΡ. ΓΕΩΡΓΙΟΣ ΠΡΙΝΙΩΤΑΚΗΣ

ΠΕΙΡΑΙΑΣ 2013

Ευχαριστίες

Η παρούσα πτυχιακή με θέμα «Ηλεκτροϊνοποίηση, χρωμικά υλικά, μίγμα νανοϊνών, υλικά επιθέματα τραυμάτων», πραγματοποιήθηκε, στο πλαίσιο της πτυχιακής εργασίας του τμήματος Κλωστοϋφαντουργίας του Τεχνολογικού Εκπαιδευτικού Ιδρύματος Πειραιά καθώς και του αντίστοιχου τμήματος του Πανεπιστημίου της Γάνδης στο Βέλγιο.

Στο σημείο αυτό αισθάνομαι την ανάγκη να εκφράσω τις ειλικρινείς μου και θερμές ευχαριστίες σε όσους συνέβαλαν στην ολοκλήρωση αυτής της προσπάθειας:

Πρώτα απόλα τον καθηγητή μου Κ. Γεώργιο Πρινιωτάκη για την καθοδηγητική του στάση. Έπειτα στην ir. Iline Steyaert διδακτορική φοιτήτρια στο Πανεπιστήμιο της Γάνδης για τη συνεχή καθοδήγηση, την αμέριστη υποστήριξη, τις ουσιώδης συμβουλές, καθώς και την αδιάκοπη συμπαράσταση και ενθάρρυνση που μου παρείχε σε όλο αυτό το διάστημα. Επίσης θα ήθελα να ευχαριστήσω ιδιαιτέρως την καθηγήτριά μου Κ. Karen De Clerck στο Πανεπιστήμιο της Γάνδης για την ευρύτερη καθοδήγηση στο δρόμο των σπουδών και της εκπαίδευσης.

Τέλος, θέλω να ευχαριστήσω τους ανθρώπους από το στενό οικογενειακό περιβάλλον που με έμαθαν να υπερβαίνω και βοήθησαν στη πραγμάτωση του ανέφικτου. Σε αυτούς που με την καθημερινή τους συμπαράσταση και υπομονή συνέβαλαν στην εκπλήρωση του στόχου μου, αφιερώνεται η εργασία αυτή.

Κωνσταντίνα Παρίτση

Αθήνα, 2013

Περίληψη

ΚΕΦΑΛΑΙΟ Ι

Εισαγωγή

Τα έξυπνα υφάσματα (smart textiles) είναι ένα πεδίο με πολλές κατευθύνσεις όπου διαχωρίζεται σε τρεις ευρύτερες κατηγορίες. Η πρώτη ονομάζεται παθητικά έξυπνα υφάσματα όπου είναι αισθητήρες, η δεύτερη ευρύτερη κατηγορία περιλαμβάνει τα ενεργά έξυπνα υφάσματα και η τελευταία αφορά τα πολύ έξυπνα υφάσματα, τα οποία είναι ικανά να προσαρμόσουν τη συμπεριφορά τους σύμφωνα με εξωτερικές συνθήκες.

Η εργασία αυτή εστιάζει στα νανοινώδη αλοχρωμικά υλικά (halochromic nanofibrous materials) τα οποία θα μπορούσαν να χρησιμοποιηθούν ως υλικά επιθέματα τραυμάτων, για παράδειγμα στη θεραπεία ενός τραύματος καψίματος (burn wound healing). Ο όρος χρωμισμός χρησιμοποιείται για την εισαγωγή των χρωμικών φαινομένων και την περιγραφή της ιδιότητας εναλλαγής του χρώματος από τις φυσικές ιδιότητες ενός υλικού. Το φαινόμενο όπου δημιουργεί τη μετατροπή αυτή είναι η αλλαγή στην περιεκτικότητα των ηλεκτρονίων στις χρησιμοποιηθούσες ουσίες, ειδικότερα την π-ή-d κατάσταση ηλεκτρονίων, ή την αλλαγή ‘τακτοποίησης’ στην υπερομοριακή δομή. Ανεξάρτητα από τους παράγοντες που ενεργοποιούν την αλλαγή του χρώματος, υπάρχουν κι άλλοι τύποι χρωμισμού ευρέως γνωστοί όπως για παράδειγμα ο αλοχρωμισμός (halochromism). Ένα αλοχρωμικό υλικό είναι το υλικό όπου αλλάζει χρώμα όταν αλλαγή pH υφίστανται. Η αλλαγή του χρώματος έγκειται στη δημιουργία χημικών δεσμών μεταξύ υδρογόνου και ιόντων υδροξειδίου στο διάλυμα. Τέτοιου τύπου δεσμοί οδηγούν σε αλλαγές του συζυγούς συστήματος του μορίου, ή σε αλλαγή της ροής των ηλεκτρονίων. Αυτό εναλάσσει το ποσό του απορροφηθέντος φωτός, το οποίο οδηγεί σε ορατή αλλαγή του χρωμάτος. Οι αλοχρωμικές ουσίες δεν αναλύουν ένα ολόκληρο εύρος χρώματος για ένα ολόκληρο εύρος pH λόγω του ότι έπειτα από συγκεκριμένες οξύτητες το συζυγές σύστημα δεν αλλάζει περαιτέρω.

Οι πεχαμετρικοί δείκτες (pH indicators) είναι αλοχρωμικές χημικές ουσίες όπου προστίθενται σε μικρά ποσά σε ένα διάλυμα ούτως ώστε το pH αυτού να μπορεί να προσδιορισθεί και οπτικά. Μια άλλη χρήση των δεικτών που είναι υπό εξέλιξη τα τελευταία χρόνια, είναι η προσθήκη των σε διάλυμα πολυμερών όπου θα ηλεκτροινοποιηθεί (electrospinning) και θα αναφέρεται ως προσθήκη χρωστικής (dye-doped) στο διάλυμα. Αυτό επιτρέπει την παραγωγή μη υφάνσιμων νανοδομών όπου μπορούν να αλλάξουν χρώμα κάτω από συγκεκριμένη επιρροή πεχαμετρικού εύρους. Αυτοί οι τύποι

των χρωμικών υλικών απελευθερώνουν τον αλοχρωμισμό και έχουν σημαντικό δυνητικό στην εξέλιξη των έξυπνων υφασμάτων.

Η εργασία αυτή εστιάζει στην παραγωγή αλοχρωμικών νανοδομών με αναστρεψιμότητα στην αλλαγή, καθώς και τη δυνητική για έλεγχο της διαδικασίας επούλωσης ενός τραύματος καψίματος χαρακτηριζόμενο από συγκεκριμένες πεχαμετρικές αλλαγές.

Νανοϊνώδης δομές ως αλοχρωμικά υλικά επιθέματα τραυμάτων

Έως τώρα μόνο μερικές φορές έχει χρησιμοποιηθεί για καλύτερη μελέτη του φαινομένου αλοχρωμισμός το σύστημα χρωστική-δείκτης όπως alizarin, bromocresol purple, brilliant yellow, nitrazine yellow σε συνδιασμό με μη υφάνσιμες ουσίες.

Νανοϊνες ανταποκρινόμενες στο pH

Ο κύριος στόχος είναι νανοϊνες ανταποκρινόμενες στο pH, ονομαστικά αλοχρωμικά υλικά. Χρωμικά υλικά είναι ο ευρύτερος όρος αναφερόμενος σε υλικά, τα οποία αλλάζουν, ακτινοβολούν και αφαιρούν το χρώμα και λόγω της ιδιότητας αυτής αναφέρονται και ως υλικά χαμαιλέων. Υφάνσιμα και μη έχουν χρησιμοποιηθεί έως τώρα για να εισάγουν τον αλοχρωμισμό. Υφάσματα όπου αλλάζουν χρώμα θα μπορούσαν να χρησιμοποιηθούν ευρέως για να προσδιορίσουν το pH μιας πληγής καψίματος μιας και το χρώμα είναι οπτικό ερέθισμα δηλαδή μια άμεση λειτουργία ειδοποιήσεως. Ένα επίθεμα ευαίσθητο στις αλλαγές του pH μπορεί να μας δώσει πληροφορίες από το χρώμα του και μόνο μιας και το pH του δέρματος στο σημείο του καψίματος ποικίλλει κατά τα στάδια της διαδικασίας επούλωσης επομένως ανεπιθύμητη απομάκρυνση των επιδέσμων μπορεί να αποφευχθεί.

Η δουλειά αυτή εστιάζει στην παρουσία του φαινομένου αλοχρωμισμού σε μη υφάνσιμα υλικά. Παρόλο που οι αλοχρωμικές χρωστικές δεν είναι διαθέσιμες στην αγορά πεχαμετρικοί δείκτες μπορούν να βρεθούν εύκολα και να χρησιμοποιηθούν ως μια εναλλακτική για να διευκολύνουν την απελευθέρωση του φαινομένου. Είναι γνωστό ότι ο χρόνος ανταπόκρισης σε υφάνσιμα είναι μεγαλύτερος σε σύγκριση με τις μη υφάνσιμες δομές. Επιπλέον, εξαιτίας των χαρακτηριστικών τους πιθανότητες λοιμώξεων ελαχιστοποιούνται, η ανάπτυξη των κυττάρων βελτιστοποιείται καθώς και παρέχεται ένας επιπλέον έλεγχος στην υγρασία της περιοχής του τραύματος.

Ένα σύστημα χρωστική-πολυμερές και χρωστική-πολυμερές-παράγοντας συμπλοκοποίησης (complexing agent) θα χρησιμοποιηθεί. Ο όρος ο οποίος θα αναφερθεί για το σύστημα αυτό με τη χρωστική είναι προσθήκη χρωστικής (dye-doped). Η χρωστική προστίθεται στο διάλυμα πολυμερούς πριν την ηλεκτροινοποίηση. Για παράδειγμα προσθήκη χρωστικής στην πολυκαπρολακτόνη με

κίτρινο nitrazine (nitrazine yellow) και προσθήκη χρωστικής στο πολυαμίδιο 6.6 με μωβ βρωμιοκρεζόλης (bromocresol purple). Επιπλέον, προσθήκη χρωστικής στο πολυαμίδιο 6 με ένα 'κοκτέιλ' πεχαμετρικών δεικτών ονομαστικά ερυθρό φαινόλης (phenol red), ερυθρό μεθυλίου (methyl red), φαινολοφθαλεΐνη (phenolphthalein), κυανό της βρωμιοθυμόλης (bromothymol blue) και πράσινο της βρωμιοκρεζόλης (bromocresol green). Μεγάλο εύρος pH επιτεύχθηκε από Agarwai et al.

Μια μεμβράνη PAN ευαίσθητη στο pH με πολυαμίδιο 6.6 αναπτύχθηκε από Zhang et al σε συσκευή ηλεκτροινοποίησης διπλού ακροφυσίου. Η επιστημονική αυτή ομάδα κατόρθωσε αλλαγή στο χρώμα από απαλό κίτρινο σε βιολετί με εύρος pH 7 - pH 14 με μια ειδική τεχνική όπου θα μπορούσε να δημιουργήσει νανοϊνώδης μεμβράνες ευαίσθητες στο pH.

Αντίληψη του χρώματος

Το χρώμα είναι ένα οπτικό ερέθισμα όπου μπορεί να χρησιμοποιηθεί για τον προσδιορισμό του σταδίου της διαδικασίας επούλωσης ενός τραύματος καψίματος. Παρόλα αυτά, η όραση είναι ένας υποκειμενικός τρόπος εκτίμησης και αξιολόγησης των πειραματικών αποτελεσμάτων για εμπορευματοποίηση των υλικών αυτών επομένως κρίνεται απαραίτητο να χρησιμοποιηθεί ένας χρωματικός χώρος προσδιορισμού. Χρωματικός χώρος ορίζεται ως τρισδιάστατος γεωμετρικός χώρος με συνιστώσες σε τιμές που ανήκουν στο ορατό φάσμα. Τα ερεθίσματα είναι μηνύματα από τον περιβάλλοντα χώρο όπου απορροφούνται από τη στοιβάδα αμφιβληστροειδούς, ενεργοποιούν μια σειρά γεγονότων και καταλήγουν στην αντίληψή μας. Αριθμητικοί χρωματικοί χώροι έχουν χρησιμοποιηθεί μέσα στα τελευταία χρόνια για τη μέτρηση του χρώματος. Σε αυτή την εργασία θα χρησιμοποιηθεί ο χρωματικός χώρος CIEL*a*b*. Η Commission Internationale de l' Eclairage, ονομαστικά CIE, εξελίχθηκε με απόπειρες μετατροπής των X, Y και Z τριών διαστάσεων τιμών σε συντεταγμένες όπου προσφέρουν ομοιομορφία. Οι τρεις παράμετροι όπου υπολογίσθηκαν είναι L* για ένα δεδομένο χρώμα και κυμαίνεται από 0 (το απόλυτο μαύρο) έως 100 (το απόλυτο λευκό), a* για το κόκκινο-πράσινο χαρακτήρα του χρώματος με θετικές τιμές για τις κόκκινες σκιές και αρνητικές για τις πράσινες σκιές και b* όπου δίνει κίτρινο-μπλε χαρακτήρα με θετικές τιμές για τις κίτρινες σκιές και αρνητικές για τις μπλε σκιές.

Οι περισσότερες αλοχρωμικές χρωστικές ουσίες αλλάζουν από ένα χρώμα σε ένα άλλο παρουσιάζοντας μια βαθοχρωμική (bathochromic) ή υψοχρωμική (hypsochromic) μετατόπιση της κορυφής φάσματος απορρόφησης επάνω σε (απο)πρωτονίωση και κατηγοριοποιούνται ως θετικές και αρνητικές αλοχρωμικές χρωστικές ουσίες αντιστοίχως. Στο γεγονός της αλλαγής χρώματος στηρίζεται η πρωτονίωση ή αποπρωτονίωση του μορίου βαφής προκαλώντας μια διαφορετική ηλεκτρονιακή διαμόρφωση με αποτέλεσμα ένα διαφορετικό χρώμα. Η ορατή αλλαγή χρώματος στις

αλοχρωμικές χρωστικές στηρίζεται κατά βάση στο άνοιγμα της αλυσίδας του μορίου της χρωστικής επάνω σε (απο)πρωτονίωση ή σε ταυτομερισμό, (τα ταυτομερή είναι ισομερή –συνταγματικά- οργανικών υλικών όπου απευθείας μετατρέπονται από μια χημική αντίδραση ονομαζόμενη ταυτομερισμός. Αυτή η αντίδραση συνήθως καταλήγει σε μετανάστευση ενός ατόμου υδρογόνου ή πρωτονίου που συνοδεύεται από αλλαγή ενός μονού δεσμού σε διπλό.) μιας και τα ταυτομερή διαθέτουν διαφορετικές χρώσεις και βαφικές αντοχές.

Στόχος πτυχιακής εργασίας

Η χρήση αλοχρωμικών υφασμάτων στην ιατρική είναι επιτακτική μιας και αυξανόμενο ενδιαφέρον παρατηρείται τα τελευταία χρόνια. Η επιστήμη σε αυτό τον τομέα μπορεί ακόμη να παρουσιάσει πρόοδο μιας και το εύρος αλλαγής pH ενός τραύματος καψίματος κατά τα στάδια θεραπείας είναι πολύ συγκεκριμένο. Η ηλεκτροινοποίηση θεωρείται μια πολύ καλή μέθοδος παραγωγής νανοϊνών καθώς οι δυνατότητες σε αυτή την περίπτωση αυξάνονται ραγδαία όπως η δημιουργία μίγματος πολυμερών και η μετέπειτα επεξεργασία για την κατασκευή ινών κάτω από την παροχή ηλεκτρικού ρεύματος. Σε αυτή την εργασία θα χρησιμοποιηθούν μίγματα πολυμερών καθώς και θα ελεγχθούν οι ιδιότητές των.

Θα πραγματοποιηθεί προσθήκη disperse red 1 και disperse red 1* στην πολυκαπρολακτόνη (PCL) και προσθήκη μωβ της βρωμιοκρεζόλης στο πολυαμίδιο 6 (PA 6) στο κεφάλαιο III. Επιπλέον, θα προστεθεί ένας παράγοντας συμπλοκοποίησης (Perfixan RDV) για την ελαχιστοποίηση της απελευθέρωσης της βαφής (dye release) σε κάθε περίσταση. Στο κεφάλαιο IV θα προστεθεί disperse red 1 και disperse red 1* στο πολυαμίδιο 6 καθώς και ο παράγοντας συμπλοκοποίησης. Θα πραγματοποιηθεί μίγμα πολυμερών PA 6 και P(M) με τη χρωστική ουσία ομοιοπολικά ενωμένη με το μόριο του τελευταίου όπου και θα ηλεκτροινοποιηθεί για τη μελέτη του φαινομένου αλοχρωμισμού. Τέλος, θα προστεθούν και θα ερευνηθούν η βαφή τροφίμων fast green και το μωβ της βρωμιοκρεζόλης στο πολυαμίδιο 6 στο κεφάλαιο V, προσθήκη παράγοντα συμπλοκοποίησης και εδώ. Μια πρώτη προσέγγιση είναι η αξιολόγηση και σύγκριση της επιρροής του παράγοντα συμπλοκοποίησης με τα πολυμερή στα οποία έχει προστεθεί κάποια χρωστική και η ανάκτηση γνώσης της ευαισθησίας στο pH. Ο επόμενος στόχος είναι η κατόρθωση μεθόδου παραγωγής αλοχρωμικών νανοϊνών με διάφορες δοκιμές προς βελτιστοποίηση.

ΚΕΦΑΛΑΙΟ ΙΙΙ

Έχει αποδειχθεί πως η προσθήκη μικρής ποσότητας μορίου σε διάλυμα προς ηλεκτροινοποίηση δεν επηρεάζει σημαντικά τη διαδικασία. Το σύστημα πολυμερές/χρωστική ουσία θα μελετηθεί σε αυτή την εργασία για την κατανόηση των μηχανισμών της διαδικασίας αυτής και την αξιολόγηση των παραμέτρων ηλεκτροινοποίησης. Ως εκ τούτου, πολυμερή, πολυμερή με προσθήκη επιλεγμένης χρωστικής και πολυμερή με τη χρωστική και προσθήκη του παράγοντα συμπλοκοποίησης θα ηλεκτροινοποιηθεί. Ο παράγοντας συμπλοκοποίησης θα προστεθεί για τη βελτιστοποίηση της διαδικασίας όπως έχει ήδη μελετηθεί από Van der Schueren and all.

Νανοίνες πολυαμιδίου 6 και πολυκαπρολακτόνης, προσθήκη χρωστικών ουσιών

Η επιλογή ενός κατάλληλου συστήματος διαλύτη είναι εξαιρετικής σημασίας για μια ομαλή διαδικασία ηλεκτροινοποίησης μιας και ο τελικός στόχος είναι η βελτιστοποίηση του συστήματος πολυμερές-χρωστική. Ηλεκτροινοποίηση νανοϊνών PA 6 σε μίγμα διαλυτών μυρμηγκικό οξύ/οξικό οξύ (formic acid/acetic acid) μελετήθηκε και χαρακτηριστήκε ως σύστημα κλειδί για σταθερή διαδικασία κάτι το οποίο είναι το πιο σημαντικό για νανοϊνες προς παραγωγή εν δυνάμη.

Σφαιρίδια πολυκαπρολακτόνης σε διάλυμα μυρμηγκικού οξέος/οξικού οξέος έχει ήδη μελετηθεί και αποδειχθεί ως πολλά υποσχόμενο από την Van der Schueren et all.

Μια χρωστική παρουσιάζει διαφορετικά χαρακτηριστικά σε διάλυμα σε σύγκριση με τις ήδη παραγμένες σε μορφή νανοϊνών. Η αλοχρωμική συμπεριφορά αλλάζει όταν μια χρωστική έχει ήδη προστεθεί απευθείας στο διάλυμα και έχει ηλεκτροινοποιηθεί για την παραγωγή νανοδομών.

Προσθήκη χρωστικής σε PA 6.6 με πορτοκαλί του αιθυλίου (ethyl orange), μωβ και μπλε την βρωμιοκρεζόλης (bromocresol purple and blue), λαμπρό κίτρινο (brilliant yellow), nitrazine yellow, κόκκινο της αλιζαρίνης (alizarine red) κ.ο.κ. Οι έρευνες που αναφέρονται σε αυτό δείχνουν πως δεν παρουσιάζεται αλλαγή στη διάμετρο των ινών καθώς και στις παραμέτρους της διαδικασίας με την προσθήκη των δεικτών αυτών. Η προσθήκη λαμπερού κίτρινου σε διάλυμα πολυκαπρολακτόνης μελετήθηκε από Van der Schueren et all και παρατηρήθηκε επιρροή στις παραμέτρους ηλεκτροινοποίησης. Η δομή των μορίων της πολυκαπρολακτόνης με προσθήκη χρωστικής μελετήθηκε επίσης μιας και πιστεύεται πως είναι ένας κρίσιμος παράγοντας προς μελέτη. Ως εκ τούτου, μοριακή μοντελοποίηση χρησιμοποιήθηκε για την ερμηνεία της αλοχρωμικής συμπεριφοράς. Παρόλο που στην εργασία αυτή δεν πραγματοποιήθηκε τέτοια διαδικασία, η μέθοδος θα εξυπηρετούσε στο μέλλον για την καλύτερη κατανόηση των μηχανισμών και αλληλεπιδράσεων μεταξύ των μορίων χρωστικών ουσιών και των μη υφάνσιμων δομών.

Η εκλογή του συστήματος πολυμερές/χρωστική ουσία

Το μέρος αυτό περιγράφει την εκλογή του κατάλληλου συστήματος, προκαταρκτικές δοκιμές πραγματοποιήθηκαν για τη μελέτη της διαδικασίας ηλεκτροινοποίησης και την αξιολόγησή της. Επιπλέον, χαρακτηρισμός του συστήματος επιτεύχθηκε για τη μέτρηση των παραμέτρων όπως απελευθέρωση βαφής και αλλαγή χρώσης κάτω από διαφορετικές τιμές pH. Τα μόρια των χρωστικών ουσιών διασποράς είναι τα μικρότερα ανάμεσα σε όλες τις χρωστικές και βασίζεται σε μόριο αζωβενζολίου ή ανθρακινόνης με γκρουπ νιτρο, αμίνη, υδροξύλιο και τα λοιπά συνδεδεμένα σε αυτό. Disperse red 1 με ή χωρίς τη λειτουργική ομάδα (disperse red 1*) θα μελετηθεί σε αυτή την εργασία.

ΚΕΦΑΛΑΙΟ IV

Σε τούτο το κεφάλαιο προσθήκη disperse red 1 και disperse red 1* σε διάλυμα πολυαμιδίου 6 θα πραγματοποιηθεί και μελετηθεί. Μίγμα πολυαμιδίου 6 και P(M) θα παραχθεί. Το μίγμα θα ηλεκτροινοποιηθεί σε εργαστηριακή κατασκευή πολυάριθμων ακροφυσίων για μεγαλύτερη σταθερότητα στη διαδικασία και δημιουργία μεγαλύτερων δοκιμίων προς μελέτη. Στις νανοδομές αλλάζουν οι αλοχρωμικές συμπεριφορές ανάλογα τον περιβάλλοντα χώρο επομένως, μεγαλύτερα δοκίμια κρίνεται απαραίτητο να δημιουργηθούν για την πραγμάτωση επιπλέον δοκιμών.

Εισαγωγή

Η συμπεριφορά των DR1 και DR1* χαρακτηρίσθηκε κάτω από συγκεκριμένες συνθήκες. Η αλλαγή στο χρώμα με pH σε διάλυμα και σε συνεργασία με νανοϊνες PA6 με προσθήκη χρωστικής μετρήθηκε. Επιπροσθέτως, μίγμα πολυμερών PA6 και P(M-co-DR1*) στο οποίο περιέχεται η χρωστική παράχθηκε με τη διαδικασία ηλεκτροινοποίησης. Το τελευταίο είναι μια λειτουργική ομάδα του DR1 (Κεφάλαιο III) ομοιοπολικά συνδεδεμένη στον κορμό του P(M).

Στόχος σε αυτό το κομμάτι είναι η προσομοίωση του φαινομένου επιρροής της disperse red 1 στη διαδικασία και ο χαρακτηρισμός των αλοχρωμικών παραχθέντων νανοϊνών. Επιπλέον, η επιρροή του ομοιοπολικού δεσμού μεταξύ χρωστικής και πολυμερούς θα αναλυθεί και τα αποτελέσματα από την κατασκευή με ακροφύσιο μονού τέλους και εκείνης με ακροφύσιο πολυάριθμου τέλους θα συγκριθούν.

Συμπεράσματα

Συμπερασματικά, η κατασκευή του λειτουργικού μορίου disperse red 1 έχει μικρή επιρροή στο χροιά της χρωστικής και η προσθήκη του παράγοντα συμπλοκοποίησης δεν έχει επιρροή. Δοκιμές pH

πραγματοποιήθηκαν και ο χαρακτηρισμός έδειξε πως το χρώμα δεν αλλάζει μεταξύ του εύρους pH 2 και pH 12. Επιπλέον, παρατηρήθηκε επιρροή της χρωστικής στη διάμετρο των ινών όχι όμως στη μορφολογία. Ο πολυμερισμός του DR1* με μονομερή P(M-co-DR1*) δεν παρουσιάζει επιρροή στο χρώμα όμως το μίγμα παρουσιάζει μεγαλύτερο βάθος για την ίδια συγκέντρωση χρωστικής. Ακόμη, σε υγρή κατάσταση το βάθος στο χρώμα του μίγματος είναι καλύτερο ενώ μεταξύ pH 2 και pH 12 δεν παρουσιάζεται αλλαγή.

Επιπλέον, δοκίμια νανοϊνών ελέχθηκαν σε πολύ χαμηλές τιμές pH (0, 0.5, 1 και 1.5) διότι το disperse red 1 είναι ασταθές σε τόσο χαμηλές τιμές. Κάτω του pH 2 παρουσιάσθηκε αλλαγή στο χρώμα μεταξύ pH 0 και pH 1.5 στο δοκίμιο με προσθήκη χρωστικής καθώς και στο δοκίμιο όπου είναι συνδεδεμένο ομοιοπολικά με τη χρωστική. Επίσης, παρατηρήθηκε μέγιστη απελευθέρωση χρωστικής σε pH 0 και στις δυο περιπτώσεις λόγω διάλυσης του πολυαμιδίου 6 σε μικρές τιμές pH. Τέλος, παρατηρήθηκε υδρόλυση των δοκιμιών με ομοιοπολικό δεσμό ως επόμενο σπασίματος του δεσμού.

ΚΕΦΑΛΑΙΟ V

Ηλεκτροϊνοποίηση PA6, PA6/FG και PA6/FG/Perfixan

Σε αυτό το τμήμα θα μελετηθεί η συμπεριφορά του Fast Green FCF υπό διαφορετικές συνθηκές. Το fast green είναι μια πράσινη βαφή (της θαλάσσης) τροφιμών όπου παρουσιάζει δυο κορυφές στο φάσμα απορρόφισης που οφείλεται στο χρωματισμό του. Το χρώμα όταν βρίσκεται σε διάλυμα διαφορετικών pH αλλάζει καθώς και όταν έχει προστεθεί σε διάλυμα πολυμερούς και παραχθεί σε νανοϊνες. Η επιρροή του παράγοντα συμπλοκοποίησης θα χαρακτηρισθεί. Η figure 36 συμβολίζει τη χημική δομή Fast Green.

Ηλεκτροϊνοποίηση PA6, PA6/BP και PA6/BP/Perfixan

Αρχικά χαρακτιρισμός της χρωστικής θα πραγματοποιηθεί ούτως ώστε να προσδιορισθεί συντελεστής αποσβέσεως του μωβ της βρομοκρεζόλης και βαθύτερη κατανόηση του χροιάς της χρωστικής σε πεχαμετρική μεταβολή από 1 έως 12. Έπειτα θα περιγραφεί η απελευθέρωση της βαφής από τις μη ηφάνσιμες νανοδομές σε διαφορετικό pH. Οι πιο βασικές δοκιμές θα πραγματοποιηθούν στην κατασκευή μονού ακροφυσίου και ο παραμείνων χρόνος σε κάθε δείγμα θα μετρηθεί ούτως ώστε η λεπτότητά τους να είναι ίδια για ελάττωση των σφαλμάτων (8 λεπτά).

Συμπεράσματα

Το fast green και το μωβ της βρωμιοκρεζόλης χαρακτηρίσθηκαν σε διάλυμα και σε δεσμό με νανοϊνες. Το πρώτο παρουσιάζει δυο κορυφές στο φάσμα της απορρόφησης σε διάλυμα και αλλαγή

στο χρώμα παρατηρήθηκε όταν δημιουργείται δεσμός με τις ίνες. Με τον παράγοντα συμπλοκοποίησης ελαχιστοποιείται το φαινόμενο της απελευθέρωσης χρωστικής σε χαμηλές τιμές pH, με την αύξηση της τιμής του η απελευθέρωση αυξάνεται αντιστοίχως. Εν κατακλείδι, το φάσμα της χρωστικής σε διάλυμα παρουσιάζει δυο κορυφές ενώ σε δοκίμιο παρουσιάζει μια κορυφή η οποία τήνει προς την αλκαλική κορυφή της χρωστικής στο διάλυμα για αυτό και κρίνεται σχεδόν αδύνατο να χαρακτηρισθεί.

Παρουσιάσθηκε αλλαγή στο χρώμα των δοκιμίων με μωβ της βρωμιοκρεζόλης. Η προσθήκη perfixan επηρέασε και τη μορφολογία των. Η αγωγιμότητα και το ιξώδες αυξάνονται και η απελευθέρωση της χρωστικής ελαχιστοποιείται. Το χρώμα του μη υφάνσιμου PA6/BP/Perfixan είναι βαθύτερο χάρη στον παράγοντα συμπλοκοποίησης συγκριτικά το μη υφάνσιμο χωρίς αυτό.

ΚΕΦΑΛΑΙΟ VI

Συμπεράσματα και μελλοντική εργασία

Σε αυτή τη δουλειά προστέθηκαν χρωστικές ουσίες στο πολυαμίδιο 6, η επιρροή του Perfixan RDV αναλύθηκε και μελετήθηκε το μείγμα PA6/P(M) ομοιοπολικά συνδεδεμένο με το μόριο του disperse red 1*.

Το disperse red 1 θα μπορούσε να χρησιμοποιηθεί ως αλοχρωμική ουσία εφόσον αλλαγή στο χρώμα παρουσιάσθηκε. Παρόλο που παρατηρείται αναστρεψιμότητα στο χρώμα, το pH του δέρματος είναι γύρω στο 6 ενώ η αλλαγή παρατηρείται στην περιοχή pH<2 έτσι περιορίζεται το εύρος των εφαρμογών όσον αφορά επιθέματα τραυμάτων. Στο μίγμα PA6/P(M) ομοιοπολικά συνδεδεμένο με disperse red 1* ελαχιστοποιείται η απελευθέρωση βαφής κάτι το επιθυμητό, έτσι η χρήση του μίγματος για επίθεμα δεν αποκλείεται.

Το μωβ της βρομοκρεζόλης θα μπορούσε να χρησιμοποιηθεί ως αλοχρωμική ουσία μιας και υπάρχει εναλλαγή χρώματος και θα μπορούσε να χρησιμοποιηθεί ως επίθεμα μιας και προσεγγίζει το pH του δέρματος όμως το εύρος είναι αρκετά στενό. Σε αυτή την περίπτωση η απελευθέρωση βαφής παραμένει θέμα προς συζήτηση, παρά το γεγονός ελαχιστοποίησής της με την προσθήκη perfixan ζητούμενο παραμένει ακόμη η βελτιστοποίηση της διαδικασίας.

Η χρωστική ουσία fast green αλλάζει χροιά όμως το εύρος είναι πολύ μικρό καθώς και δεν είναι ιδιαίτερα ξεκάθαρο. Το χρώμα είναι ένα άμμεσο οπτικό ερέθισμα για αυτό και είναι ιδιαίτερα σημαντικό η αλλαγή να είναι ξεκάθαρη ούτως ώστε η διαδικασία επούλωσης να μπορεί να παρακολουθηθεί. Παρομοίως στο σύστημα πολυαμίδιο 6/μωβ της βρομοκρεζόλης, η απελευθέρωση

βαφής περιορίζεται με την προσθήκη Perfixan όμως καθαρότητα στην αλλαγή παραμένει άλυτο ζήτημα.

Οι αλοχρωμικές ουσίες μελετήθηκαν ευρέως σε αυτή την εργασία. Επιπλέον, εξαιρετικής σημασίας είναι η ευδιάκριτη αλλαγή στη χροιά της χρωστικής ουσίας και η απελευθέρωσή της παραμένει ζήτημα προς μελέτη μιας και τα επιθέματα τραυμάτων οφείλουν να είναι βιοσυμβατά με την πληγή. Ένα μίγμα πολυμερών μελέτηθηκε, η απελευθέρωση βαφής θα μπορούσε να μελετηθεί περαιτέρω.

Contents

Chapter I

Introduction and literature study

1. Introduction

Smart textiles are an area with a lot of directions that can be divided in three major categories. The first one is called passive smart textiles which are sensors, the second category contains active smart textiles and the last one treats very smart textiles, which are able to adapt their behavior to the circumstances. [32][66]

This work focuses on halochromic nanofibrous materials that could be used as wound dressing materials, e.g. in burn wound healing. Chromism is a term widely used to introduce chromic phenomena and describe a reversible colour change of the physical properties of a material. It is based on the phenomena that generate the change of the electron density of substances, especially π-or-d electron state, or the change in the arrangement of the substance supramolecular structure. Independently of the factors that trigger reversible colour change, several kinds of chromism are known such as halochromism. A halochromic material is a material which changes colour when a pH change occurs. The colour change of halochromic substances occurs when the chemical binds to existing hydrogen and hydroxide ions in solution. Such bonds result in changes in the conjugate systems of the molecule, or the range of the electron flow. This alters the amount of light absorbed, which in turn results in a visible change of colour. Halochromic substances do not display a full range of colour for a full range of pH because, after certain acidities, the conjugate system will not change further. [36][55][58]

PH indicators are halochromic chemical compounds that are added in small amounts to a solution so that the pH of the solution can be determined visually. Normally the indicator causes the colour of the solution to change depending on the pH. Another use of pH indicators developed the last years, is the addition of it in a polymer solution that will be electrospun, also referred to as dye-doping of the electrospinning solution. This enables the production of nanofibrous nonwovens that can change colour under the influence of a pH-variation. Those types of chromic materials reveal the halochromic phenomena and they have a significant potential in the development of smart textiles. [1][4][5][7][11][22][23]

This work focuses on the production of nanostructured halochromic materials having a reversible colour change, provided by the incorporation of dyes, and their potential to monitor the healing procedure of a burn wound characterized by specific pH-changes.

2. Wound dressing materials

2.1 Requirements for a good wound dressing

A wound is a type of skin injury caused by mechanical, thermal, electrical and chemical injuries. Wound dressings are materials used to cover the wounds and promote healing. Dominant condition for a good wound dressing is to avoid strikethrough and to protect the injured site from contamination and further injuries. A burn is a subcategory of wounds caused by heat, electricity, chemicals, light, radiation or friction. There are superficial burns which heal by rapid re-epithelialization with minimal scarring, and deep burns requiring surgical therapy. A burn wound passes through a very complex process during the healing procedure defined by the initial injury and that is why a good wound dressing is crucial. [2][13][20][44]

Wound dressings are divided into traditional and new types. The latter are mostly smart materials that are believed to help in the healing procedure of a wound and provide information about it. However, it is a field in progress. There are many structures that have already been used as dressings with or without cooperation of another substance for healing such as alginates, hydrogel, honey and chitosan because of its antimicrobial properties. [1][4][21][32][33][44][49]

It is important to know the pH range of a wound because chemical reactions each require a certain optimum pH value that is modified by endogenous and exogenous factors such as the ambient temperature during the healing procedure. With a pH scale from 0-14, the pH of a wound varies between 4 and 6 depending on the age of the person and the anatomical location. Acute wounds can take 8-12 weeks to heal whereas chronic wounds can take more than 12 weeks (Figure 1, Figure 2). [14][33][52]

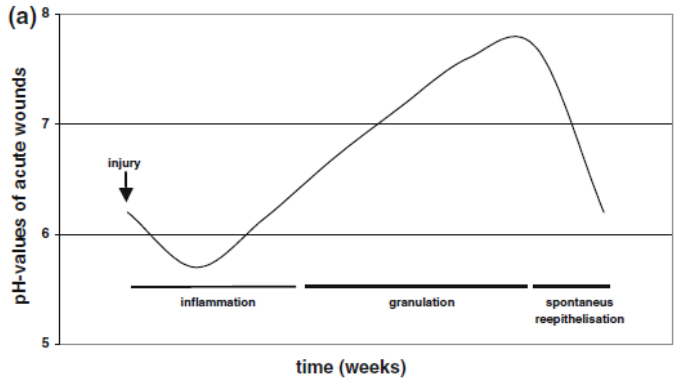


Figure 1: PH values of acute wounds [14]

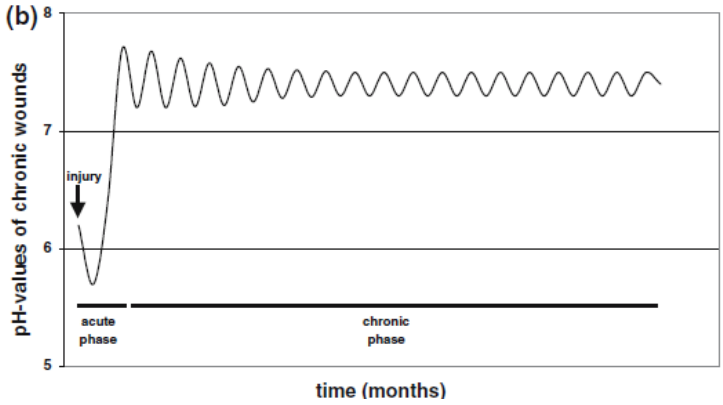


Figure 2: PH-values of chronic wounds [14]

It is known that wound healing needs moisture. An open wound which is exposed to air dehydrates, which results in the formation of a scab. The latter forms a mechanical barrier against migrating epidermal cells, causing them to move through a deeper level of tissue, retarding healing. A moist environment prevents the formation of scab and allows the cells to move unhampered (Figure 3). The 5 stages of the healing procedure are hemostasis, inflammation, migration, proliferation and maturation. The first step can be promoted by a good wound dressing with a porous surface. [14][32][33][45][50]

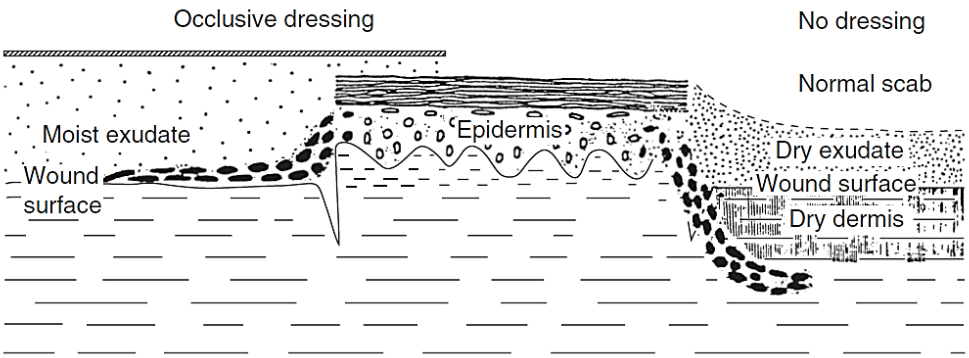


Figure 3: Healing under a moisture environment [32]

Classical biocides function either by inhibiting the growth of bacteria (biostatic) or by killing them (biocidal). Medical textiles should have quick biocidal functions. The requirements for a good wound dressing are storage durability, sterilization of steam or ethylene oxide and weathering and UV resistance. Challenges are the sterilization that can destroy many active biocides and also biocidal surfaces can be covered by dead bacterial cells or dusts. [24][25][54]

To conclude, the pH and the moisture of a wound are decisive parameters for the metabolism and meaningful for the therapeutic interventions in wound care. Therefore we can easily conclude that the use of a pH-indicator during the healing of a wound could be very useful. [1][4][14][34]

2.2 Nanofibrous structures produced by electrospinning

"Nanofibre" originates from the Greek word nano- (νάνο) that means dwarf and can be determined only in the nanoscale. These are fibrils with diameter less than 1000 nm (nanometers) and have great properties because of their small size such as low density, large surface area, high pore volume, tight pore size and flexibility. Because of their properties, nanofibrous structures have a wide range of applications such as biomedical, protective clothing, filtration, tissue scaffold, drug delivery, sensors, wound dressings, space applications et cetera that can be classified in major applications such as Bioengineering, Environmental Engineering & Biotechnology, Energy & Electronics and Defense & Security. [10][11][41]

There are a lot of production methods that have been determined through the years such as drawing technology for producing micro/nanofibres using a micropipette with a diameter of a few micrometers; template synthesis of carbon nanotubes, nanofibre arrays and electronically conductive polymer nanostructures; and thermally induced phase separation method for producing nanofibres. Electrospinning is one of the methods that after numerous of patents was re-discovered in 1995 by Doshi and Reneker in order to provide a method for drawing very fine fibres from a liquid. It is the cheapest and the most straightforward way to produce nanomaterials. This method uses a high voltage source that is applied to a polymer fluid so that charges are induced within the fluid. A well-defined droplet erupts from the tip of the nozzle and a jet is formed. Between the droplet and the jet a cone is formed with the name Taylor cone. Solvents of solution evaporate and pure polymer creates a thin deposition of nanofibres on the collector plate. The polymer chain entanglements within the solution will prevent the electrospinning jet from breaking up. [3][10][15][16][39]

Because significant influence on the fibre performance, high quality and precise morphology of the fibres is demanded, a controlled manner of production is important. The electrospun fibrils can be

deposited either randomly to form a nonwoven web or in an oriented manner to give an aligned nanofibre array. The fibre orientation depends on the collector that will be used for example a rotating collector drew fibres according to the rotation. Figure 4 indicates collectors used for regulating the fibre collection process. [1][4][17][31][35][41][47][48][51]

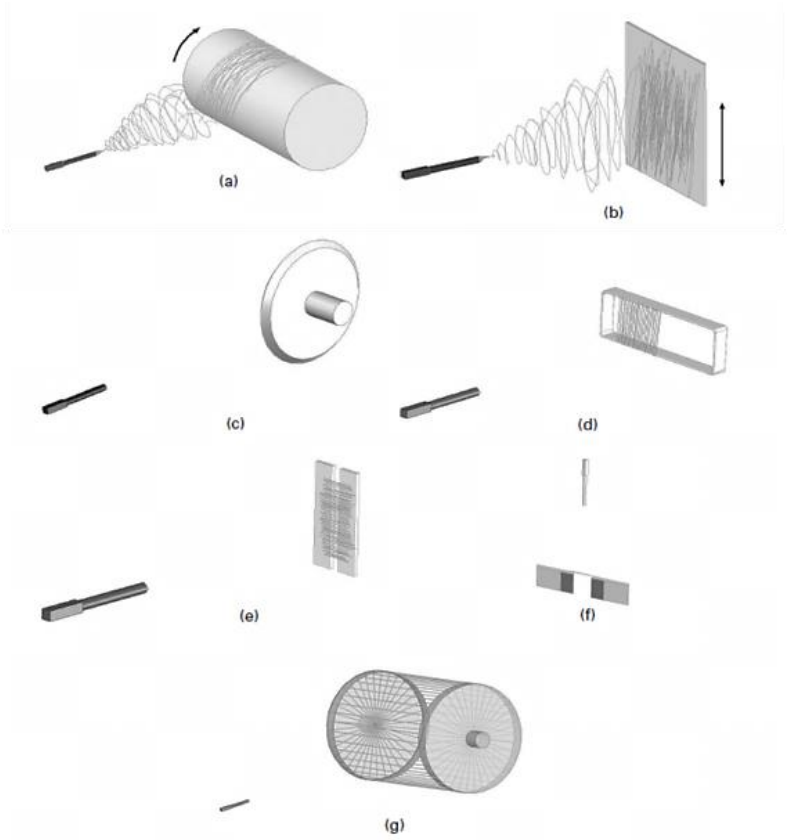


Figure 4: a. rotating roller, b. vibrating plate, c. sharp edge rotating disc, d. frame, e. fork, f. point collector and g. drum [47]

In the electrospinning process a combination of polymers could be also used by blending in order to produce a new material with added functionality. This way, the advantageous properties of the components can be combined, raising the quality of the new material. A polymer blend is a mixture of at least two polymers that are blended together to create a new material – hybrid - with different physical properties. A polymer blend must have good compatibility between the two components in order to have reasonable mechanical properties and a good adhesion between the phases. The best way of preparing a blend of two or more polymers is not to change the properties of the components drastically, but to capitalize on the maximum possible performance of the blend. A few examples of polymer blends are PET/PBT, PET/PC, PBT/ABS, PET/PTFE, PVC/IBA, Wang et all electrospun field responsive surperpamagnetic polymeric fibers from colloidallystable suspensions of magnetic nanoparticles in PEO and PVA solutions et cetera. [1][4][11][29][30][26][51][53]

Polymer blends belong to a greater group of hybrids called functionalized polymers, which can be achieved in many ways such as surface modification, membrane filtration, coatings, friction, blending, et cetera. Functionalization on the surface with a coating is defined as a material being applied onto a surface and appears as either a continuous or discontinuous film after drying. Coatings are separated into organic and inorganic forms. Inorganic coatings are mainly applied for protective coatings, whereas organic coatings are mostly used for decorative and functional applications. Although organic and inorganic coatings may be used individually for industrial applications, for specific requirements a combination of both systems – termed hybrid coating – is favored. Microencapsulation provides the possibility of combining the properties of different types of material (for example organic and inorganic). [6][10][24][25][28][37][42][48]

Functionalization in the structure of a polymer namely blend is the direct mixture into the polymer solution before electrospinning. The latter will be used in this project since a good wound dressing should be porous. With the use of a coating such as sol-gel, the initial structure and therefore also the porous properties are being changed, especially in the biodegradable polymer nanofibres. [10]

2.3 Synthetic polymers

Polyamide 6 is being used for this project and has been electrospun many times in the past in different ways. Nylon 6 is a polymer developed to reproduce the properties of nylon 6-6 without violating the patent on its production. Unlike most other nylons, nylon 6 is not a condensation polymer but instead is formed by ring-opening polymerization. This makes it a special case in the comparison between condensation and addition polymers and is a semicrystalline polyamide. Nylon 6 fibres are tough, possess high tensile strength, as well as elasticity and lustre. Polyamide 6 is prepared by ring opening polymerization of ε-caprolactone using a catalyst such as stannous octoane. (Figure 5) [6][17][18][19][23][25][40]

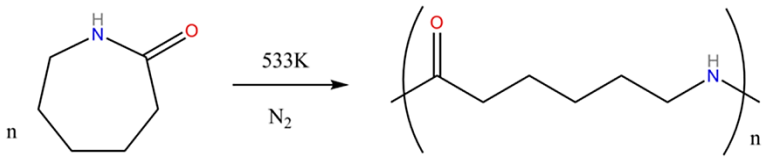


Figure 5: Caprolactam ring opening polymerization

Ring opening polymerization is formed of chain growth polymerization in which the terminal end of a polymer acts as a reactive center, where further cyclic monomers join to form a larger polymer

chain through ionic propagation. The treatment of some cyclic compounds with catalysts brings about cleavage of the ring followed by polymerization to yield high-molecular-weight polymers.

It has been done surface functionalization of the polyamide 6 as-spun nanofibres by Cu (copper) coating though it is not the case for this project. The diameters of the nanofibers increase after the Cu deposition. Plasma treatment improves the water adsorption of the nanofibres, this can be attributed to the fact that the treatment has an effect on surface etching which brings a microscopic roughness to the fibre surfaces. [6]

Polyamide 6.6 is a polymer of nylon class and is made of hexamethylenediamine and adipic acid which give nylon 6-6 a total 12 carbon atoms in each repeating unit. Electrospin polyamide 6.6 is being referred since nylon 6 (that will be used in this project) has similar properties of nylon 6-6 that it is not the case (figure 6). It has a melting point of 268°C that makes it resistant to heat and friction and enables it to withstand heat setting for twist retention. Nylon 6-6 is frequently used when high mechanical strength, great rigidity and good stability is required and some popular applications are carpet fibres, apparel, airbags, tires, zip ties, ropes, conveyor belts and hoses.

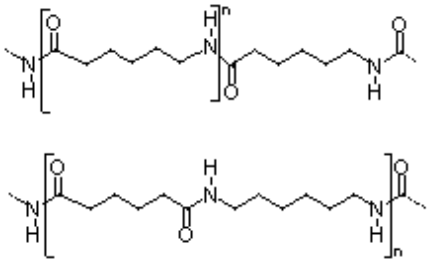


Figure 6: Structure of nylon 6 (above) and nylon 6.6 (below)

Another polymer that will be used in this project is polycaprolactone (PCL) a biodegradable polyester with a low melting point of around 60 °C and a glass transition temperature of about -60°C and is often used as an additive for resins to improve their processing characteristics and their end use properties.

Poly(dadmac) is a polymeric complexing agent that will be used for the reduction of the leaching dye. It can be produced by free radical addition polymerization of diallyldimethylammonium chloride using persulfate initiator. Poly(DADMAC) is usually delivered as a liquid contentrate having a solids level in the range of 10 to 50% and it is a high charge density cationic polymer. This polymer is been used in waste water treatment, for controlling disturbing substances in the paper making process and in water purification.[46]

P(M) is a polymer that produced by a free radical polymerization and is an organic compound. It is appeared as white crystals and is soluble in alcohols and common organic solvents but is insoluble in water. It is often used as a foamer in plastics and rubber and as a radical initiator. It is consider as an explosive compound, decomposing above 65°C.

In conclusion, while the size scale and orientation of nanofibre can be used to influence cell functions such as adhesion, proliferation and migration even greater enhancement over the control of cellular function can be achieved by attaching bioactive molecules to the surface of the nanofibrous scaffold. The development of new collectors has demonstrated the importance in choosing the correct collector properties in order to obtain the desired scaffold properties as an example pore size and fiber density. Additionally different collectors can be used to control not only the scaffold geometry but also the fiber alignment, which can be used to control the mechanical properties as well as the biological response to the scaffold. Research has shown that surface modification of electrospun fibers can be used to further enhance the scaffold's interaction with cells in tissue engineering applications. The ability to electrospin synthetic (biodegradable or non-degradable), natural and hybrid materials allows for precise tailoring of the scaffold properties to the desired application, and new materials are constantly being electrospun. [43]

A few examples of nonwoven wound dressings are gauze dressings, compression bandages, plasters, scaffolds, vascular prosthesis, surgical gowns and so on. Moreover, surgical gowns, caps and masks, absorbent layers, fleeces, wipes, protective clothing et cetera and these fields are being in development continuously. [54]

3. Nanofibrous structures as halochromic wound dressing materials

Until now only few times a dye-indicator such as alizarin, bromocresol purple, brilliant yellow, nitrazine yellow combined with a nonwoven structure has been used to study better the appearance of halochromic phenomena. However, an increased interest in this area is observed. A combination of a pH-indicator with conventional textiles is also been used to provide pH sensitive materials. [1][4][5][22]

3.1 PH responsive nanofibres

The main objective is pH responsive nanofibres, namely halochromic material. Chromic materials are the general term referring to materials, which change, radiate or erase color and due to colour changing properties very often referred to us chameleon materials. [58] Textile and nanofibrous

structures have been used up until now to introduce the halochromism. Textiles that change color could be widely used in order to indicate the pH of a burn wound since the color is a visual stimuli and a first warning function. A pH sensitive dressing could provide information just by its color since the skin pH of a wound varies during the healing process therefore unnecessary removal of the bandage can be avoided. [4][5][7][34][59][59]

The focus of this project is in nanofibrous structures with presence of halochromic phenomena. Although halochromic dyes are not available on the market pH indicators could be easily found and alternatively used to facilitate the halochromism in the nanofibrous structures. It is known that the response time in conventional textiles is increased in comparison to nonwoven substances. Therefore nanofibrous structures have been used in this project to indicate this phenomena. Moreover, thanks to their characteristics a decreasing risk on infections and a promotion of cell growth and a control of fluid drainage in the wound area are provided. [7][59][59]

A system dye-polymer and dye-polymer-CA (Complexing Agent) will be used. The term that will be referred for the system with the dye is dye-doped. The dye is been added in the polymer solution before the electrospinning. For instance polycaprolactone dye doped by Nitrazine yellow [4] and polyamide 6.6 dye doped by bromocresol purple [5]. Moreover, polyamide 6 dye doped by a "cocktail" of pH indicators namely Phenol Red, Methyl Red, Phenolphthalein, Bromothymol Blue and Bromocresol Green [34]. A great pH range is been succeeded by Agarwai et al.

A pH sensitive membrane of PAN with PA 6.6 is been developed by Zhang et all [11] in a two-nozzle electrospinning set up. The group accomplished color change from pale yellow to violet in pH range from 7 to 14 with a special technique that could be evolved to succeed pH responsive nanofibre membranes (figure 10).

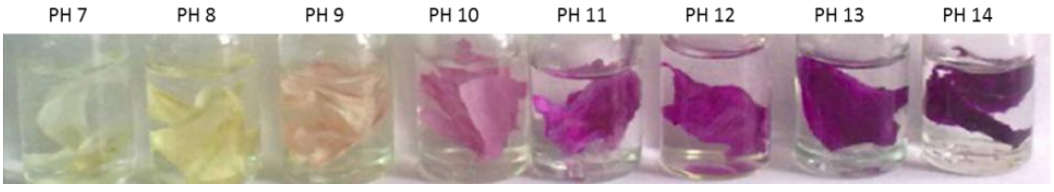


Figure 10: The color change properties of pHS-NF membranes in different pH buffer solutions. [11]

3.2 Apprehension of the color

Color is a visual stimuli and can be used to indicate the healing process of a burn wound. Nevertheless, vision is an objective way to estimate the color and evaluate the experimental results for commercial stimuli responsive materials so it is imperative a color space is used. A color space is a three dimensional geometric space with axes defined so that symbols for all possible color

perceptions of humans can be defined. The stimuli are to us messages from the outside world absorbed by the retinal layer and trigger a complex of events and result in our perceptions. Numerical color spaces have been used through the years for color measurements; in this project CIEL*a*b* color space will be used. The Commission Internationale de l' Eclairage, nominally CIE, was developed from earlier attempts to transform the X, Y and Z tristimulus values into coordinates that would provide better uniformity. The three parameters calculated are L* for a given color varies between 0 (perfect black) and 100 (perfect white), a* for the red-green character of the color with positive values for red shades and negative for green shades and b* that gives yellow-blue character with positive values for yellow shades and negative for blue shades. [8][64]

Most halochromic dyes change from one colour to another showing a bathochromic or hypsochromic shift of the absorption peak upon (de)protonation and are classified as positive and negative halochromic dyes respectively. At the base of the colour changes lies a protonation or deprotonation of the dye molecule causing a different electron configuration and thus a different colour. The visible colour change of halochromic dyes is mostly based on a ring opening of the dye molecule upon (de)protonation or on a tautomerism, (tautomers are isomers –constitutionals- of organic compounds that readily interconvert by a chemical reaction called tautomerization. This reaction commonly results in the formal migration of a hydrogen atom or proton accompanied by a switch of a single bond and adjacent double bond. Because of the rapid interconnections, tautomers are generally considered to be the same chemical compound.) as tautomers have different colours and tinctorial strengths. [22]

4. Objective of the thesis

The use of halochromic textiles in medicine is imperative since increasing interest is observed lately according to the literature. The focus and the research is still in progress for a good pH indicator since the pH range of a burn wound during healing process is very specific. Electrospinning is believed to be a good production process for nanofibres and many materials could be blended to produce desirable nowoven structures. Polymer blends combine the properties of the polymers that used to create a material with generated properties and it will be tested as well.

Polycaprolactone doping by disperse red 1 and the functionalized DR1 and polyamide 6 doping by bromocresol purple will occur in Chapter III. A complexing agent will be added as well to eliminate the leaching of the dye in each occasion. In Chapter IV polyamide 6 doped by disperse red 1 and the functionalized dye again doped by the complexing agent will be carried out. A blend of polymers PA 6 and P(M) will be used and the dye covalently bonded to the backbone of the later polymer will be electrospun as well to investigate halochromism from this scope. And last but not least polyamide 6 doping by Fast Green and by Bromocresol Purple will be researched in Chapter V, doped by the complexing agent as well. A first objective is to evaluate and compare the influence of the complexing agent with the dye doped polymers and to obtain a better knowledge in the pH-sensitivity. A second goal is to maintain a production method for halochromic nanofibres by different tests that will optimized.

Chapter II

Materials and methods

1. Materials

All polymers necessary to perform the experiments were obtained from Sigma-Aldrich and are used as received. The P(M) was obtained from the Chemical Department of University of Gent. The polycaprolactone (PCL) pellets were from the same lot having a number average molecular weight (Mw) of 114,000 g mol^{-1} and a weight average molecular weight (Mw) of 191,000 g mol^{-1} and the Nylon 6 pellets with molecular weight (Mw) 12,321 g mol^{-1} were obtained from Sigma Aldrich. Different solvents were used in the experiments, all obtained from Sigma-Aldrich: 98-100v% formic acid, 99,8v% acetic acid and acetone. The solutions were stirred with a magnetic stir bar. Also all of the colourants used, namely Bromocresol Purple and Litmus were obtained from Sigma-Aldrich. The azo dyes Fast Green, Disperse Red 1 and the functionalized dye Disperse Red 1* were obtained from the Chemical Department of University of Gent. Perfixan RDV, a polyquaternary complexing agent, was obtained from Sigma Aldrich.

2. Electrospinning equipment

2.1 Mononozzle electrospinning setup

For the preparation of the nanofibrous samples, a mononozzle electrospinning devise was used. The specifications of the used devise are concluded in the following Table 1 and are schematically represented, figure 1. The measurements were taken under room temperature and room humidity, none of both controlled. In each experiment, the conditions were measured and written down.

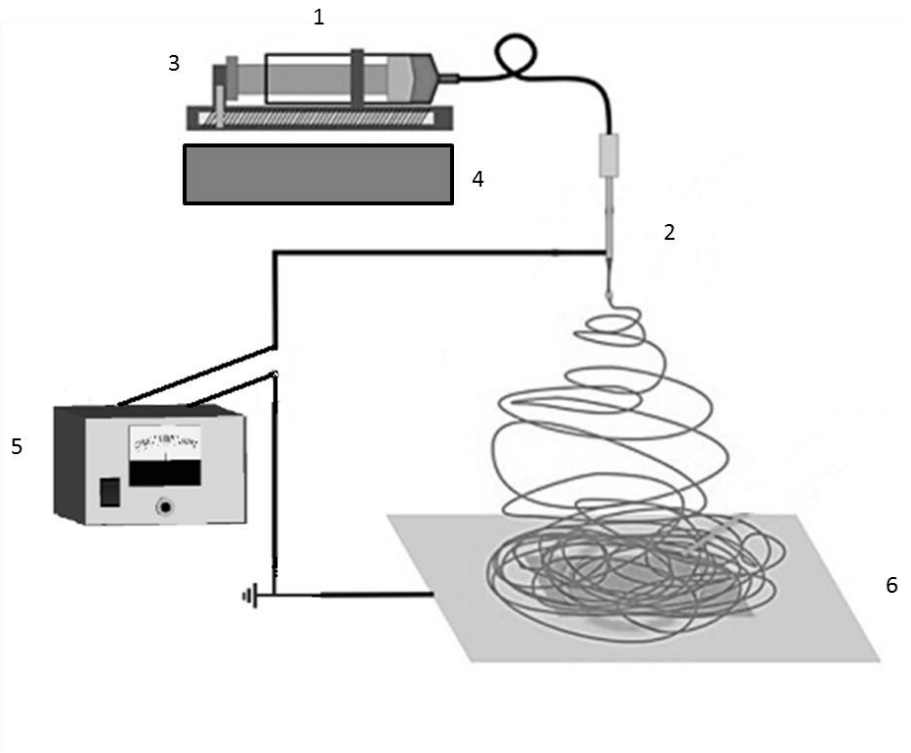


Figure 5: Schematic of monozzle eletrospinning set up [15]

Table 1: Specifications of the mononozzle electrospinning setup

n	Parts of the devise	Characteristics
1	Syringe	20 ml Norm-jet of Henke SassWolf
2	Needle	Sigma Aldrich stainless steel 316 syringe needle, pipetting blunt 90° tip -> Length: 15,24 cm -> Size: 18 gauge (nominal internal diameter of 0,838 mm)
3	Infusion pump	KD Scientific Syringe Oumo Series 100
4	Laboratory jack	Used to adjust TCD by measuring the distance between the needle tip and the collector
5	High voltage source	Glassman High Voltage Series EH -> Output voltage: 0 - 30 kV
6	Collector	Grounded collector plate covered with aluminium foil (or other suitable substarte)

2.2 Multinozle electrospinning setup

When there is need for thicker and larger samples, the stability or the electrospinning process needs to be tested, a multinozzle electrospinning setup can be used. This setup is basically the same as the mononozzle setup, with the possibility to use more needles and the collector can move, creating a semi-continuous process. The needles are connected to the syringes using PVC tubing and to the high voltage sources by a metallic wire in a serial mode to transfer the applied voltage. They are supported by the upper element, which is made of an isolating material because of the electric field. The placement and the number of the needles can be adjusted. The TCD can be adjusted by changing the position of the collector conveyor belt. The setup is located in a controlled environment, quaranteeing a temperature of 21±20°C and the relative humidity of 45±5%. To be aware of anomalies, the humidity and temperature were written down with each experiment.

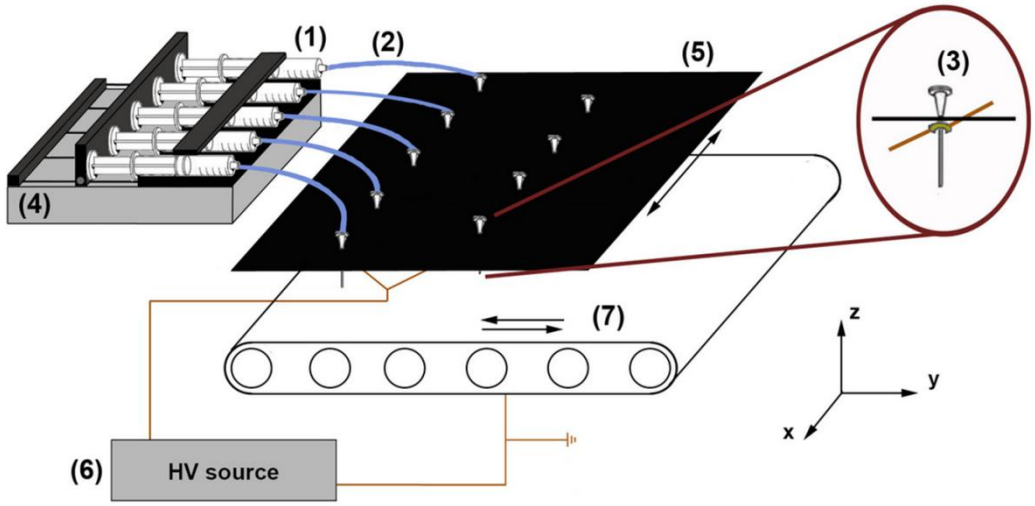


Figure 2: Experimental set up of multinozle [1]

Table 2: Specifications of the multinozzle electrospinning setup

n	Parts of the devise	Characteristics
1	Syringe	20 ml Norm-jet of Henke SassWolf
2	Tubing	Sigma Aldrich PVC laboratory tubing -> Inner Diameter: 1,588 mm -> Outer diameter: 3,175 mm
3	Needle	Terumo mixing needles without bevel -> Length: 40 mm -> Size: 18 gauge (nominal internal diameter of 0,838 mm)
4	Infusion pump	KD Scientific Syringe Pump Series 220-CE
5	Upper element	PVC plate -> Thickness: 1 cm -> Movement: possible along the x-axis driven by a three plase ac motor
6	High voltage source	Glassman High Voltage Series WK 125P5 -> Output voltage: 0 - 125 kV
7	Collector	Grounded aluminium foil supported by a conveyor belt -> Size: 0,5 x 1,5 m -> Movement: along the y-axis

3. Color fastness

For the fasteness of the color of the specimens ISO 105 PT*E01:2010 will be followed. A test device, an oven and the adjacent fabrics need to be used. Test device, consisting of a frame of stainless steel into which a weigh-piece of mass approximately 5 kg and base of 60 mm x 115 mm is closely fitted, so that the pressure of 12.5 kPa can be applied on test specimens measuring 40 mm x 100 mm placed between acrylic-resin plates measuring approximately 60 mm x 115 mm x 1.5 mm. The test device shall be constructed so that, if the weight-piece is removed during the test, the pressure of 12.5 kPa remains unchanged. The oven is maintained at 37 °C ± 2 °C and the adjacent fabrics that will be used are polyamide and wool.

4. Characterization

4.1 Conductivity and Viscosity

The electrospinning solutions were characterized by measuring their conductivity and viscosity. The former was measured using a Brookfield viscometer LVDV-II, the last using a CDM210 conductivity meter (Radiometer Analytical).

4.2 Scanning Electron Microscopy (SEM)

The formation of the nanofibrous structures were examined using a scanning electron microscope (Jeol Quanta 200 F FE-SEM) at an accelerating voltage of 20 kV. A gold coating was applied using a sputter coater (Balzers Union SKD 030), which is responsible for the cracks that sometimes appear on the fibres in the SEM images. The nanofibre diameters were measured using UTHSCSA ImageTool version 3.0, developed by the University of Texas Health Science Center. The average fibre diameters and their standard deviations are based on 50 measurements per sample.

4.3 pH measurements

Several aqueous solutions with hydrochloric acid (Sigma-Aldrich 1 mol l^{-1}) and sodium hydroxide (Sigma-Aldrich 50 wt %) were prepared for the determination of pH of each halochromic sample. In the aforementioned solutions potassium nitrate was added (1 g l^{-1}) in order to a constant coefficient activity be ensured during the procedure. The pH was tested with a combined reference and a glass electrode (SympHony Meters VMR).

After the immersion in pH-baths, the samples are placed on a dry nanofibrous polyamide nonwoven in order to see the colour and enable handling of the samples. In further descriptions, this nonwoven will be referred to as the support.

4.4 UV-VIS spectroscopy

The ultraviolet-visible (UV-Vis) spectra were recorder with a Perkin-Elmer Lambda 900 spectrophotometer, which is a double beam spectrophotometer. For the reflection measurements on the fabrics an integrated sphere (Spectralon Labsohere 150mm) was used. The spectra were recorded from 380 to 780 nm, with a data interval of 4nm.

4.5 Grey scale

Since the color yield of a dyeing is the depth of color that a unit mass of a dye is able to impart to the dyed substrate it can be assessed visually; grey scale for assessing change in color, complying with ISO 105-A01, and grey scale for assessing staining, complying with ISO 105-A01.

Chapter III

Preliminary tests on PCL and PA6 doped by colorants and complexing agent

It has been established that the addition of small molecular units in the electrospunning solution has no significant influence on the electrospinning process. The system polymer/dye is investigated in this essay in order to understand the mechanisms of this process and to evaluate all the electrospinning parameters. Therefore, pure polymers, polymers doped by a selected dye and polymers doped by the dye (different in each occasion) and a complexing agent will be electrospun. A complexing agent is being added to optimize dye release that has been noted by Van der Schueren and all. [5]

1. Pure PA6 & PCL nanofibres, colorants incorporated with nanofibrous structures

Selection of the solvent system is meaningful for steady state electrospinning since the final goal is to optimize the polymer-dye system. Electrospinning PA 6 nanofibres in a formic acid/acetic acid solvent mixture, has been established and characterized as the key for steady state conditions, which is really important in the case of producible nanofibres. [63]

	Volume fraction of acetic acid in the formic acid/acetic acid mixtures					
wt% PA 6	25 v% AA	33 v% AA	40 v% AA	45 v% AA	50 v% AA	55 v% AA
12						
13					1.5	
14			2	2.5	3	
15		2	2.5	3	4.5	
16		2.5	3	3.5	5	
17		2.5	3	3.5	5.5	
18		3	3.5	4	6.5	
19		3.5	4	4.5	7.5	
20		3.5	4	5	6.5	
21						

Figure 3: The grey area indicates "no steady state possible", the black area is for the polymer that was not dissolved completely. (Voltage = 30 kV and TCD = 6 cm)

[63]

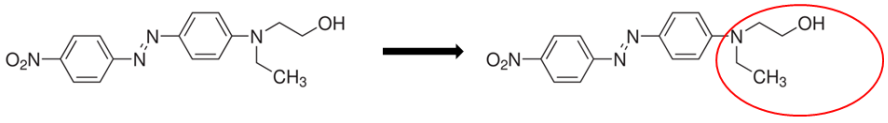
Polycaprolactone pellets in formic acid/acetic acid solvent system is also been proved to be promising by Van der Schueren et all. [61]

A colorant presents different characteristics in solution compared to the incorporated substances in the nanofibres. The halochromic behavior alters when a colorant has been added directly to the solution and then electrospun to produce the halochromic nanofibrous structures. [5]

Dye-doping of PA 6.6 with ethyl orange, bromocresol purple & blue, brilliant yellow, nitrazine yellow alizarine red et cetera has already been examined. Any type of pH indicator doped in the polymer solution do not alter the fibre diameter and in the electrospinning parameters. [5] The influence of nitrazine yellow in PCL solution has been studied by Van der Schueren et all. Influence in the solution and the electrospinning parameters have been noted. The structure of the molecules of the dye-doped PCL is also been deliberated since it is believed that is a very important factor to evaluate. Therefore, molecular modelling is been used for the construction of the halochromic behavior. Though it is not the case in this project, this method would help in a future work to understand better the mechanisms and the interactions between the dye molecules and the nonwovens structures. [4]

2. The selection of polymer/dye system

This chapter describes the selection of a suitable polymer/dye system, preliminary tests were done in order to study the system during electrospinning and to evaluate the procedure. Moreover, characterization of this system has been accomplished to measure parameters such as dye release and colour change under different pH values. Disperse dye molecules are the smallest dye molecules among all dyes and is based on an azobenzene or athraquinone molecule with nitro, amine, hydroxyl et cetera groups attached to it. Disperse red 1 or the functionalized one (Figure 6) is been used in this project.



Disperse red 1 Disperse red 1*

Figure 6: Disperse red 1 and the acrylate Disperse red 1*

3. Preliminary tests on PCL dye doped by Disperse Red 1 and the functional group

Three solutions were prepared; the first one with 14 wt% PCL, to the second one is been added 0.5 %omf of disperse red 1 and a third solution with the same amount of dye and 4 %omf of the complexing agent. The solutions with the functional group are been prepared in exact the same quantities of substances. These tests were held to characterize the influence of disperse red 1 and the functional group on PCL during the electrospinning process. Diameters of the deposition on the collector plate is been measured after SEM analysis as descripted in Chapter II. In figure 6 the numbers 1 and 2 indicate the electrospinning day for the same solutions. The relative humidity and temperature in day 1 are 53.5% and 22.1°C whereas in the 2nd day are 49% and 21.9°C respectively.

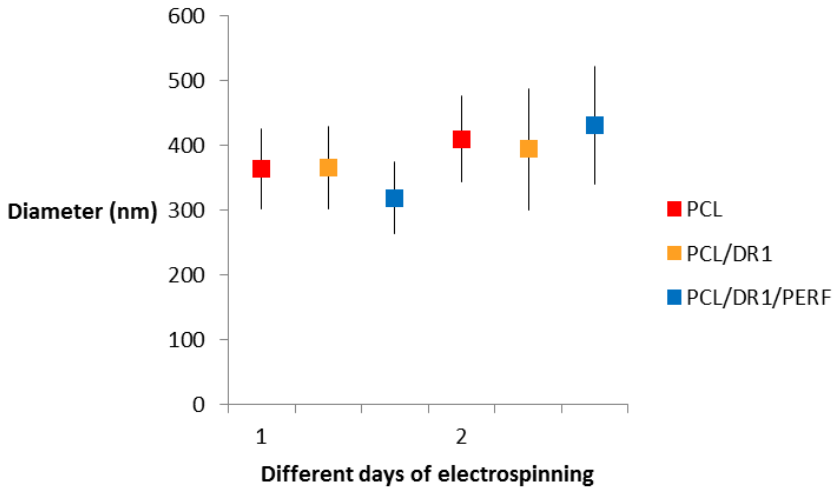


Figure 6: Preliminary tests on PCL dye doped by disperse red 1, electrospun in two different days.

The humidity is slightly greater in the first day compare to the humidity the second day but this is not the case since only great range of this parameter can affect significantly the diameters of the nanofibres. Disperse dyes are charged molecules therefore the charges of the solution are increased caused by repulsion of the charges in the surface consequently conductivity is increased with the addition of the dye. (Table 3) Moreover, figure 6 indicates a reduction in diameters of the solutions with Perfixan that electrospun the first day but within the margin of error so not significant influence.

Table 3: Characterization of the solutions PCL, PCL/DR1 & PCL/DR1/PERFIXAN and PCL, PCL/DR1-A & PCL/DR1-A/PERFIXAN

CONDUCTIVITY			
mS/cm			
PCL	0.0148	PCL	0.0495
PCL/DR1	0.0673	PCL/DR1*	0.103
PCL/DR1/PERFIXAN	0.0108	PCL/DR1*/PERFIXAN	0.188

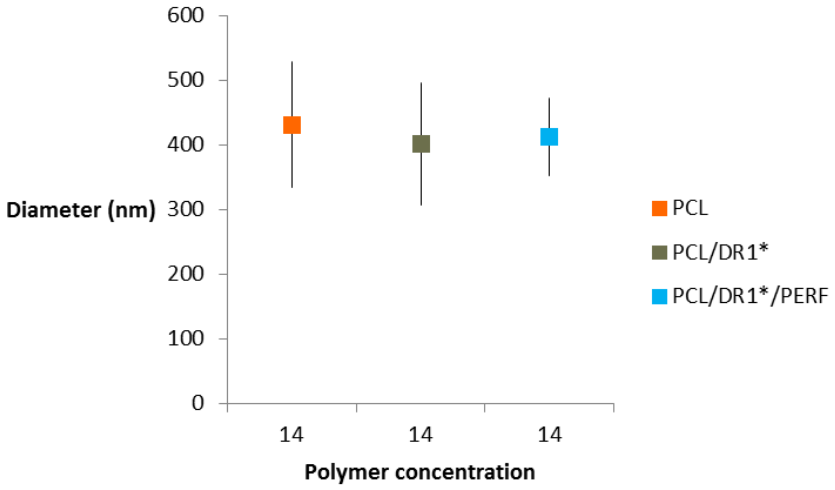


Figure 7: Preliminary tests on PCL dye doped by disperse red 1*

Figure 7 indicates the diameters of the dye doped electrospun nanofibres with the functionalized disperse red 1. There is no significant influence of the dye in the polymer solutions likewise in figure 6.

There is no significant difference on the fibre diameter between PCL dye doped by DR1 and PCL dye doped by DR1* (figure 8). Although the humidity during the electrospinning of the DR1* is 38.9% and the temperature 21.3℃ it is expected greater average diameters compared to the DR1 dye doped samples because humidity applies an extra plasticizer effect that results in thinner fibers. Moreover, diameters is in agreement with literature that is been noted a range of 364 ± 83 nm in humidity 50%. [61]

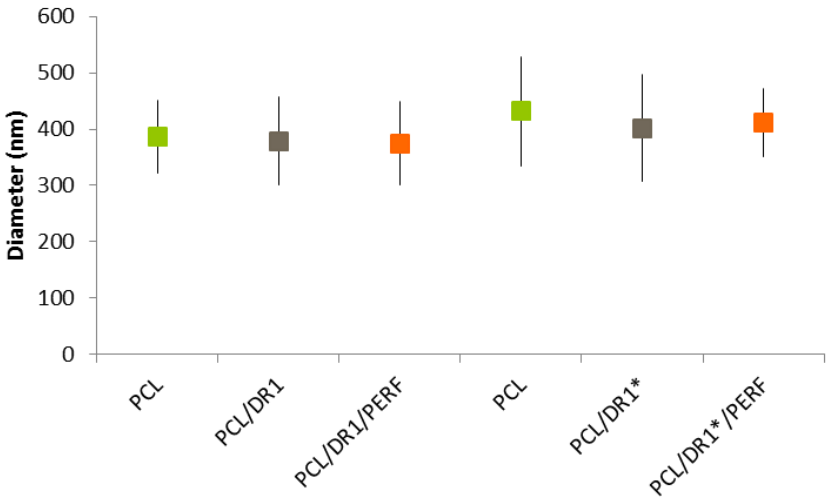


Figure 8: Diameters of PCL dye doped by DR1 compared to PCL dye doped by DR1*

4. Preliminary tests on PA6 dye doped by Bromocresol Purple

For this trial two solutions were prepared with bromocresol purple. Bromocresol purple is a pH-indicator that changes color from yellow to purple when pH changes from acid (below pH 5.2) to alkalic (above pH 6.8) respectively and above pH 6.8 the colour is blue. It was investigated if the polymer solutions are easy to electrospin on the mononozle and dye leaching tests were performed to characterize the dye release of the samples with and without the addition of the complexing agent.

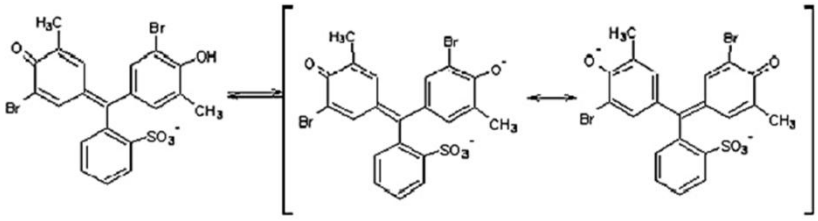


Figure 9: Equilibrium of the bormocresol purple between acid and alkali pH range. [5]

4.1 Electrospinning of PA6/BP and PA6/BP/Perfixan (BP=Bromocresol Purple)

Two polymer solutions were prepared with PA 6 in 16 wt% and 50/50 AA/FA. To the first one 0.5% omf bromocresol purple was added and to the second one the same amount of dye and 4% omf of the complexing agent were added. The ambient humidity and temperature were 51.1 % and 18.5°C

respectively during the electrospinning process and the parameters were kept constant (speed = 2ml/h, voltage = 22 kV and TCD = 6cm).

The dye doped polymer solution is quite stable to electrospin. After a while the voltage source turned off and on and the jet doubled, so two jets came out of the tip that is within the start–up phase. Then, a gradual range on the voltage was performed from 22 to 23.5 kV, the jet remained stable. The solution with the complexing agent is not been as stable as the dye doped. It took a few seconds to make it stable and still the jet was not straight as in the dye doped polymer solution.

To conclude, the addition of the pH indicator bromocresol purple and the complexing agent to the polymer solution do not have significant influence on the electrospinning process although obtaining a stable electrospinning process is more difficult when also Perfixan was added. Thorough tests will clarify this. Last but not least, it was noted that after the solvent evaporated (5 hours after the solutions were electrospun) PA6/BP and PA6/BP/Perfixan nanofibre samples changed color from yellow to light green and from yellow to dark green respectively, which can be explained by the evaporation of the solvent.

4.2 Dye leaching tests on PA6/BP and PA6/BP/Perfixan

The dye leaching tests performed in stock solution with potassium nitrate (10^{-2} M) in pH 2, 7 and 12. Samples were prepared (5mg of each type) and were immersed in 5ml stock solution for 24 hours. Afterwards, the spectrum of each solution was measured by UV-Vis spectroscopy and characterization of dye release occurred.

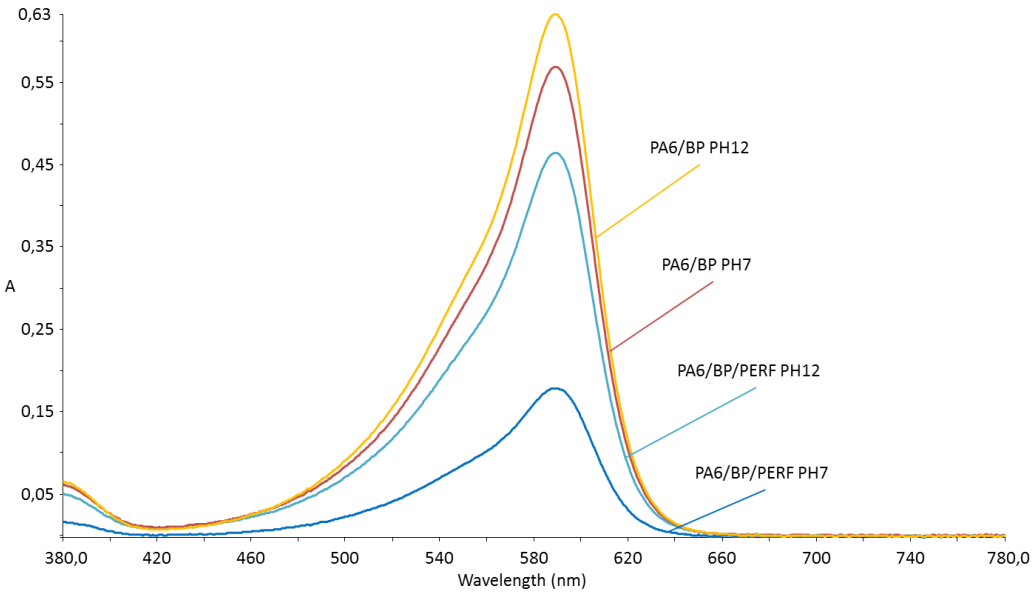


Figure 8: Dye leaching tests, absorbance spectra of PA6/BP and PA6/BP/PERF in pH (7 – 12).

There is no dye release between pH 2 and 7 but there is dye release between pH 7 and 12. Moreover samples with the complexing agent decreased dye release compare to samples without Perfixan. (Figure 8) The color change of both samples is illustrated in figure 9.

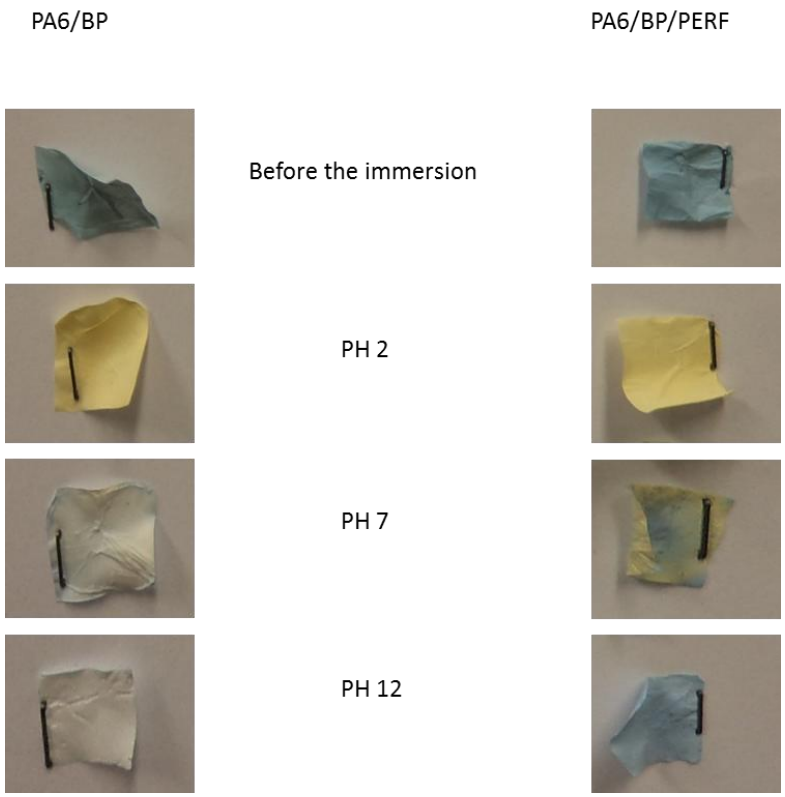


Figure 9: Dye leaching tests between pH 2 and 12 after 24 hours immersion, 5mg samples in 5ml stock solution

Chapter IV

Electrospinning PA 6, dye doped and blended

In this chapter doping of polyamide 6 by disperse red 1 and the functionalized dye will be investigated. Blend of polyamide 6 and the polymer P[M] will be produced. The blend nanofibres will be electrospun on the multinozle apparatus for a very stable process and large samples. Nanofibrous structures alter their halochromic properties according the environment conditions. Therefore, great samples will be needed and further tests will be held out.

1. Introduction

The behavior of DR1 and DR1* was characterized under several circumstances. The colour change with pH in solution and when incorporated in PA6 nanofibres by dye doping was measured. Additionally, blend nanofibres containing the dye were produced, by electrospinning a polymer blend of PA6 and P(M-co-DR1*). The latter is a copolymer with the DR1* (Chapter III) covalently bonded to the backbone of P[M].

The goal of this section is to illustrate the effect of disperse red 1 on the electrospinning process and to characterize the performance of the produced halochromic nanofibres. Additionally, the influence of the covalent bond between the dye and polymer will be analyzed and the results from the mononozzle and multinozzle setup will be compared.

2. Characterization of PA6 nanofibres containing DR1 and DR1* by dye-doping

The color change and the extinction coefficient of DR1 and DR1* were characterized. Additionally, the influence of functionalization on the color of the dye, the color change of PA6/DR1 and PA6/DR1* with pH in solution and the influence of the complexing agent (Perfixan RDV) on the color of the dye were characterized.

At first, DR1 and DR1* solubility was tested in potassium nitrate stock solution 10^{-2} M. For the electrospinning of the dye-doped solutions a 16 wt% PA6 solution was used in 50/50 acetic

acid/formic acid and a dye concentration of 0.5 %omf. To minimize dye release, 4 %omf of Perfixan was added to the electrospinning solution. Samples were prepared on the mononozle setup and additional tests were held on the multinozle and were characterized by SEM. The influence of the dye and the complexing agent on the solution characteristics (conductivity, viscosity) and the electrospinnability (stable or not) were investigated whereas the electrospinning parameters were kept constant (E=23kV, FR=2ml/h, TCD=6cm). The colour change of DR1 and DR1* dye-doped constant nanofibres on the polymer solution was measured at pH 2, 7 and 12 with and without presence of the complexing agent (Perfixan RDV). PH-sensitivity and dye release were measured by UV-Vis spectroscopy.

DR1 and DR1* did not dissolve in stock solution. Disperse dyes have slight water solubility because of the presence of polar substituents in their molecular structures such as HydroxyEthyloAmino. In their structure there are dispersants that are either a non-surface active polymers or a surface active polymer added to improve the particle separation. The solid forms of the dye contain much more dispersant, than pasts and liquid forms, to prevent particle aggregation during drying. Granular forms pour easily dust lest and facilitate weighing. The interaction of such polar groups with water, by polar interactions are hydrogen bonds, is crucial for water solubility. [8]

There is a small increase in conductivity with the addition of DR1 to a PA6 solution and even more with the addition of Perfixan. A complexing agent is a charged chemical substance thus the conductivity is increased even more. Influence of RH% and T on conductivity and viscosity is very small, not to be considered. (Figure 10)

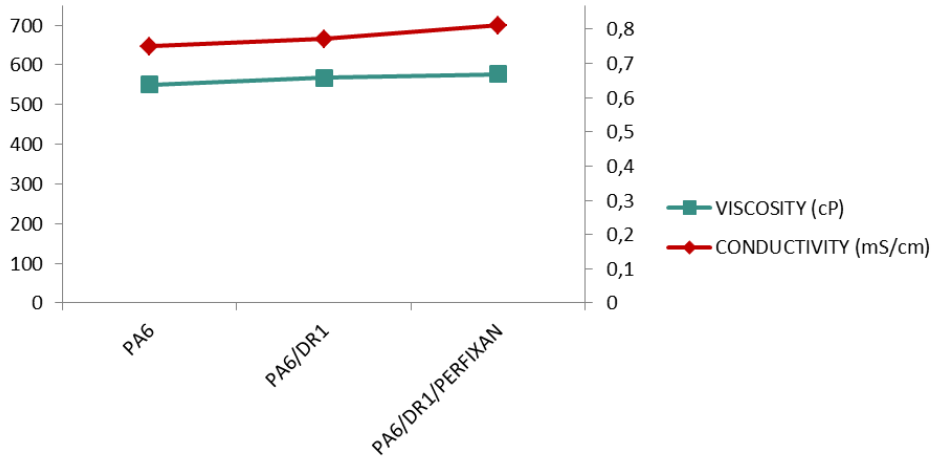


Figure 10: Viscosity and conductivity of PA6/DR1 and PA6/DR1/PERFIXAN nanofibre samples

Electrospinning of PA6 with DR1 and DR1* was quite stable. Moreover, a visible colour change in turn from red, orange and in the end pink was observed during the procedure and not in all of the

samples. The first, third and fifth samples (Figure 11) prepared in parallel the same day in order to compare. The same was as for the second, fourth and sixth sample. When samples were electrospun for the first group (PA6, PA6/DR1 and PA6/DR1/PERFIXAN) humidity and temperature was higher. Humidity affects the fibre diameter, diameter decreases with increasing humidity for PA 6.

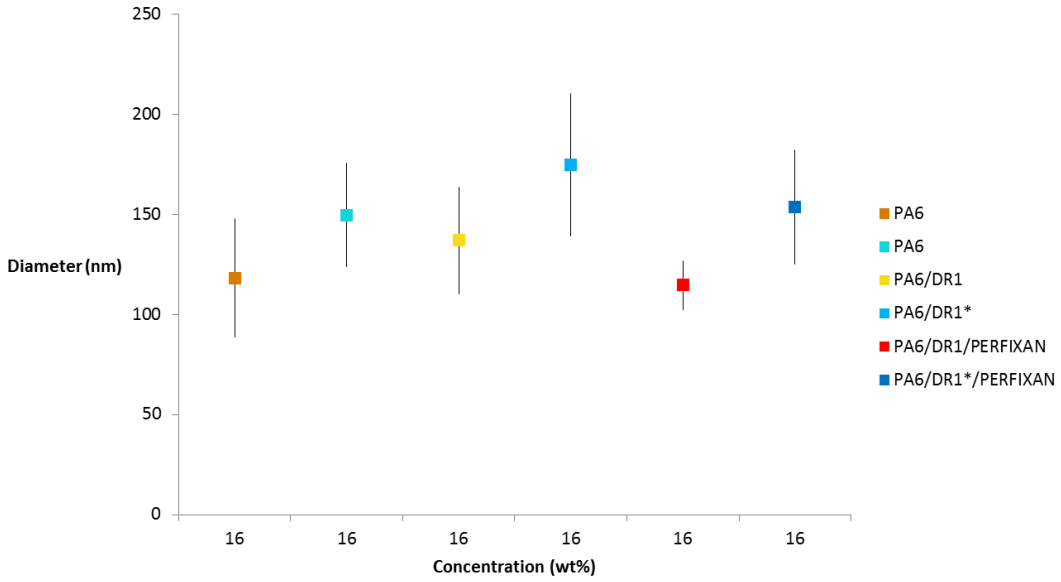


Figure 11: Influence of DR1 and DR1* in fibre diameter with and without Perfixan

Polyamide 6 blank solution, dye doped by disperse red 1 and doped by the dye and the complexing agent are been electrospun in the multinozle as well. The procedure was continued for at least 3 hours on the multinozle set up. By analyzing the fibre dimensions and morphology at the start and the end of this period, the long term stability of the process can be characterized. The fibre diameters show no significant change so it is assumed that the electrospinning process is stable in all three cases. (Figure 12)

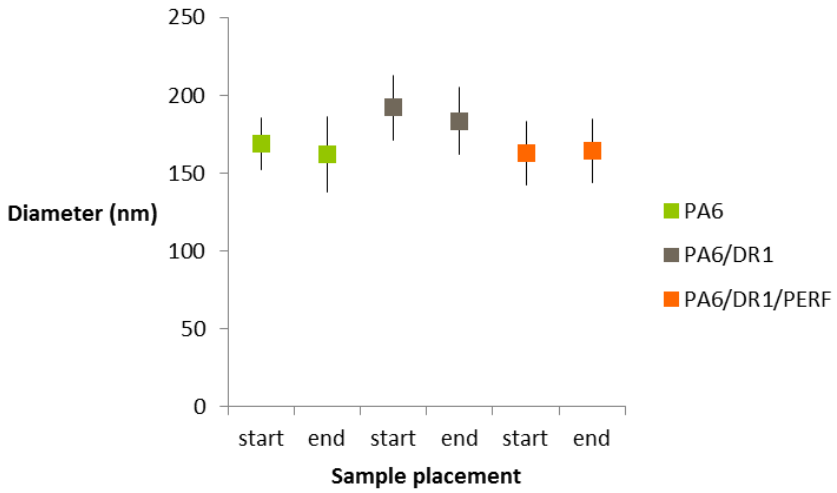


Figure 12: Electrospinning PA6, PA6/DR1 and PA6/DR1/Perfixan on the multinozle

The higher ambient humidity has an increased plasticizing effect on the polyamide 6 as it is been mentioned. This results also in a smaller variation of the average fiber diameter. The addition of dye in the polymer solution affects the average fibre diameter. The addition of Perfixan as it is observed from the graphs restore average fibre diameter but all within margin of error so no significant influence.

Although, it is known that the addition of small molecular weight components may alter the process conditions and fibre morphology, morphology of PA6/DR1 and PA6/DR1* have not changed as it is observed from SEM images (Figure 13). In pure PA6 were noted cracks on the fibre structure whereas PA6/DR1* nanofibre samples are without cracks that is from the gold coating before imaging and is thus due to sample preparation of SEM (Chapter II – Materials and Methods).

a b

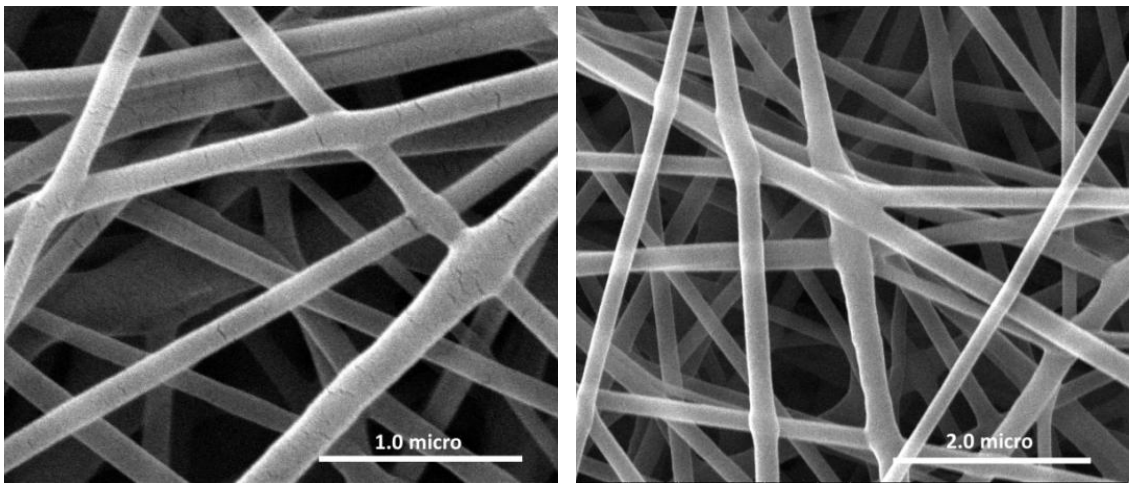


Figure 13: SEM images of PA6 (16 wt%) of pure PA6 (a) and PA6/DR1* (b)

Moreover, it was observed a greater colour depth in PA6/DR1 samples than in PA6/DR1*. Additional, it was noted from the normalized Kubelka-Munk graph that there is a small colour change between PA6/DR1 and PA6/DR1*. In conclusion, functionalization has small influence on the colour of the dye. (Figure 14)

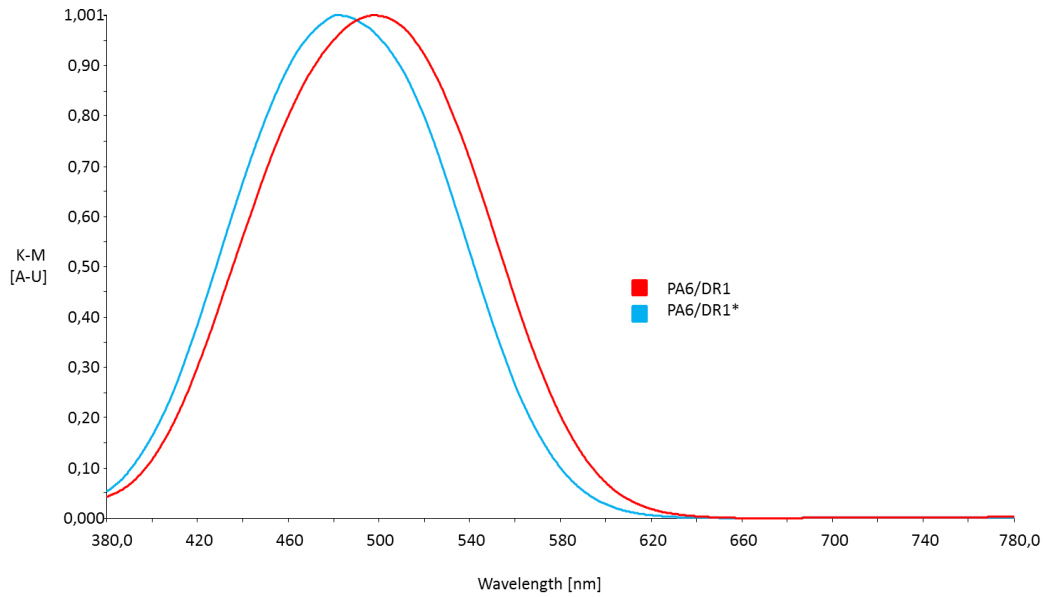


Figure 14: Normalized Kubelka-Munk spectra of PA6/DR1 and PA6/DR1* dry samples, mononozle

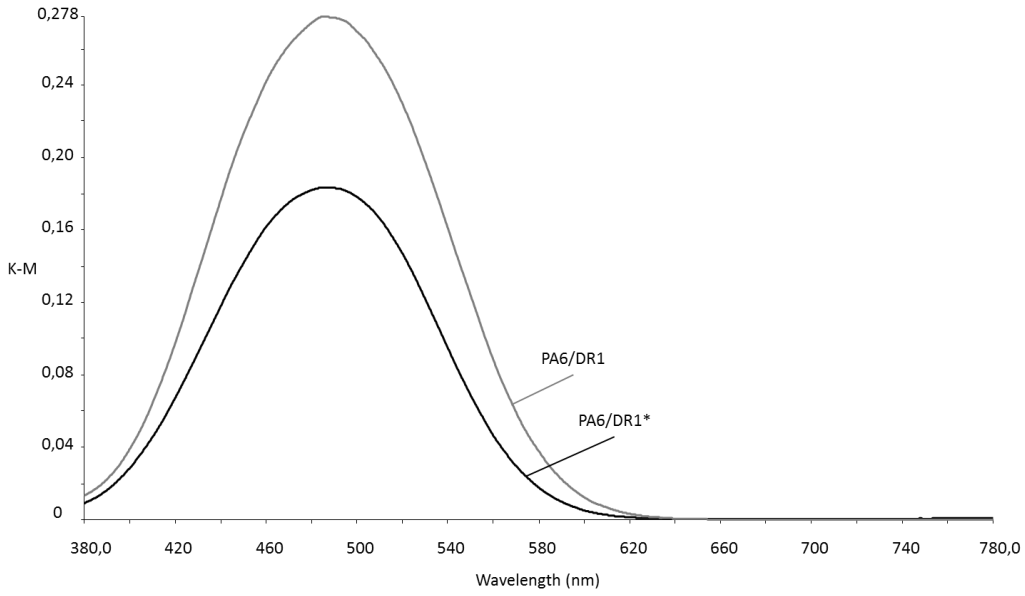


Figure 15: PA6/DR1 and PA6/DR1* electrospun in the multinozle

The as-spun nanofibres that is been doped by disperse red 1 appears to have deeper color in comparison to disperse red 1* according to the Kubelka-Munk spectra in the UV-Vis. No colour change is been noted (figure 15).

The addition of Perfixan in the polymer solution has shown a greater colour depth on (dry) nanofibre samples in both cases (PA6/DR1 and PA6/DR1*) without any influence on colour. So, I conclude that there is no influence on colour due to Perfixan. (Figure 16)

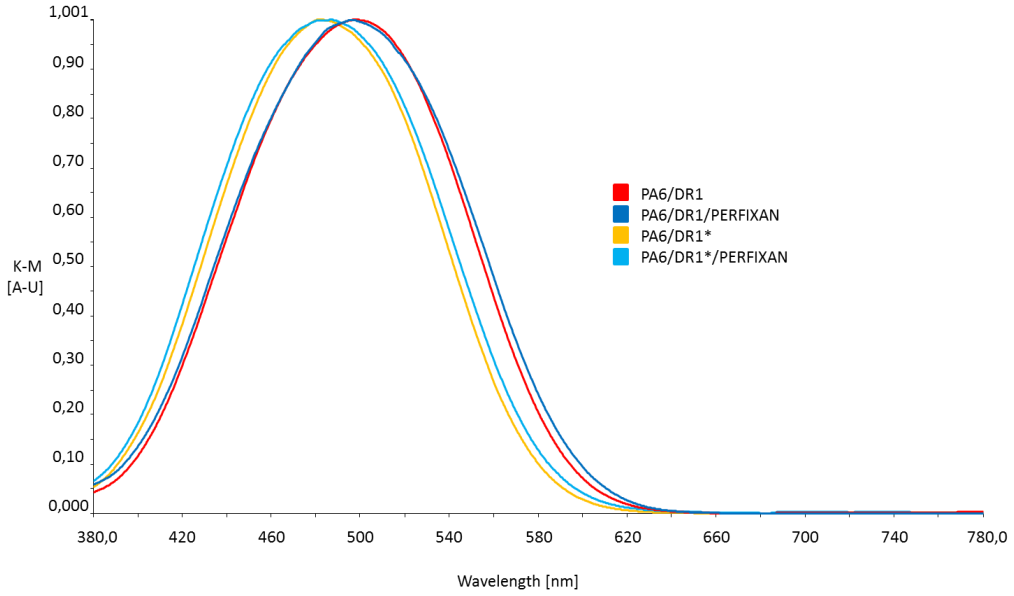


Figure 16: Normalized Kubelka-Munk spectra of PA6/DR1, PA6/DR1/PERFIXAN and PA6/DR1*, PA6/DR1*/PERFIXAN dry samples

Moreover, there is no color change between pH 2 and 12 in PA6/DR1 nanofibres and PA6/DR1/Perfixan. The same has been remarked concerning PA6/DR1* and PA6/DR1*/Perfixan.

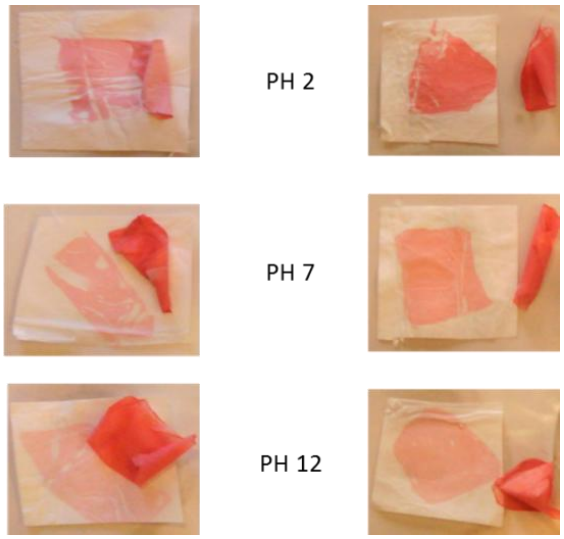


Figure 17: Introduction of PA6/DR1 (on the left) and PA6/DR1/Perfixan (on the right) samples upon colourless polymeric support

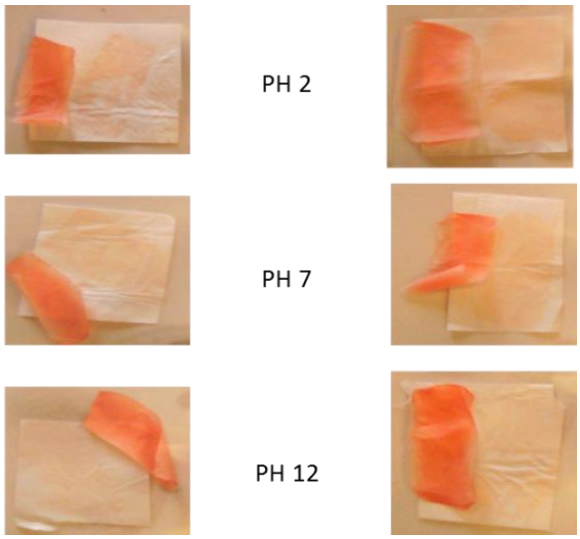


Figure 18: Introduction of PA6/DR1* (on the left) and PA6/DR1*/Perfixan (on the reight) samples upon colourless polymeric support

In figure 17 and 18 a polyamide reference is been used as it is mentioned in Chapter II to introduce the nanofibres after immersion in each pH solution. It is noted that there is dye release after reference and dye doped samples get in contact. Moreover, the colour is different between the doped as-spun samples by disperse red 1 and the doped with the functionalized dye as it is been indicated by figure 14 as well.

3. Characterization of blend nanofibers containing P(M)

This section is directly connected to the first part of this chapter. Three polymer solutions were prepared to electrospin on the multinozzle, namely PA6, PA6/DR1* and PA6/P(M-co-DR1*). The amounts of the polymers of the blend are PA6/P(M) in ratio 84/16 and dye concentration 0.64 % omf. The amount of DR1* is approximately the same in both cases. The colour change of the dye doped PA 6 and the blend constant nanofibres on the polymer solution were measured at different pH values. Finally, dye release and hydrolysis of the dye were characterized.

3.1 Comparison of PA6/DR1 and PA6/P(M-co-DR1*) and characterization of colour change*

Electrospinning was continued for several hours on the multinozzle setup as it is mentioned in the doping of polyamide 6 with disperse red 1. By analyzing the fibre dimensions and morphology at the beginning and the end of this period, the long-term stability of the process can be analyzed. The fibre diameters show no significant change so it is assumed that the electrospinning process is stable in all three cases. (Figure 19) Additionally, PA6/P(M-co-DR1*) samples have smaller average diameter which proves that combining two polymers namely blend could be advantageous and it results in finer fibres.

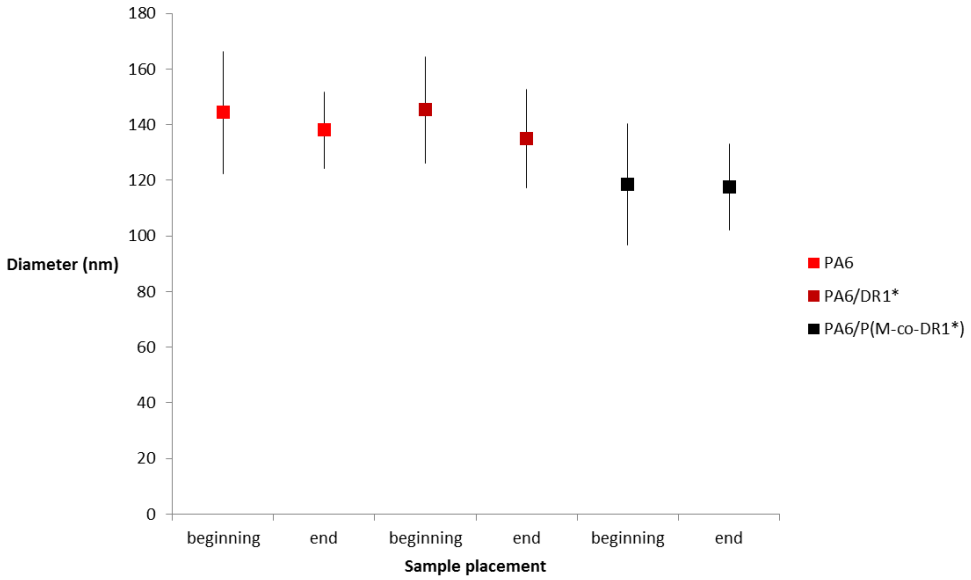


Figure 19: Fibre diameter of PA6, PA6/DR1* and PA6/P(M-co-DR1*)

The blend polymer solution compared with the PA6/DR1* solution presents a reduction in conductivity and viscosity so combination of PA6 and P(M) polymer results in lower viscosity and conductivity measurements. (Figure 20)

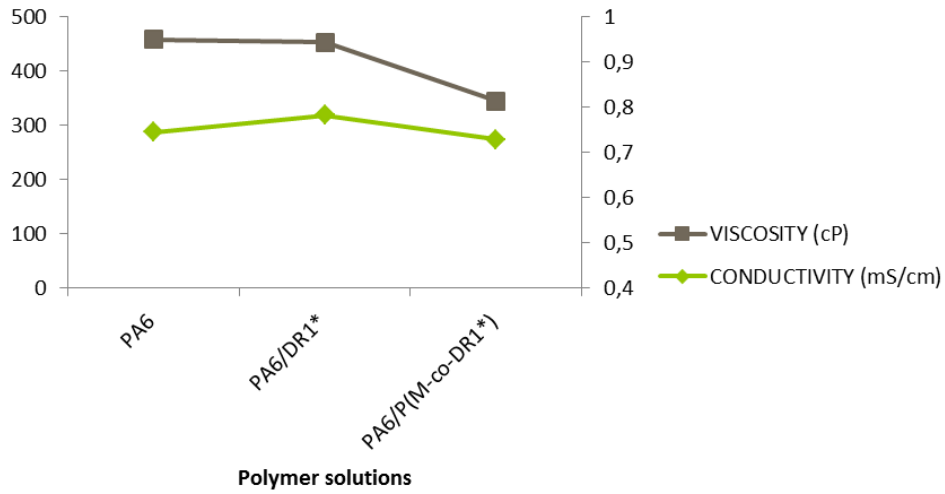


Figure 20: Comparison of viscosity and conductivity parameters

Nanofibrous samples were measured by UV-Vis spectrophotometry in dry and wet state under pH 2, 7 and 12. Kubelka-Munk graph in figure 21 indicates the difference in the colour depth of the two samples. The covalently bonded nanofibre sample has higher colour depth for the same dye concentration than PA6/DR1*.

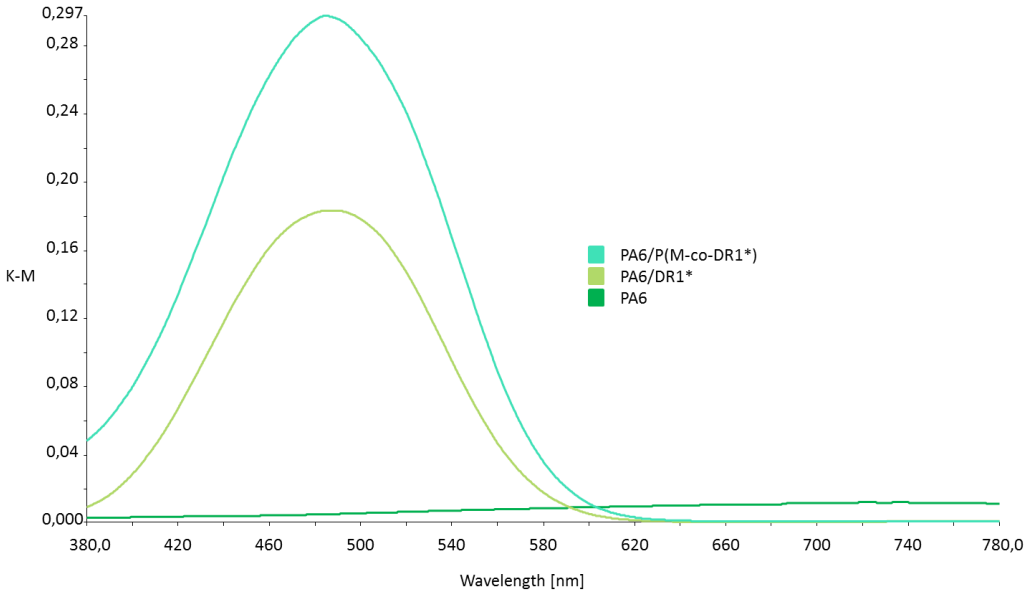


Figure 21: Comparison of the colour depth in dry state of pure, dye-doped and blend PA6

Additionally, there is no colour change between pH 2 and 12 in the dye-doped and blend nanofibres so polymerization of DR1* to P(M-co-DR1*) does not have influence on the colour. (Figure 23)

Although it is not the case in this graph, it is observed a narrower range of PA6/DR1* wet samples in neutral pH bath than PA6/P(M-co-DR1*) which means dye-doped polymer has smaller reflectance range.

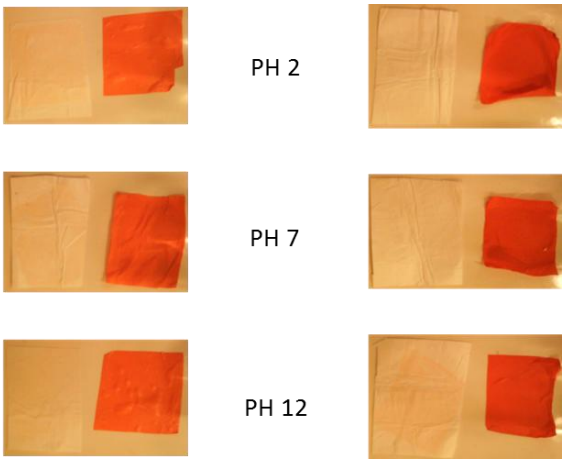


Figure 22: Introduction of PA6/DR1* (on the left) and PA6/P(M-co-DR1*) (on the right) samples upon colourless polymeric support

In figure 22 is the introduction of the samples upon the nonwoven reference samples and is clearly obvious the dye release of the covalently bonded in pH 12.

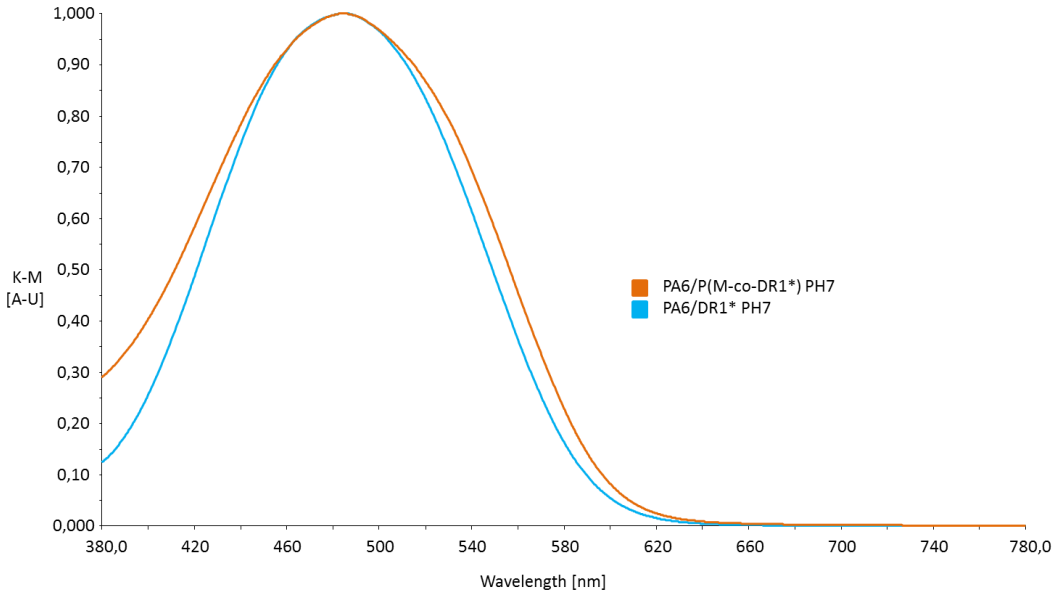


Figure 23: Normalized Kubelka-Munk graph of PA6/P(M-co-DR1*) and PA6/DR1* nanofibres, neutral pH bath

Significantly dye release was noted from the blend nanofibres at pH 12 that was mentioned (figure 22) and the diameters increases after the 24 hours immersion of PA6/DR1* and PA6/P(M-co-DR1*) samples. Figure 24 indicates absorbance spectra of pH 12 bath from both of the submerged samples.

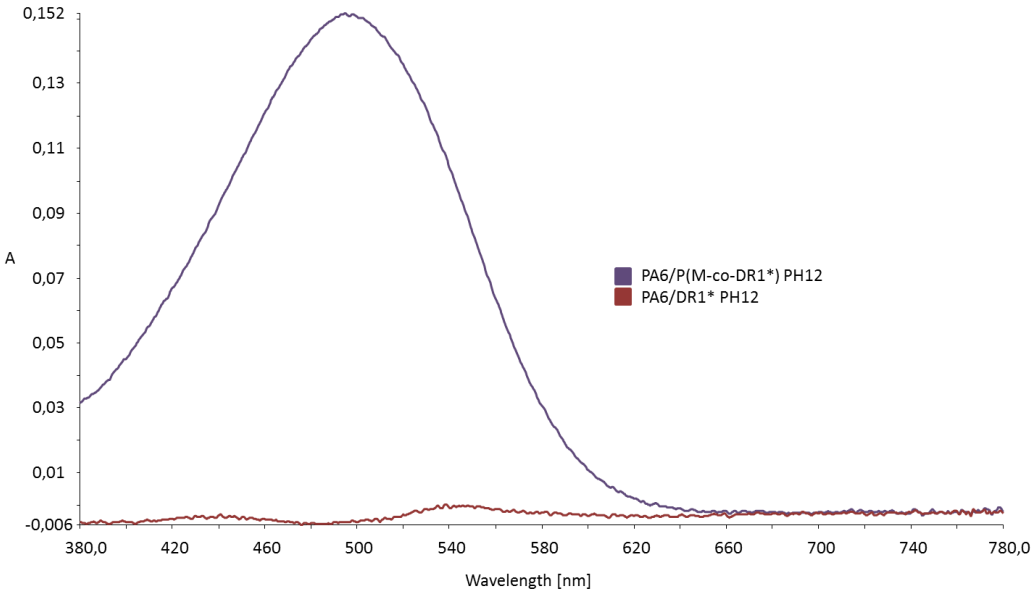


Figure 24: Dye release, pH bath of PA6/P(M-co-DR1*) after immersion in stock solution for 24 hours

In order to characterize fibre morphology after the immersion diameters were measured as well. After 24 hours immersion the diameters of the nonwoven samples are increased in every case. This could be due to the fact that polyamide 6 is a hydrophilic polymer and nanofibres have porous surface so absorption of the water is occurred and nanofibres are swelled after immersion. (Figure 25)

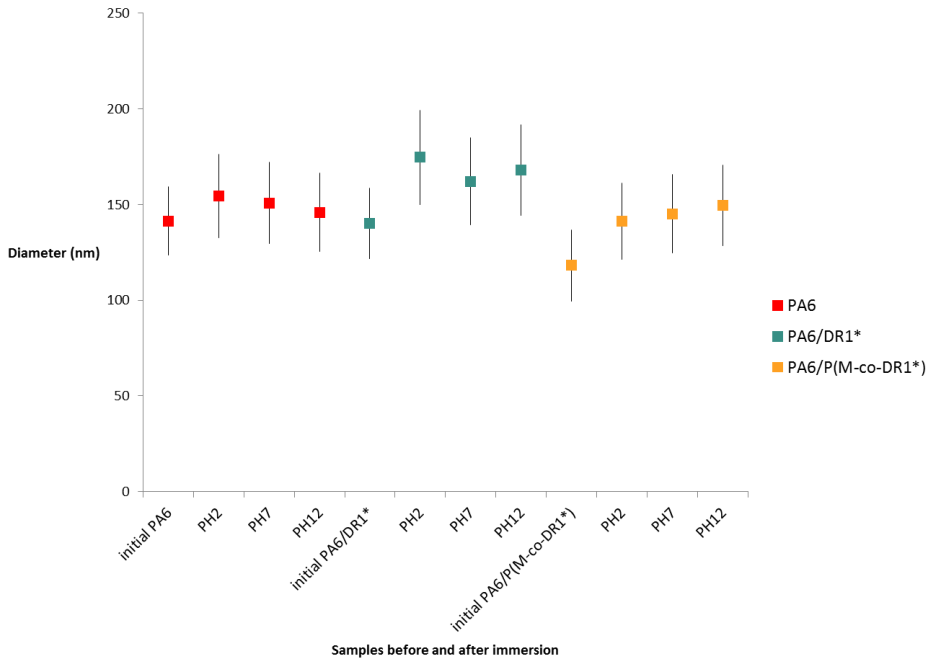


Figure 25: Diameters after immersion of the nanofibres in stock solution form 24 hours

In the Kubelka-Munk graph it was observed a colour change from each sample of PA6/DR1* in turn from pH 1.5 to 0. The largest colour depth was noted in the sample that immersed in pH 0. In the samples that were submerged between pH 1.5 and 1 there is no colour change whereas the samples in pH 0.5 have a first colour change and in pH 0 a second relocation. In conclusion, there is significant colour change between pH 0 and 1.5. The same was observed as it concerns the colour depth of PA6/P(M-co-DR1*) nanofiber samples with an exception of the sample that immersed in pH 0.5. Colour depth of the covalently bonded sample is the lowest in pH 0.5. Additional, in the normalized graph was noted a small colour change between pH 1.5 and 1 whereas between pH 1 and 0.5 there is a greater colour change. (Figure 26)

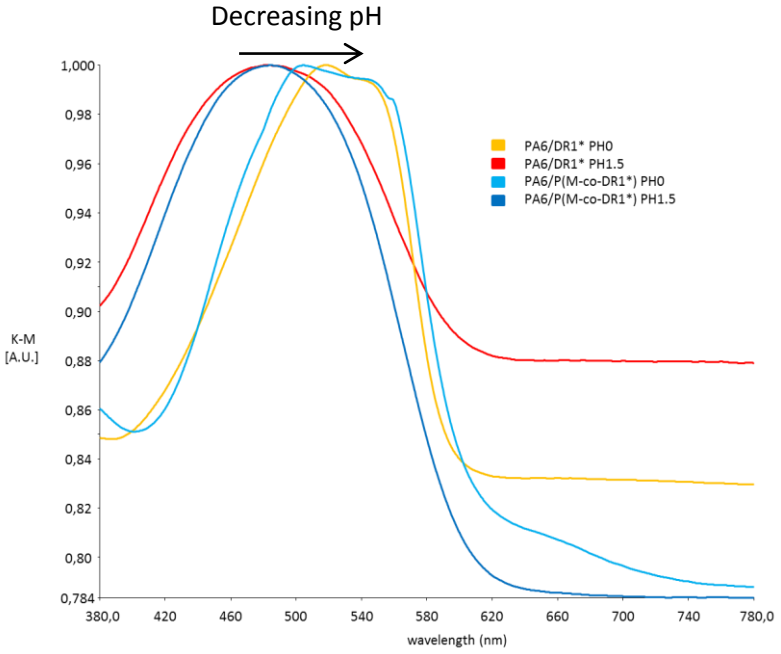


Figure 26: Comparison of dye doped DR1* and conalently bonded DR1* with P(M) in low pH values (0, 0.5, 1 and 1.5)

PH baths were prepared in 0, 0.5, 1 and 1.5 values and nanofibrous samples were submerged in them for 24 hours. Then, the absorbance of each pH bath was measured in UV-Vis spectrophotometry. PH 0 bath has the greatest absorbance compare to the others. (Figure 27 & 28) Both of the samples, dye doped and covalently bonded, that submerged in pH 0 and 0.5 baths dissolved totally during the remaining time in ambient conditions, only some droplets left was observed.

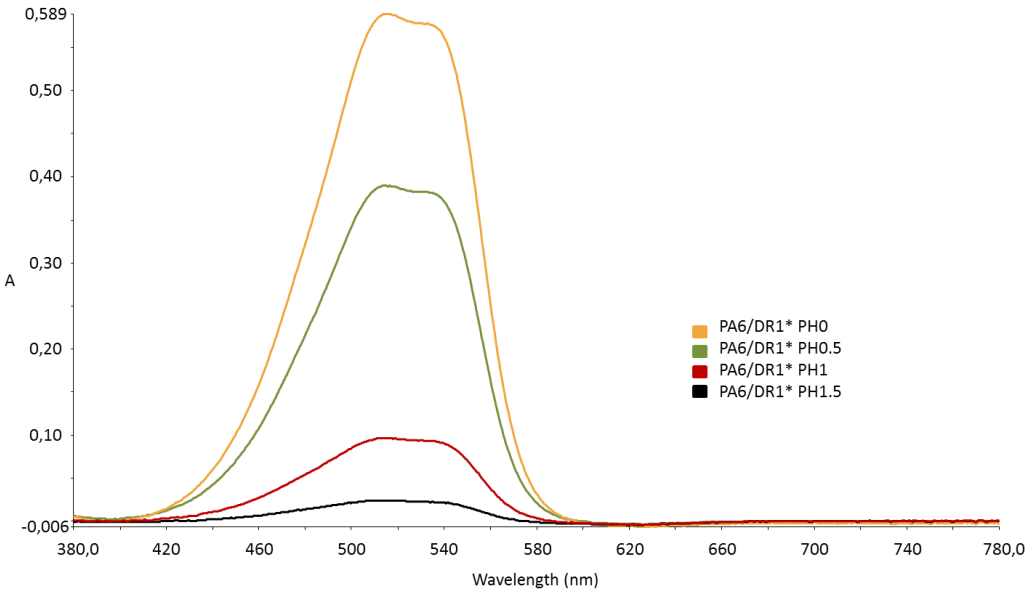


Figure 27: Absorbance graph of the pH baths of PA6/DR1* after 24 hours soaking (0, 0.5, 1 and 1.5)

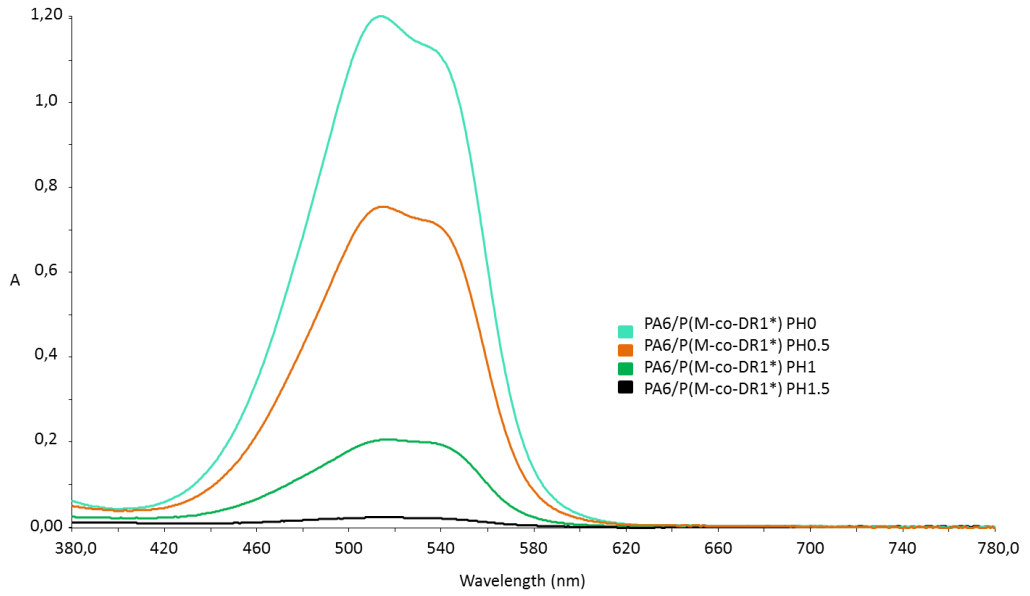


Figure 28: Absorbance graph of the pH bath of PA6/P(M-co-DR1*) after 24 hours soaking (0, 0.5, 1 and 1.5)

3.2 Dye release study and hydrolysis of PA6/DR1 and PA6/P(M-co-DR1*)*

It was observed a significant dye release of the blend nanofibres in solution at pH 12 (figure 24) so further tests were carried out such as water fastness to characterize dye release. Additionally, in the covalently bonded polymer dye release was observed at pH 12 due to hydrolysis of the functional group of the dye molecule, so pH baths (10 and 11) were fulfilled to remark in which pH value the hydrolysis of the dye starts.

3.2.1 Dye release

Color fastness tests are a method for determining the resistance of the color of textiles of all kinds and in all forms to immersion in water. Preliminary tests were done with different types of references to result the ideal one for this test. PES, wool, polyamide, cotton and nanofibre polyamide 6 references were used in this test. The references were stitched together with the PA6/DR1* and then with the PA6/P(M-co-DR1*) nanofibre sample. It is presumed that wool and polyamide references are the best to indicate dye release. Thereafter, wool and polyamide references were stitch together with each nanofibrous sample and immersed in stock solution 50 by the weight of each sample with potassium nitrate 10^{-2} mol/l and different pH baths (2, 7 and 12) for 30 min. Then placed one above each other (each separated from the next by one acrylic-resin plate) under pressure and clamped for 4 hours in the oven which has been preheated in 37 °C ± 2 °C and let dry for at least 24 hours. Afterwards, the spectra of each sample were measured in UV-Vis spectrometry and dye release was characterized.

There is no color change between the dried samples of PA6/DR1* and PA6/P(M-co-DR1*) and the treated ones. Nevertheless, dye release is observed on the wool reference in the dye-doped samples between pH 2 and 12. The greatest dye release was noted in pH 2 and 12 and in the polyamide reference dye release is noted in all three pH baths. (Figure 29 & 30) Polyamide reference is the ideal reference for this test compared to wool since wool is naturally colored and the transmitted color upon the reference substrate after water fastness tests is not sufficient.

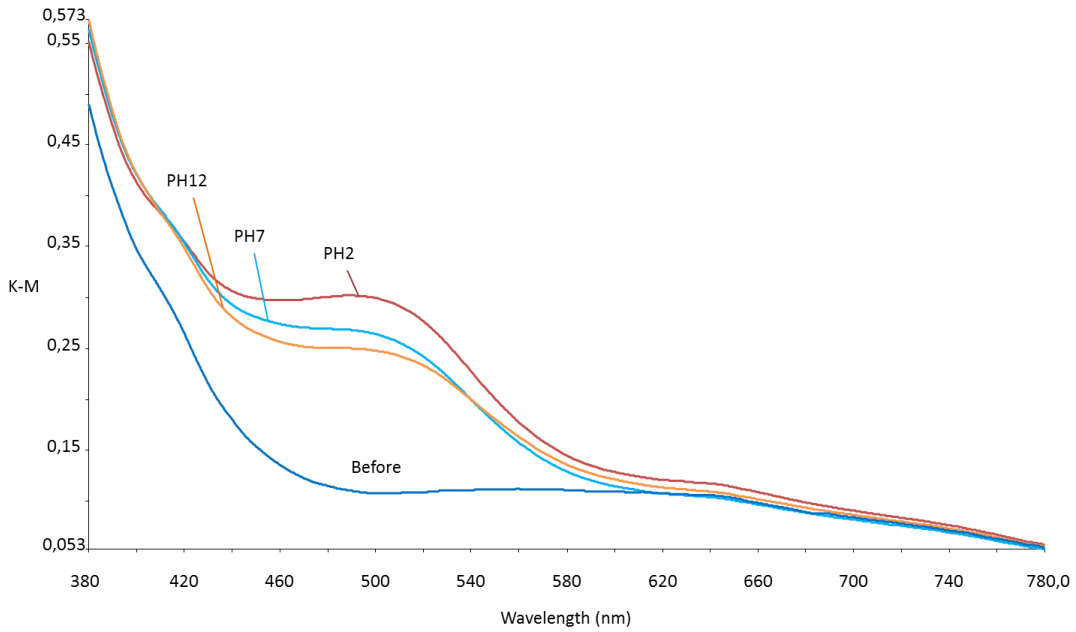


Figure 29: Kubelka-Munk spectra, wool reference in PA6/DR1*, before and after the immersion

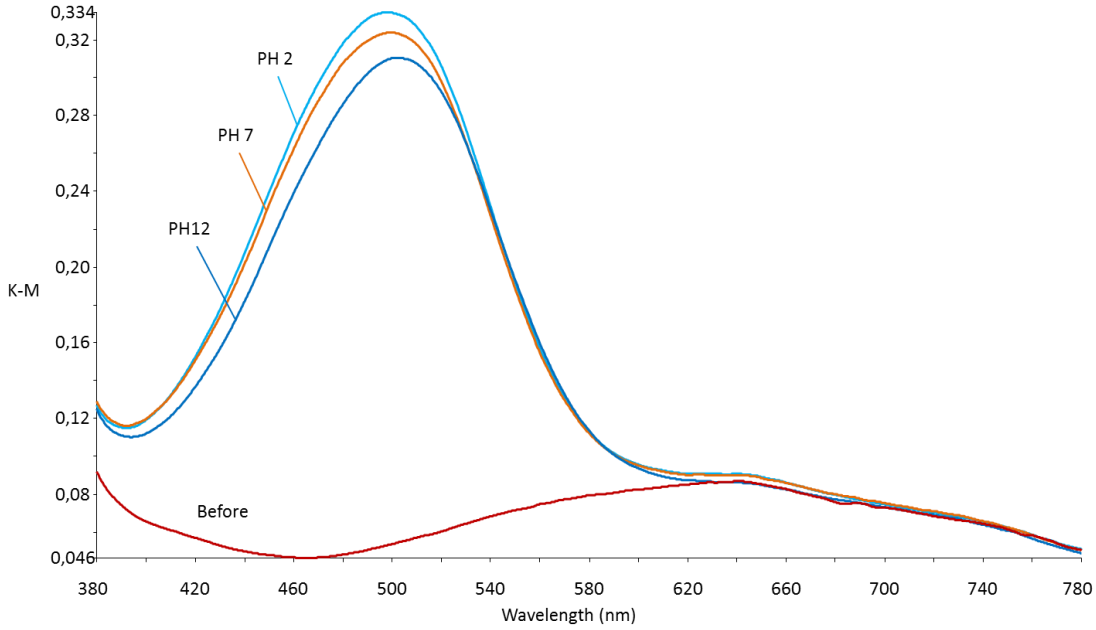


Figure 30: Kubelka-Munk spectra, polyamide reference in PA6/DR1*, before and after immersion

For the covalently bonded samples, there is dye release on wool reference between the three pH baths and the dried wool sample. In the polyamide reference it was noted dye release between the dried samples and pH 2 and 7 whereas samples that submerged in pH 12 have the greatest dye release. (Figure 31 & 32)

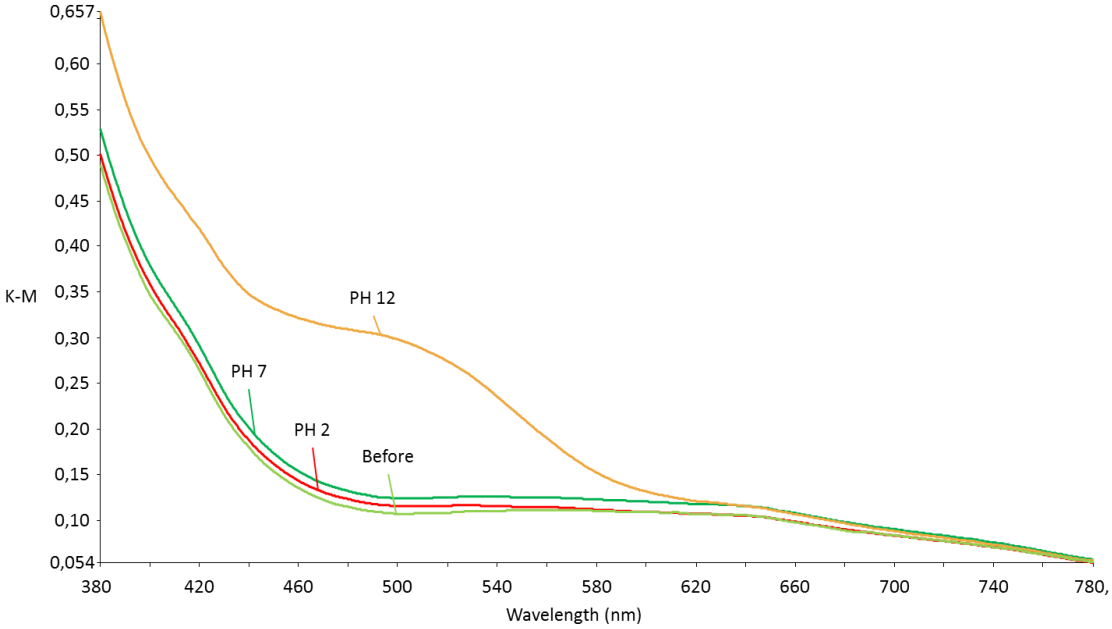


Figure 31: Kubelka-Munk spectra, wool reference in PA6/P(M-co-DR1*), after the immersion

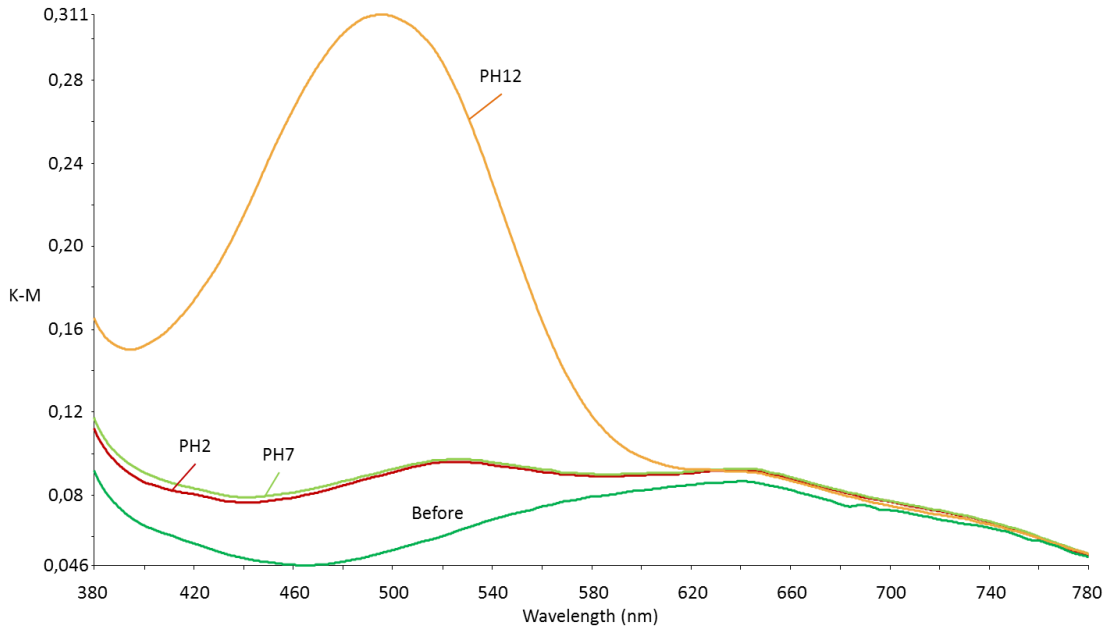


Figure 32: Kubelka-Munk spectra, polyamide reference in PA6/P(M-co-DR1*), before and after the immersion

The PA6/DR1* samples in a scale from 1 (the largest colour transfer) to 5 (no colour change) have dye release ¾ in the wool reference according to the Grey scale and 2/3 in the polyamide reference in pH 2. In pH 7 and 12 the wool reference has shown ¾ and 3 colour change respectively in comparison to the initial and 2/3 and 2 in the polyamide reference respectively. Additionally, in the PA6/P(M-co-DR1*) samples there is no colour transfer in wool reference in pH 2 and 7 whereas it is ¾ in pH 12. And the polyamide reference has 4/5 in pH 2 and 7 and 2/3 in pH 12.

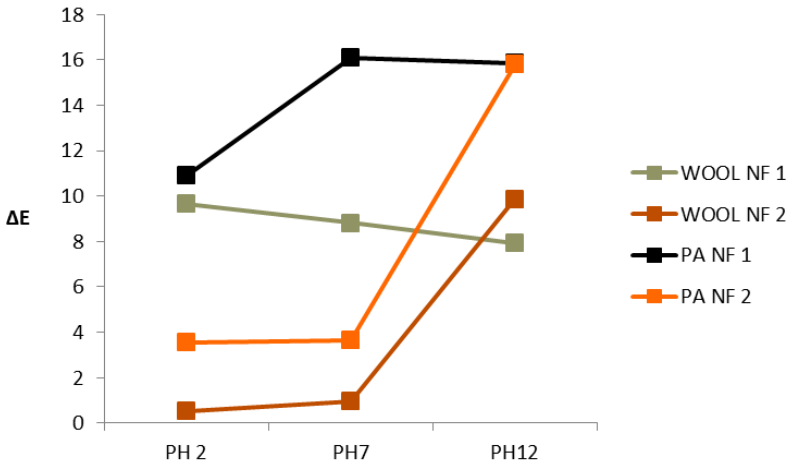


Figure 33: Dye release of nanofibre structures on the references, water fastness test.

[NF 1] indicates: PA6/DR1*

[NF 2] indicates: PA6/P(M-co-DR1*)

Colour of each pH was compared according to CIEL*a*b* colour space as indicated in Chapter I. with the other by calculating total color difference (ΔE) by the $\Delta E = [(\Delta L)^2 + (\Delta \alpha)^2 + (\Delta b)^2]^{1/2}$ equation as it is showed in figure 33. ΔL indicates brightness difference between samples, Δα is the redness difference between the samples and Δb is the yellowness between the samples. If ΔE is greater than 5 it means colour is distinguished and if value is greater than 12 then the colour belongs to completely different space. [34]

3.2.2 Hydrolysis

For this trial 5mg of each sample was soaked in 5 ml of each pH bath (10 and 11). Then, the pH baths were measured in UV-Vis spectrophotometer and the samples were remained under ambient conditions until dry.

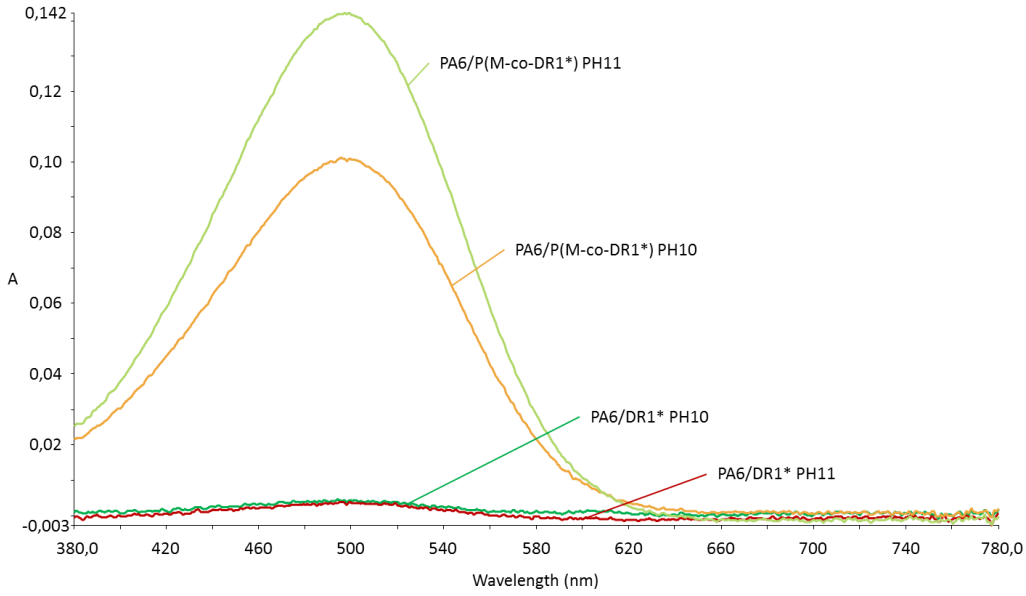


Figure 34: Absorbance spectra of 10 and 11 pH baths of PA6/DR1* and P(M-co-DR1*) samples after 24 hours soak in the pH baths

Figure 34 indicates the absorbance spectra of the pH baths of each submerged sample. In the covalently bonded sample the greater dye release is been appeared in pH 11 compared to the dye doped one.

3.3.3 Hydrolysis and dissolution of nanofibres

Polyamide 6 dissolves in low pH baths (below pH 2) as it is been indicated in figure 33 that is also the dye is leaching out of the as spun according to figure 27 & 28. Above pH 10 is been noted hydrolysis of the covalently bonded that could be explained by the fact that the functional group of the dispersant agent hydrolyses in alkali environment and the covalent bond between the back bone molecule and dye molecule breaks. (Figure 35)

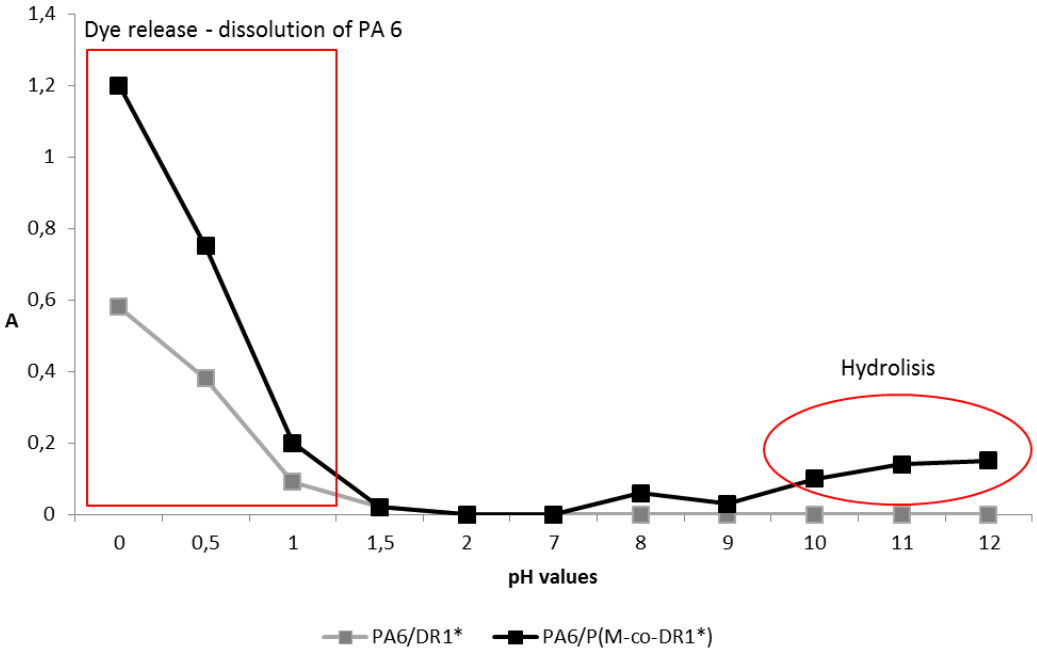


Figure 35: Absorbance spectra of PA6/DR1* and covalently bonded to the back bone after 24 hours immersion, hydrolysis and nanofibres dissolution, pH 0-12

4 Conclusions

To conclude, functionalization of disperse red 1 has small influence on the colour of the dye and the addition of complexing agent has no influence. PH tests occurred and the characterization has shown that there is no colour change between pH 2 and 12. Additionally, it was noted influence of the dye in the fibre diameter but not in the morphology. Polymerization, of DR1* to P(M-co-DR1*) does not have influence on the colour but the blend has higher colour depth for the same dye concentration. Also, in wet state the colour depth of blend is better whereas between 2 and 12 pH bath there is no colour change.

Moreover, nanofibre samples were tested in lower pH values (0, 0.5, 1 and 1.5) because disperse red 1 is not stable in low pH values. Below pH 2 is been noted colour change between pH 0 and 1.5 in the dye doped and in the covalently bonded nanofibrous sample. Thus in pH 0 the largest dye release in both cases was noted due to dissolution of the polyamide 6 in low pH baths. Hydrolysis of the covalently bonded samples it was noted as a consequence of the break of the covalent bond.

Chapter V

Electrospinning PA6 doped by Fast Green and by Bromocresol Purple

1. Electrospinning PA6, PA6/FG and PA6/FG/Perfixan

In this section the behavior of Fast Green FCF under several circumstances will be presented. Fast green (FG) is a sea green triarylmethane food dye that presents two peaks in absorbance graph owing to its colour. [62] The colour change with pH is been measured in solution and also when incorporated in PA6 nanofibres by dye-doping. The influence of the complexing agent is been characterized. Figure 36 represents the chemical structure of Fast Green.

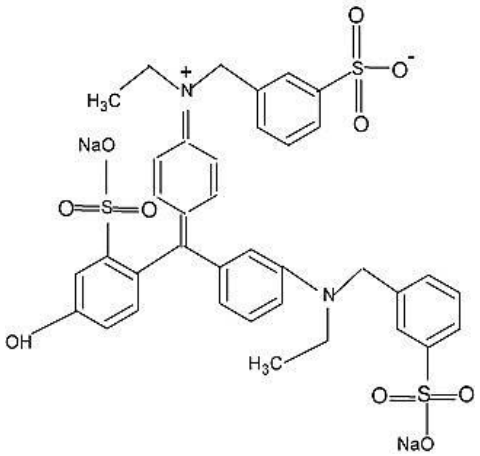


Figure 36: Chemical structure of Fast Green FCF [62]

1.1 Characterization of Fast Green in solution

Due to appearance of two peaks abovementioned when characterization of the colour occur in the nanofibres with Kubelka-Munk the research is been focused in the non-normalized graphs. Investigation of the peaks should be performed. An amount of 2 mg/l of fast green is been added to potassium nitrate stock solution (10^{-2} mol/l) (0,5 mg/l the solution of the dye and all the pH values in with a range scale from 1 to 12 and in 1 mg/l only the solution of the dye) and the hydrolysis of the dye was measured at pH 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12. The stock solution was used to ensure a constant activity coefficient during measurement. The colour change was characterized by UV-Vis spectrophotometer. (Figure 37 & 38)

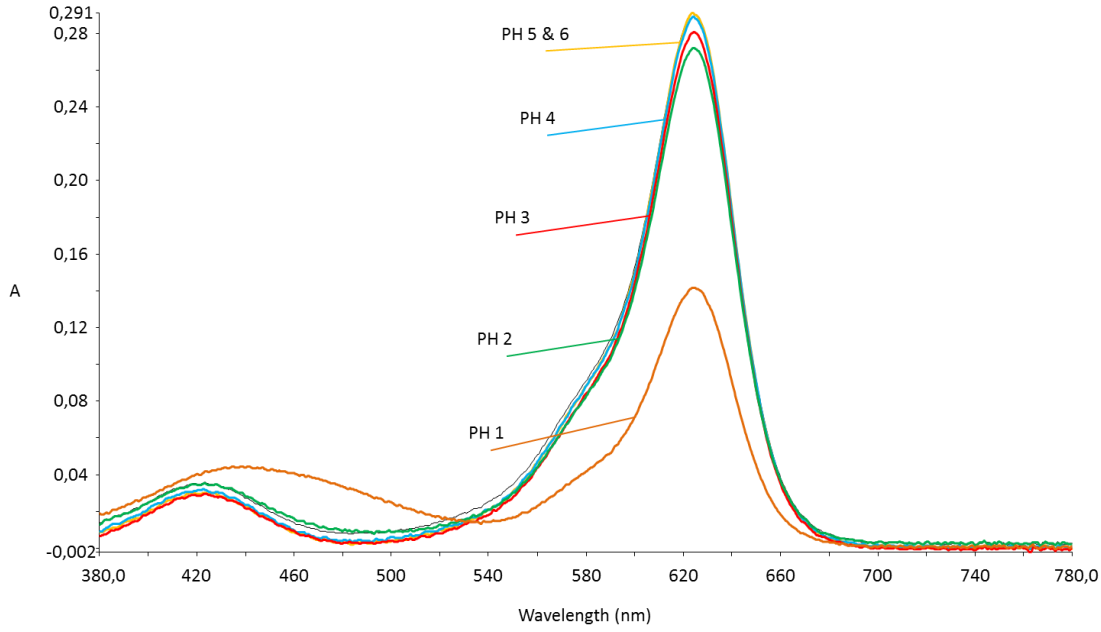


Figure 37: Absorbance spectra of Fast Green in solution-acid baths, 2mg/l

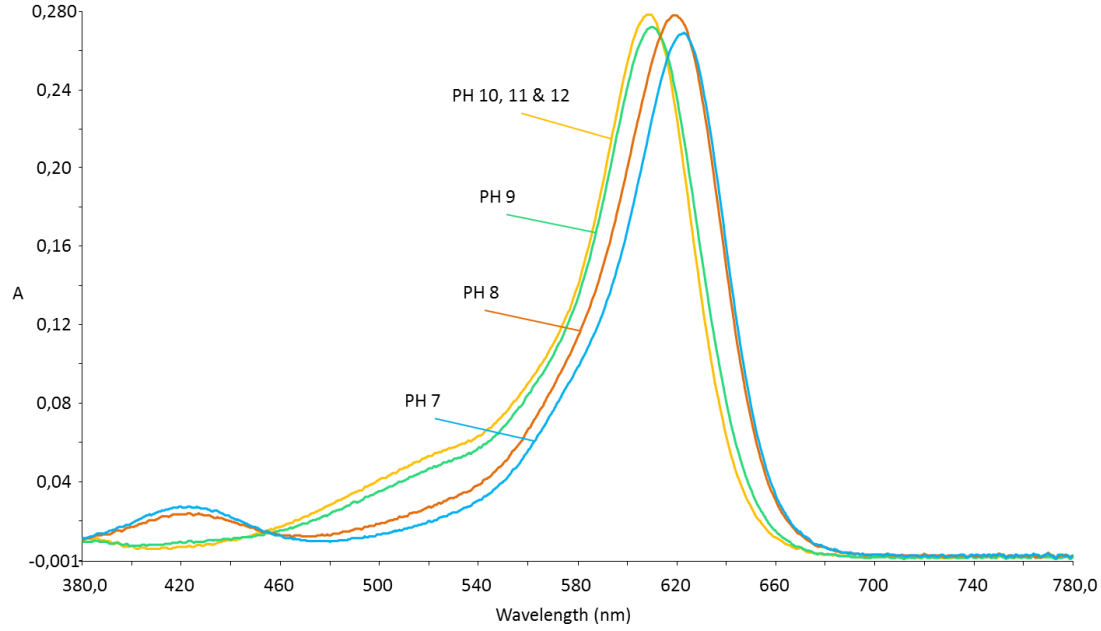


Figure 38: Absorbance spectra of Fast Green in solution-basic baths, 2mg/l

1.2 Characterization of Polyamide 6 nanofibres containing Fast Green by doping

For the electrospinning of the dye doped solutions a 16 wt% Nylon 6 was added in the solvent system acetic acid/formic acid in ratio 50/50. A dye concentration of 0.5 %omf was tested and to minimize the dye release 4% of complexing agent (Perfixan RDV) was added to the electrospinning solution. This will be compared to the results without complexing agent. Three solutions were

prepared with 40 ml of PA6 in 50/50 AA/FA, the first one is polyamide 6, to the second it is added 0.5%omf of Fast Green and to the third 0.5%omf and 4% of the complexing agent Perfixan RDV is been added.

The viscosity and conductivity of the solutions were measured to characterize each solution that had been electrospun on the multinozzle set up.

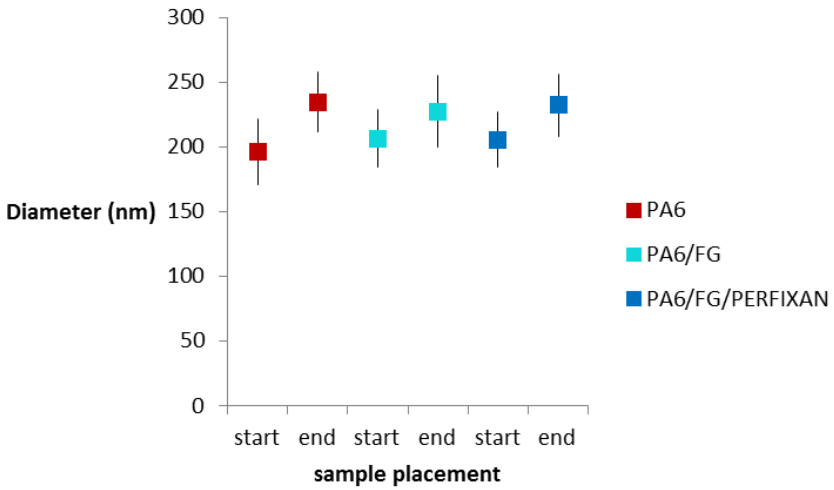


Figure 39: Nanofibrous samples diameters, sample start-end placement

Electrospinnig was continued for several hours on the multinozle setup, it is mentioned in Chapter IV, and the process is quite stable. The fibre diameters show no significant change so it is assumed that the electrospinning process is stable in all three cases (figure 39).

1.3 PH sensitivity of the PA6/FG and PA6/FG/Perfixan samples

PH baths were prepared in a pH range from 2 to 12. The samples were initially immersed for 1 min in each pH bath and then the color of the nanostructures was measured by the UV-Vis spectrophotometer. It was noted that Fast Green has great reaction time so the method was repeated and the samples now where immersed for 10 min. (figure 40)

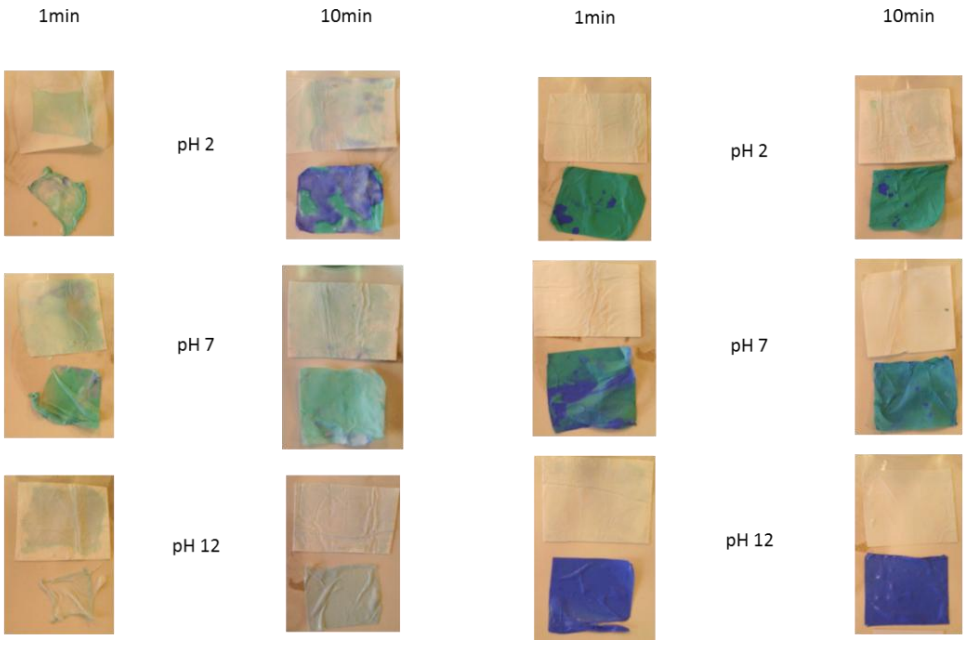


Figure 40: Introduction of PA6/BP –on the left- samples PA6/BP/Perfixan –on the right- samples

The color change was measured again after 10 minutes immersion. (Figure 41 & 42)

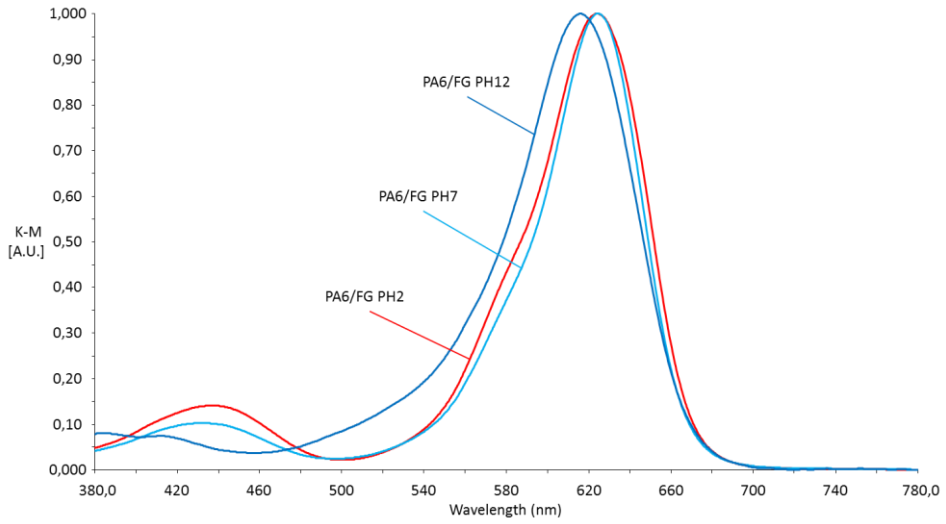


Figure 41: Normalized Kubelka-Munk graph of PA6/FG nanofibers after immersion in pH baths (10 min)

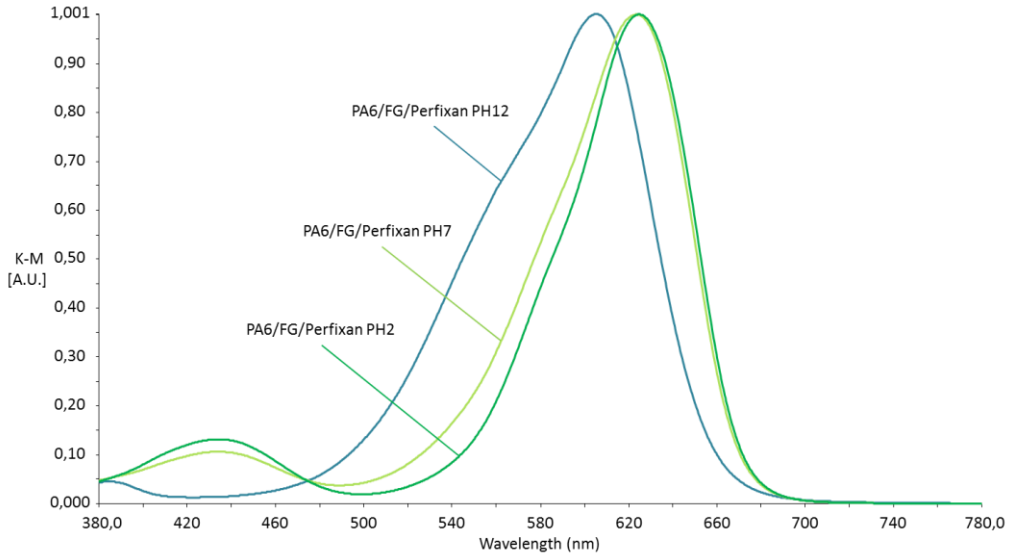


Figure 42: Normalized Kubelka-Munk graph of PA6/FG/PERFIXAN nanofibre samples after after immersion in pH baths (10 min)

In both cases with and without the use of compexing agent is observed in the one-minute immersion that there is no color change between pH 2 and 7 whereas between pH 7 and 12 there is color change. The same as for the ten-minute immersion that is between pH 2 and 7 there is no color change and between pH 7 and 12 there is color change. Moreover, it was noted influence of Perfixan on the color of the dye in the dry state and in pH 12 the color change due to Perfixan is greater than the PA6/FG samples. (Figures 41, 42 & 43)

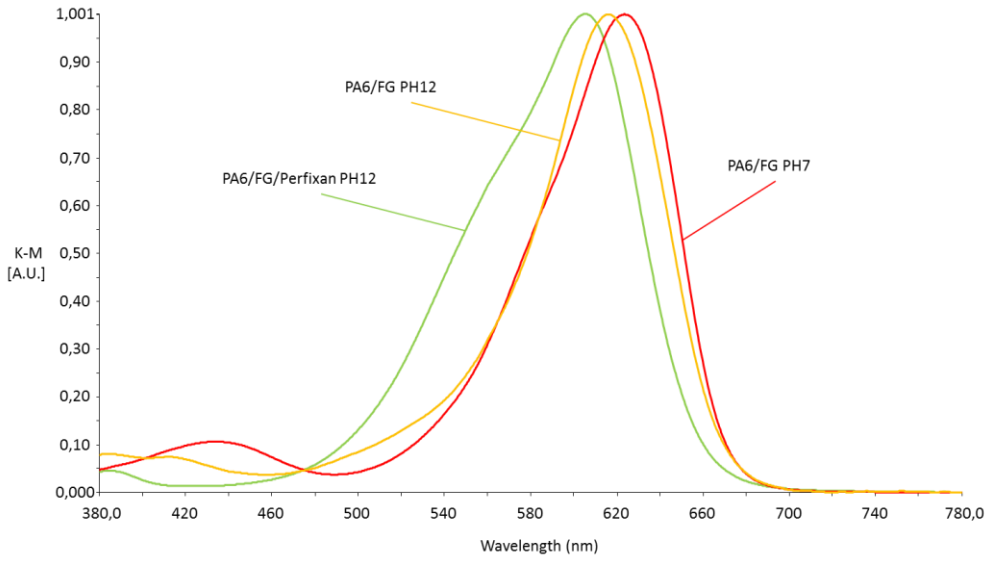


Figure 43: Normalized Kubelka-Munk graph, compare PA6/FG with PA6/FG/PERFIXAN nanofibre samples after immersion in pH baths (10 min)

Additional tests were done on PA6/FG/PERFIXAN specimens in pH range 3, 4, 5, 6, 8, 9, 10 and 11. The samples is been placed upon polyamide as spun reference, dye release is noted. (figure 44)

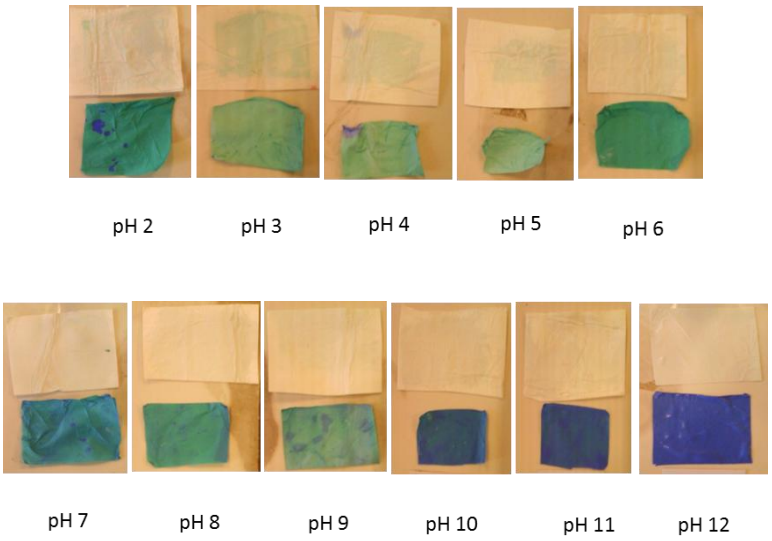


Figure 44: PA6/FG/PERFIXAN specimens upon polyamide as spun references, 10 min immersion.

1.4 Testing dye-leaching of the PA6 samples electrospun on the multinozzle

Initially, three samples were prepared for this performance of each constant nanofibre PA6/FG and PA6/FG/Perfixan weighing 5mg and the spectra of the pH baths from 24 hours soaked samples was measured in each case.

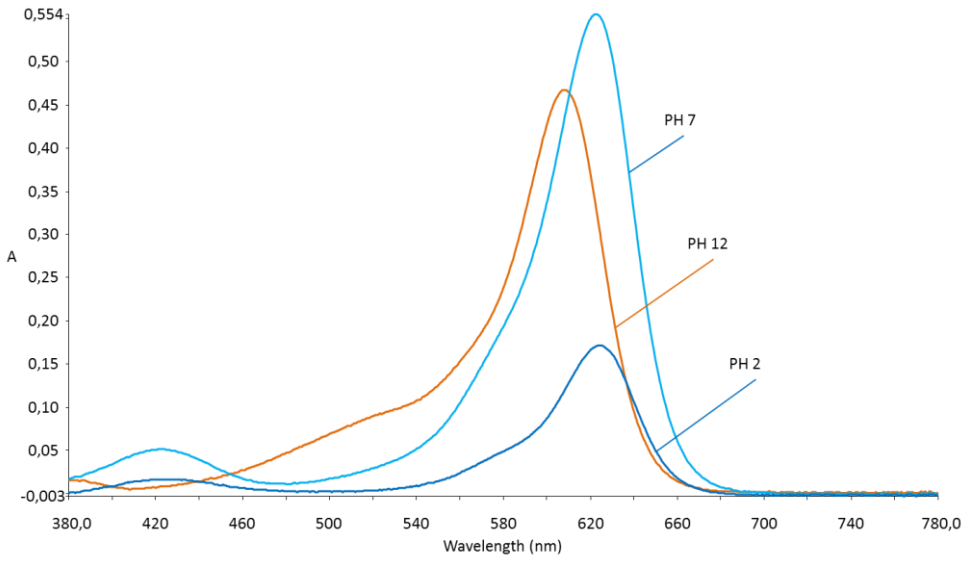


Figure 45: Absorbance spectra of Polyamide-6 doped by Fast Green, 24 hours immersion

The dye leaching of the PA6/FG samples is the highest in pH 7. There is a color change in the dye leaching baths between pH 12 and 7 and there is no color change between pH 7 and 2. (Figure 45)

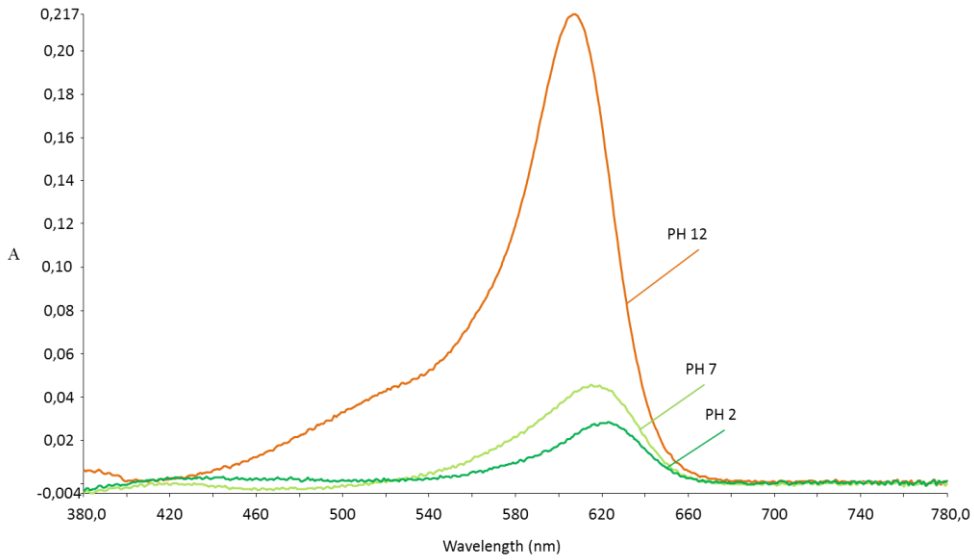


Figure 46: Absorbance spectra of Polyamide-6 doped by Perfixan and doped by Fast Green, 24 hours immersion

Dye release increased in pH 12 whereas in pH 2 and 7 a very small dye release is observed. Moreover, the color changed between pH 2 and 12. (Figure 46)

The dye release is increased in the dye doped specimens compare to the ones doped by Perfixan and the dye which demonstrates that the use of a complexing agent is indispensable in order to fulfill a successful remaining color.

Dye release increased between pH 2 and 12. Specimens doped by the complexing agent presents much less dye release compare to the dye doped nanofibrous samples, and it could be by the elimination of polyvalent metal ions that caused by the complexing agent. [65]

Table 4: Dye release of treated samples doped by Fast Green and by the complexing agent at pH 2, 7 and 12

	Dye release at pH 2 (% omf)	**Dye release at pH 7 (% omf)**	**Dye release at pH 12 (% omf)**
PA6/FG	26	75	90
PA6/FG/Perfixan	3	5.5	41

2. Electrospinning of PA6, PA6/BP and PA6/BP/Perfixan

Initially dye characterization will be done in order to determine extinction coefficient of bromocresol purple and better understanding of the color of the dye in pH range from 1 to 12. Later the dye release of the as-spun nonwoven will be described in different pH. The main tests will be done on the mononozle and the remaining time of each sample will be counted in order to succeed the same thickness in each sample (8min). The chemical structure of 0.04wt % bromocresol purple in H_2O is indicated in figure 3 (Chapter IV – Preliminary tests on PA6/BP).

2.1 Bromocresol purple characterization

Dye characterization is been carried out in stock solution containing soft water and 10^{-2} M potasium nitrate from pH 1 to 12. Bromocresol purple changes colour between pH 5-7 and turns from yellow to purple and then to blue.

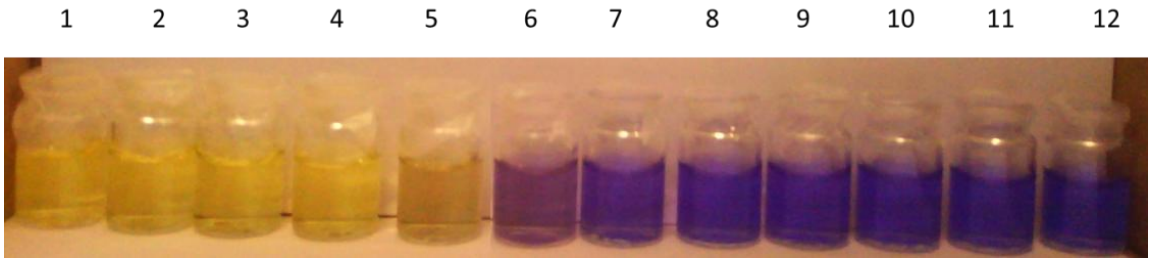


Figure 47: Colour change of bromocresol purple in pH solution 1-12 with a concentration 7.5mg/l

Bromocresol purple has two peaks, the acidic one in 433 nm wavelength that is a mono anionic molecule and the alkalic in 590 nm wavelength that is di-anionic molecule (figure 48). [5] In low pH the spectra shifts to the left and a yellowish color appears whereas in high pH the color changes from yellow to blue.

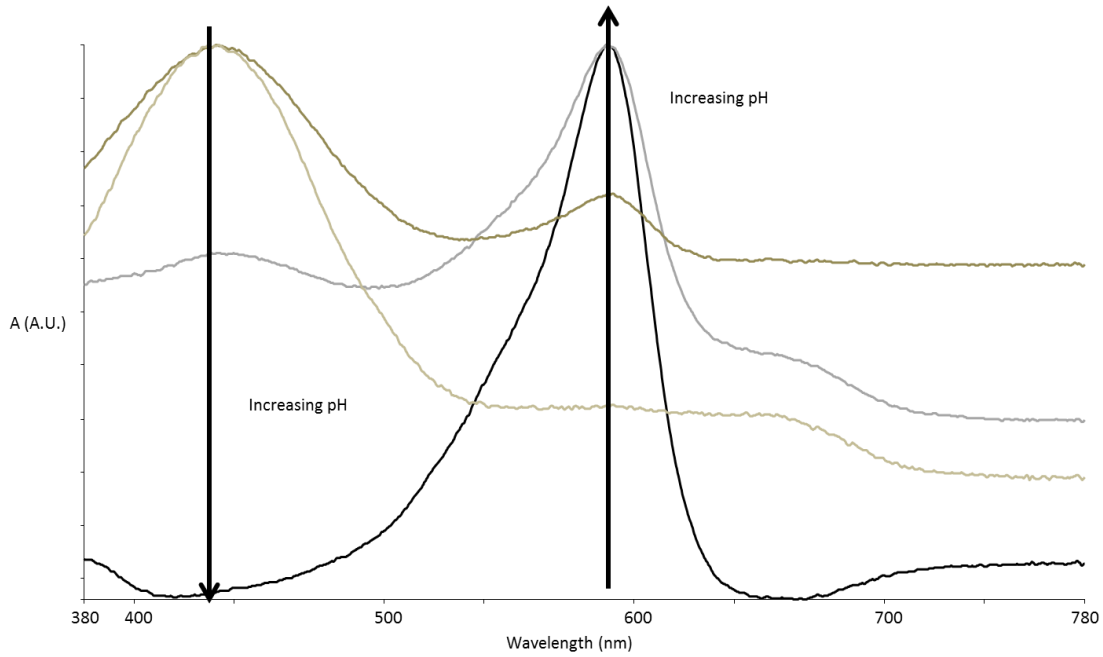


Figure 48: Acidic and alkali peak of bromocresol purple in solution, absorbance range 380nm – 780nm.

2.2 Characterization of the as spun PA6, PA6/BP and PA6/BP/Perfixan

Three polymer solutions were prepared with PA6 16 wt% in 50/50 AA/FA. The first is polyamide 6 with acetic acid and formic acid, to the second one it was added 0,5% omf bromocresol purple and to the third one it was added the same amount of dye and 4% omf of the complexing agent. The ambient humidity and temperature were 28,2 % and 20,3 °C respectively during the electrospinning process and the parameters were kept constantly (speed = 2ml/h, voltage = 23 kV and TCD = 6cm).

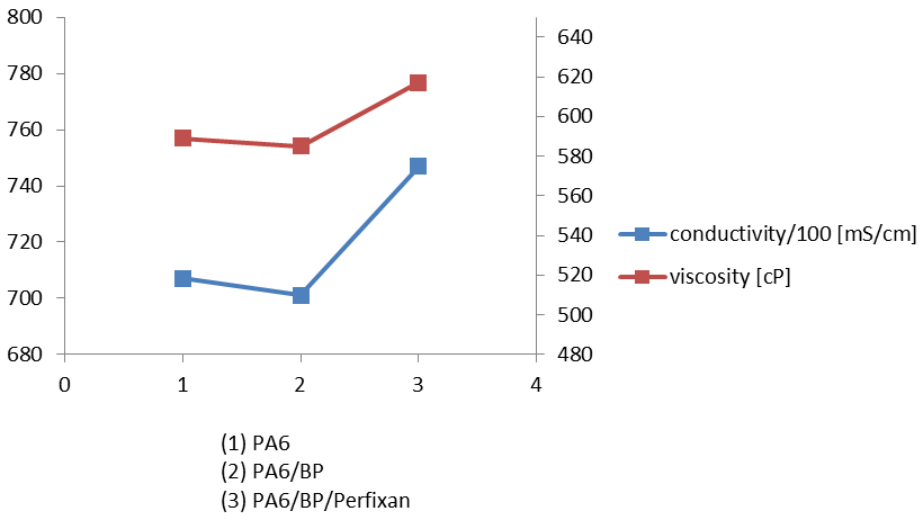


Figure 49: Characterization of the polymer solutions; PA6, PA6/BP and PA6/BP/PERFIXAN

Conductivity and viscosity increases when perfixan has been added in the solution. The dye has no influence in the polymer solution; the complexing agent is a charged molecule and influences the solution. (figure 49)

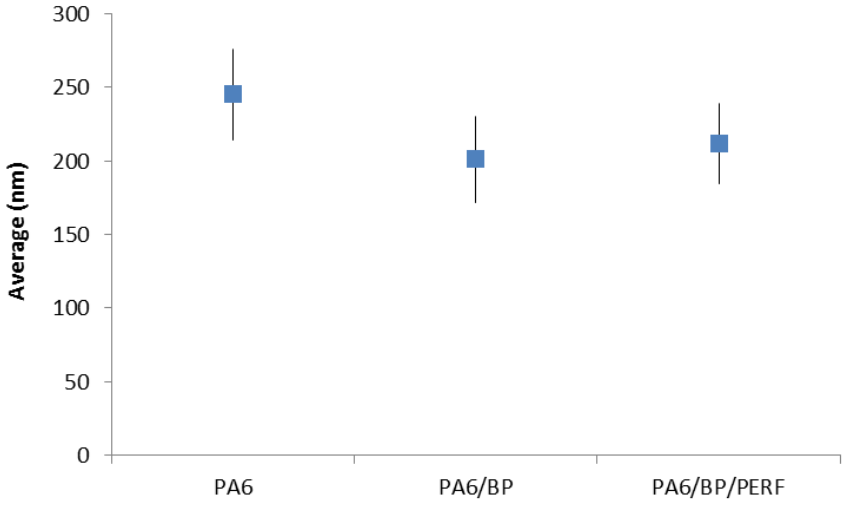


Figure 50: Diameters of the as spun; pure PA6, PA6/BP and PA6/BP/PERFIXAN

The dye influences fibre morphology, since diameters decreasing with the addition of bromocresol purple (figure 50) and perfixan has no influence in the fibre diameter.

2.3 Dye leaching tests on PA6/BP and PA6/BP/Perfixan

In order to characterize the dye leaching of the doped samples with bromocresol purple and the doped samples with the complexing agent and the dye, tests were held between pH 2 and 12.

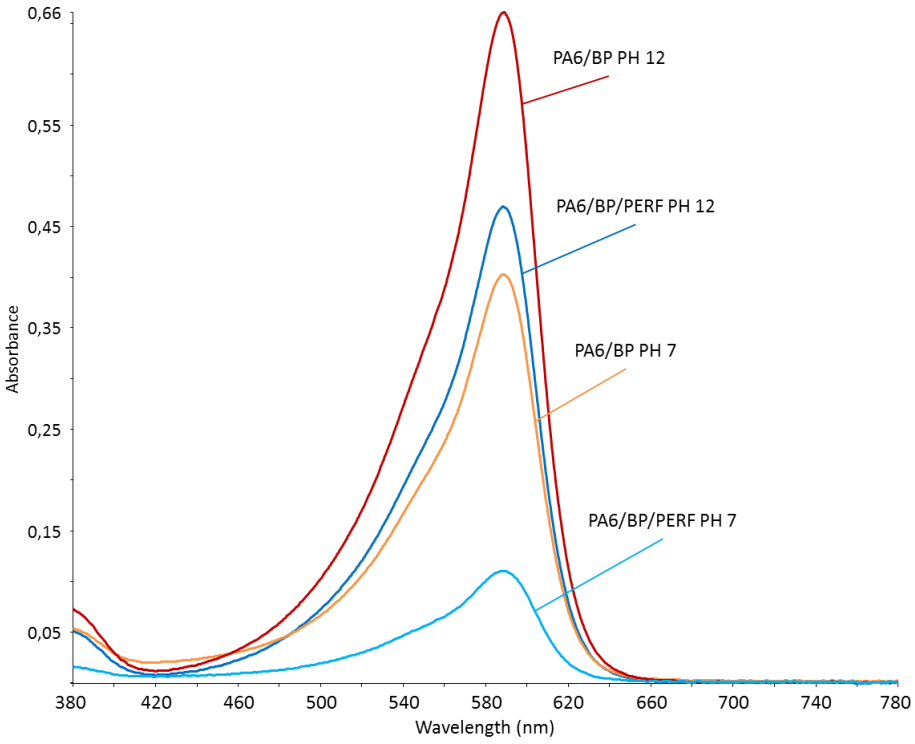


Figure 51: Absorbance of PA6/BP and PA6/BP/PERF after 24 hours immersion

It is observed that the nanofibrous samples without perfixan appear greater dye release than the samples with the complexing agent. Also, the dye release increases as the pH increases (Figure 51).

3. Conclusions

Fast green and bromocresol purple is been characterized in solution and when incorporated with the nanofibres. Fast green has two absorption maximum in solution and color change has been noted when fast green is incorporated with the nanofibres. The complexing agent minimizes the leaching of the dye in low pH, as pH increases release of the dye increases as well. In conclusion, fast green spectrum is very difficult to characterize; the dye in solution performs two peaks as above whereas in sample presents one peak that is very close to the alkalic peak of the dye in solution.

It has been noted colour change in the nonwovens doped by bromocresol purple. The addition of perfixan has influence in the morphology as well. Conductivity and viscosity increases and leaching of the dye minimizes. The colour of the PA6/BP/PERF as spun is deeper due to perfixan in compare to the dye doped nonwovens.

Chapter VI

Conclusions and future work

In this work polyamide 6 doped by colorants has been studied, the influence of Perfixan RDV has been analyzed and the blend PA6/P(M) covalently bonded with the functional group of the disperse red 1 has been deliberated on.

Disperse red 1 could be used as a halochromic substance since the colour changes. Although reversibility of the colour could characterize this dye the skin pH is around 6 and the colour change occurs below pH 2; therefore the range of applications in wound dressings is limited. Blend of PA6/P(M) with the functional dye covalently bonded to the back bone eliminates dye release which is desirable in this case, therefore use of the blend as a wound dressing is not excluded.

Bromocresol purple could be used as a halochromic substance since colour alters and it could be used as a wound dressing as well since pH range is identified to the skin pH but still the range is very narrow. In this system dye release is the case, although leaching of the dye decreases with the addition of perfixan optimization of the process is still the object.

Fast green changes colour but the range is quite narrow and not very clear. Since colour is a visual perceptual stimuli it is important the colour change to be sufficient so that the healing process of a burn wound could be monitored. Similarly to polyamide 6 / bromocresol purple system, dye release is limited with the addition of perfixan nevertheless sufficient colour change is the case.

Halochromic substances are been established in this work. Moreover, distinct colour change is meaningful and leaching of the dye is still a matter of case since a good wound dressing should have excellent biocompatibility. A polymer blend system is been demonstrated and the dye release could still be optimized.

APPENDIX I

1. *Influence of the humidity on the polyamide 6 diameters*

Influence of the humidity on the diameters of the polyamide nanofibres; data is been selected in different electrospinning days and analyzed. Humidity has a plasticizer effect on the diameters, when humidity increases diameters decrease which is the case for a good wound dressing since absorptivity is crucial. (figure 52)

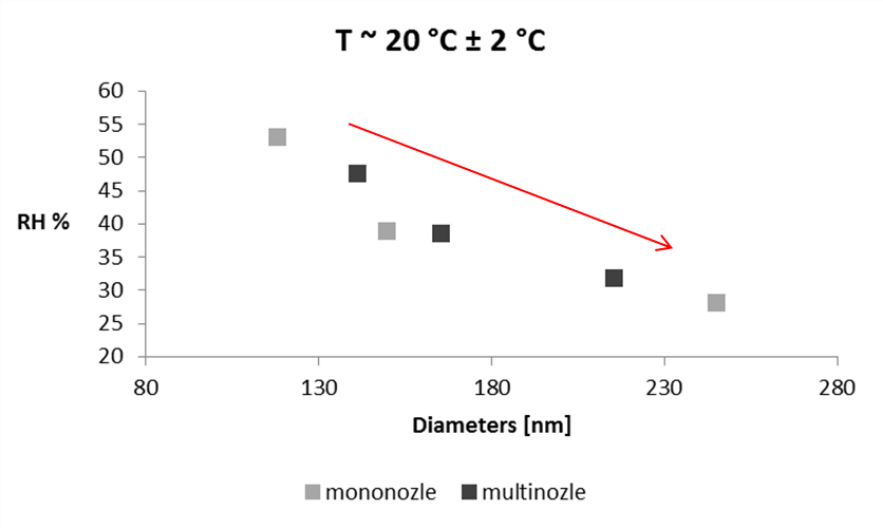
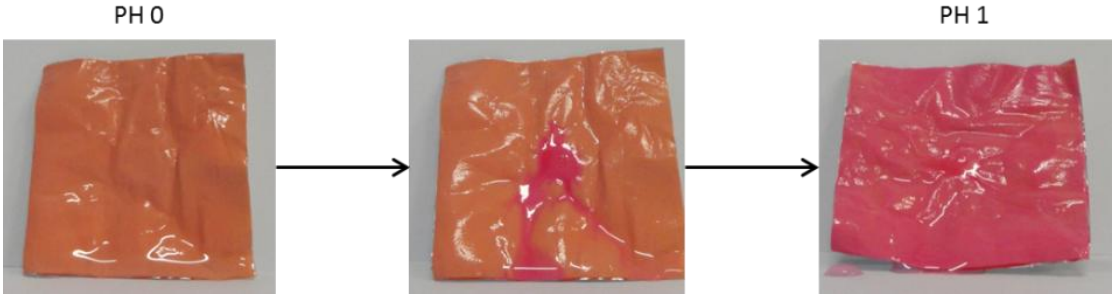


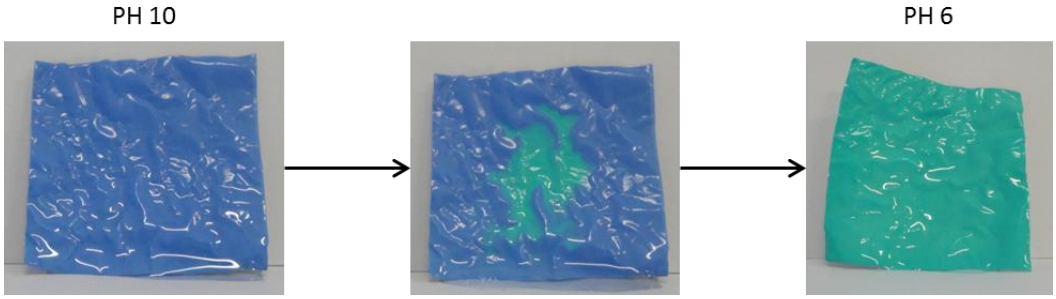
Figure 52: Diameters of polyamide 6 as spun in relation to air humidity, SEM images, each measurement is from different day of electrospinning. Mononozle – Multinozle

2. *Influence of the pH in the colour of polyamide 6 specimens.*

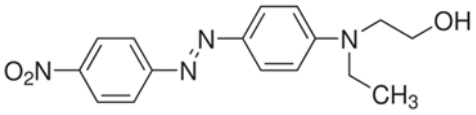
Polyamide 6 as spun doped by disperse red 1. The first sample in the line is in pH 0, then pH 0 with a pH 1 droplet and the last one pH 1.



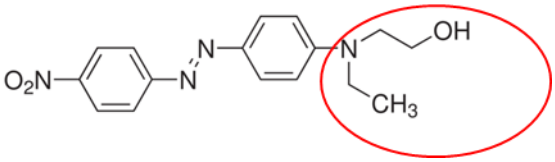
Polyamide 6 as spun doped by Fast Green (FCF). The initial specimen is in pH 10, then in pH 10 with a pH 6 droplet and the last one in pH 6.



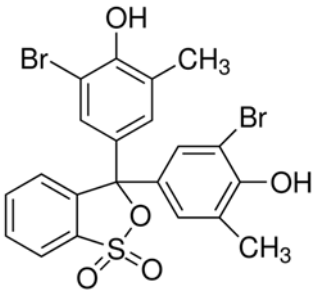
APPENDIX II – COLOURANTS MOLECULE STRUCTURE



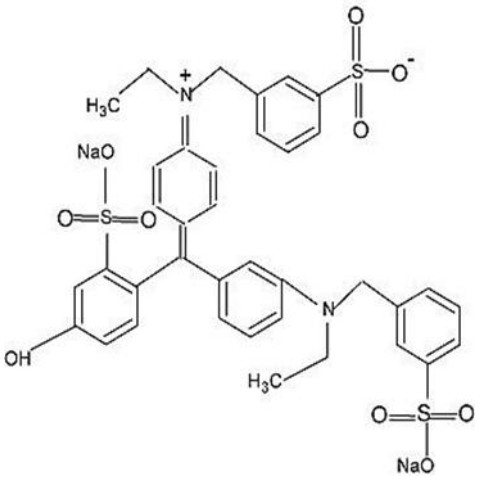
DISPERSE RED 1



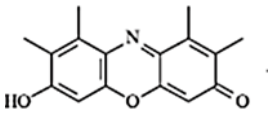
DISPERSE RED 1*



BROMOCRESOL PURPLE



FAST GREEN



LITMUS

REFERENCES

[1] Iline Steyaert (2010-2011) Hydrid Electrospun Structures for pH- Sensitive Wound Dressings, *Unpublished master's thesis*. Gent University, Department of Textiles, Belgium

[2] Peters Shakerpeare (2001) Burn wood healing and skin substitutes. *Burns, 27*, pp. 517-522

[3] Jon Stanger, Nick Tucker and Mark Staiger (2005) Electrospinning, *Smithers Rapra Technology*. Volume 16, Number 10

[4] Lien Van der Schueren, Thierry De Meyer, Illine Steyaert, Ozgur Ceylan, Karen Hemelsoet, Veronique Van Speybroek, Karen De Clerck (2012) *Polycaprolactone and polycaprolactone/chitosan nanofibres functionalized with the pH-sensitive dye nitrazine yellow.* Carbohydrate polymers 91, pp. 284-293

[5] Lien Van der Schueren, Tybo Mollet, Ozgur Ceylan, Karen De Clerck (2010) *The development of polyamide 6.6 nanofibres with pH-sensitive functionalize by Electrospinning.* European Polymer Journal 46, pp. 2229-2239

[6] Dan Tao, Qufu Wei, Yibing Cai, Qiuxiang Xu, Lingyan Sun (2008) *Functionalization of polyamide 6 nanofibers by electroless deposition of copper.* European J. Coat. Technol. Res., 5 (3), pp. 399–403

[7] Lien Van der Schueren, Karen Hemelsoet, Veronique Van Speybroek, Ozgur Ceylan, Karen De Clerck (2012) *The influence of polyamide matrix on the halochromic behavior of pH-sensitive azo dye Nitrazine Yellow.* Dyes and pigments 94, pp. 443-451

[8] Arthur D. Broadbent (2001) Basic Principles of Textile Coloration. *Society of Dyers and Colourists*

[9] Steven S. Zumdahl (2009) *Chemical Principles*. New York: Houghton Mifflin Company, 6th edition, pp. 319–324. http://www.google.be/books?hl=el&lr=&id=hsuV9JTGaP8C&oi=fnd&pg=PR3&dq=Steven+S.+Zumdahl+%282009%29.+Chemical+Principles&ots=76dMKsh0on&sig=iMIfWz68P1ADSfyATDKhdK2mNiY&redir_esc=y#v=onepage&q=Steven%20S.%20Zumdahl%20%282009%29.%20Chemical%20Principles&f=false

[10] Lynn A. Melton, C. W. Lipp, R. W. Spradling & K. A. Paulson (2002) *Chemical Engineering Communications.* Volume 189, Issue 3, pages 322-338

[11] Chaoqun Zhang, Yapeng Li, Wei Wang, Naiqian Zhan, Ning Xiao, Shuai Wang, Yaoxian, Qingbiao Yang (2011) A novel two-nozzle electrospinning process for preparing microfiber reinforced pH-sensitive nano-membrane with enhanced mechanical property. European Volume 47, Issue 12, Pages 2228–2233

[12] *Resources:* http://textilelearner.blogspot.be/2012/01/nanofibers-nanofibers-in-nonwoven.html Thursday 15th Novemver 2012

[13] Stan Monstrey, Henk Hoeksema, Jos Verbelen, Ali Pirayesh, Phillip Blondeel (2008) Assessment of burn depth and burn wound healing potential. *Burns*, Volume 34, Issue 6, pp. 761–769

[14] Lars Alexander Schneider · Andreas Korber, Stephan Grabbe · Joachim Dissemond (2007) Influence of pH on wound-healing: a new perspective for wound-therapy?. *Arch Dermatol Res* 298:413–420

[15] Ji-Huan He, Yong Liu, Lu-Feng Mo, Yu-Qin Wan and Lan Xu (2008) Electrospun nanofibres and their applications. Smithers Rapra Update

[16] Seeram Ramakrishna, Kazutoshi Fujihara, Wee-Eong Teo, Teik-Cheng Lim, Zuwei Ma (2005) Electrospinning and Nanofibers. National University of Singapore, World Scientific Publishing

[17] Chidchanok Mit-uppatham, Manit Nithitanakul, Pitt Supaphol (2004) Ultrafine electrospun polyamide-6 nanofibres: effect of solution conditions on morphology and average fiber diameter. *Macromolecular chemistry and physics*, pp. 2327-2338

[18] Pitt Supaphol Chidchanok, Mit-uppatham, Manit Nithitanakul (2005) Ultrafine electrospun polyamide-6 nanofibres: effect of emmiting electrode polarity on morphology and average fibre diameter. *Journal of polymer science*, pp. 3699-3712

[19] Pirjo Heikkila, Ali Harlin (2008) Parameter study of electrospinning polyamide-6. European polymer journal, pp. 3067-3079

[20] *Resources*: Medical Encyclopedia, Medline Plus http://www.nlm.nih.gov/medlineplus/burns.html Tuesday 13th November 2012

[21] Fwu-Long Mi, Yu-Bey Wu, Shin-Shing Shyu, An-Chong Chao, Juin-Yih Lai, Chia-Ching Su (2003) Asymmetric chitosan membranes prepared by dry/wet phase separation: a new type of wound dressing for controlled antibacterial release. *Journal of Membrane Science* 212, pp. 237-254

[22] Lien Van der Scueren and Karen De Clerck (2008) Colouration and application of pH-sensitive dyes on textile materials, Society of dyers and colorists, *Coloration technology*, 128, pp.82-90

[23] Mazeyar Parvinzadeh (2009) A new approach to improve dyeability of nylon-6 fibre using a subtilisin enzyme, Society of dyers and colorists, *Coloration technology,* 125, pp. 228-233

[24] Edited by Swapan Kumar Ghosh (2006) Functional coatings by polymer microencapsulation. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

[25] Edited by N.Pan and G. Sun (2011) Functional textiles for improved performance, protection and health. *Woodhead Publishing Limited*, Number 120

[26] Ramakrishnan Ramaseshan, Subramanian Sundarrajan, Yingjun Liu, R SBarhate, Neeta L Lala and S Ramakrishna (2006) Functionalized polymer nanofibre membranes for protection from chemical warfare stimulants. *Nanotechnology*, 17, pp. 2947–2953

[27] Amarildo Otavio Martins, Edson Luiz da Silva, Eduardo Carasek, Norberto S. Gonçalves, Mauro C. M. Laranjeira, Valfredo T. de Fávere (2004) Chelating resin from functionalization of chitosan with complexing agent 8-hydroxyquinoline: application for metal ions on line preconcentration system. *Analytica Chimica Acta*, 521, pp. 157–162

[28] Fernando Wypych, Kestur Gundappa Satyanarayana (2005) Functionalization of single layers and nanofibers: a new strategy to produce polymer nanocomposites with optimized properties, *Journal of Colloid and Interface Science*, 285, pp. 532–543

[29] Adbulakh K. Mikitaev, Mukhamed Kh. Ligidov, Gennady E. Zaikov (2006) "Polymers, polymer blends, Polymer Composites and Filled Polymers: Synthesis, Properties and Applications". *Nova Science Publicers*

[30] Zbigniew K. Walczak (2002) "Processes of fiber formation". *Elsevier Science Ltd.*

[31] B. L. Deopura, R. Alagirusamy, M. Joshi and B. Gupta (2008) Polyesters and Polyamides. *Woodhead Publishing Limited*

[32] S. Rajendran (2009) Advanced textiles for wound care. *Woodhead Publishing Limited*

[33] Payam Zahedia, Iraj Rezaeiana, Seyed-Omid Ranaei-Siadat, Seyed-Hassan Jafaria and Pitt Supapholc (2010) A review on wound dressings with an emphasis on electrospun nanofibrous polymeric bandages. *Polymers Advanced Technologies*, 21, pp. 77–95

[34] Anshika Agarwala, Anant Rahejaa, T.S. Natarajanb, T.S. Chandraa (2012) Development of universal pH sensing electrospun nanofibers, *Sensors and Actuators B* 161, pp. 1097– 1101

[35] Ajay Tambralli, Bryan Blakeney, Joel Anderson, Meenakshi Kushwaha, Adinarayana Andukuri, Derrick Dean2 and Ho-Wook Jun (2009) A hybrid biomimetic scaffold composed of electrospun polycaprolactone nanofibers and self-assembled peptide amphiphile nanofibers. *Biofabrication 1*, 025001 (11pp)

[36] Peter Bamfield and Michael G. Hutchings (2010) Chromic Phenomena Technological Applications of Colour Chemistry. *RSC Publishing*, 2nd edition

[37] Yong-Tang Jia, Jian Gong, Xiao-Hua Gu, Hark-Yong Kim, Jiong Dong, Xin-Yuan Shen (2007) Fabrication and characterization of poly (vinyl alcohol)/chitosan blend nanofibers produced by electrospinning method, *Carbohydrate Polymers 67*, pp. 403–409

[38] R. Jayakumar, M. Prabaharan, S.V. Nair, H. Tamura (2010) Novel chitin and chitosan nanofibers in biomedical applications. *Biotechnology Advances 28*, pp. 142–150

[39] Audrey Frenot, Ioannis S. Chronakis (2003) Polymer nanofibers assembled by electrospinning, *Current Opinion in Colloid and Interface Science 8*, pp. 64–75

[40] Zhi-Juan Pan, Hong-Bo Liu, Qian-Hua Wan (2008) Morphology and Mechanical property of Electrospun PA 6/66, www.tbisociety.org

[41] Prasanth Raghavan, Du-Hyun Lim, Jou-Hyeon Ahn, Changwoon Nah, David C. Sherrington, Ho-Suk Ryu, Hyo-Jun Ahn (2012) Electrospun polymer nanofibers: The booming cutting edge technology. *Reactive & Functional Polymers*

[42] Margaret W. Frey, Ph.D. and Lei Li, Ph.D. (2007) Electrospinning and Porosity Measurements of Nylon-6/Poly(ethylene oxide) Blended Nonwovens. *Journal of Engineered Fibers and Fabrics* Volume 2, Issue 1

[43] Travis J. Sill, Horst A. von Recum (2008) Electrospinning: Applications in drug delivery and tissue engineering. *Biomaterials*, 29, pp. 1989-2006

[44] L. Van Langenhove (2007) Smart textiles for medicine and healthcare. *Woodhead Publishing Limited*

[45] Professor Subhash Anand Bolton Institute (2001) MEDICAL TEXTILES. *The Bolton Institute*

[46] W Johna, CA Buckleyb, EP Jacobsc and RD Sandersonc (2002) SYNTHESIS AND USE OF POLYDADMAC FOR WATER PURIFICATION. Paper presented at the Biennial Conference of the Water Institute of Southern Africa (WISA) Durban, South Africa www.wisa.co.za ISBN Number: 1-86845-844-X

[47] Nanofibers and Nanotechnology in Textiles (2007) Woodhead Publishing Limited

[48] Songting Tan, Xianwei Huang and Bolin Wu (2007) Mini-review: Some fascinating phenomena in electrospinning processes and applications of electrospun nanofibers. *Polymer International,* 56, pp. 1330–1339

[49] Xuri Yan, Michael Gevelber (2010) Investigation of electrospun fiber diameter distribution and process variations, *Journal of Electrostatics,* 68, pp. 458-464

[50] CHEN Jiong, HAN Chun-mao, SU Guo-liang, TANG Zhi-jian, SU Shi-jie and LIN Xiao-wei (2007) Randomized controlled trial of the absorbency of four dressings and their effects on the evaporation of burn wounds. *Chinese Medical Journal; 120(20), pp. 1788-1791*

[51] Ashok Kumar (2010) Nanofibres. Intech

[52] Osti E. (2008) Skin pH varations from the acute phase to re-epithelialization in burn patients treated with new materials (BURN SHIELD®, SEMIPERMEABLE, ADHESIVE FILM, DERMASILK®, AND HYALOMATRIX®) non-invasive preliminary experimental clinical trial, *Annual of Burns and Fire Disasters, vol XXI, n.2*

[53] Long Yu, Katherine Dean, Lin Li (2006) Polymer blends and composites from renewable resources. *Progress in Polymer Science*, 31, pp. 576–602

[54] B. L. Deopura, R. Alagirusamy, M. Joshi and B. Gupta (2008) Polyesters and Polyamides *Wound Publishing Limited,* ISBN 978-1-84569-298-8

[55] Euk Seok Gil, Samuel M. Hundson (2004) Stimuli-responsive polymers and their bioconjugates, Progress in polymer science, 29, pp. 1173-1222

[56] H. Beecken, E-M Gottschalk, U. v. Gizycki, H. Kramer, D. Maassen, H-G Matthies, H. Musso, C. Rathjen, UI. Zdhorszky (2003) Orcein and Litmus. Biotechnic & Histochemistry, pp. 289-302

[57] G. A. F. Hendry, J. D. Houghton (1996) Natural food colorants. *ISBN 0 7514 0231 1* e-book

[58] H. R. Mattila (2006) Intelligent Textiles and Clothing. *Woodhead Publishing Limited*, ISBN-13: 978-1-85573-546-0; ISBN-10: 1-85573-546-6

[59] L. Van Der Schueren, K. De Clerck (2010) The road to a unique textile material nanofibres with a pH sensitive function, *4th International Technical Textiles Congress*, 16-18 May, Istanbul-TURKEY

[60] Lien Van Der Schueren, Karen De Clerck (2011) PH sensitive textile materials as innovative wound dressings. *FiberMed11*, Tampere, Finland

[61] Lien Van Der Schueren, Bert De Schoenmaker, Özlem I. Kalaoglu, Karen De Clerck (2011) An alternative solvent system for the steady state electrospinning of polycaprolactone. *European Polymer Journal* 47, pp. 1256-1263

[62] Alok Mittal, Dipika Kaur, Jyotti Mittal (2009) Butch and bulk removal of a tryarylmethane dye, Fast Green FCF, wastewater by adsorption over waste materials. *Journal of Hazardous materials 163*, pp. 568-577

[63] Sander De Vrieze, Bert De Schoenmaker, Özgur Ceylan, Jara Depuydt, Lieve Van Landuyt, Hubert Rahier, Guy Van Assche, Karen De Clerck (2010) Morphologic Study of Steady State Electrospun Polyamide 6 Nanofibres. *Journey of applied polymer science 119*, pp. 2984-2990

[64] Rolf G. Kuehni (2003) Color space and its divisions, *John Wiley and Sons Publication*, ISBN 0-471-32670-4

[65] John Shore (2002) Colorants and auxiliaries 2nd edition, Society of Dyers and Colorists, ISBN 0 901956 76 3

[66] P. Westbroek, G. Priniotakis and P. Kiekens (2005) Analytical electrochemistry in textiles, *Woudhead Publishing Limited*, ISBN 0 8493 3485 3