New Solvent for Polyamide 66 and its use for Preparing Single-Polymer Composite Coated-Fabric

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Abstract

Polyamides (PAs) are one of the most important engineering polymers; however, the difficulty in dissolving them hinders their applications. Formic acid (FA) is the most common solvent for PAs, but it has industrial limitations. In this contribution, we proposed a new solvent system for PAs by replacing a portion of the FA with urea and calcium chloride (FAUCa). Urea imparts the hydrogen bonding and calcium ion from the calcium chloride, as a Lewis acid was added to the system to compensate for the pH decrease due to the addition of urea. The results showed that the proposed solvent (FAUCa) could readily dissolve PAs, resulting in less decrease in the mechanical properties during the dissolution. The composite prepared using the FAUCa has almost the same properties like the one prepared using the FA solution. The solution was applied on a polyamide 66 fabric to make an all-polyamide composite coated-fabric, which then was characterized. The FAUCa solution had a higher viscosity than the one prepared using the neat FA solvent, which can be an advantage in the applications which needs higher viscosity like preparing the all-polyamide composite coated-fabric. A more viscose solution makes a

denser coating which will increase the water-/gas-tightness. In conclusion, using the FAUCa solvent has two merits: 1. replacement of 40 % of the FA with less harmful and environmentally-friendly chemicals and 2. enabling for the preparation of more viscouse solutions, which makes denser coating.

Keywords:

Polyamide solvent, composite, coated-fabric, Nylon, single-polymer composite, all-polyamide composite coated-fabric

Introduction

Aliphatic polyamides (PAs), also called Nylons, are a class of semi-crystalline polymers that contain amide groups which are intercalated along linear alkane chains [1]. Solution processing of aliphatic PAs is quite challenging due to the fact that only a few solvents, such as formic acid (FA) and cresol [2], or fluoric solvents [3], can dissolve them. All of the solvents being used for the dissolution of PAs have severe environmental challenges. A few attempts have been made [2] to replace the existing solvents or propose new solvents. Papadopoulou *et al*. [2] mixed FA with trifluoroacetic acid and acetone. Charlet *et al*. [4] studied the crystallization and dissolution behavior of polyamide 6-water systems under pressure. Nirmala *et al*. [5] used FA 85 wt%, acetic acid, dichloromethane, 1,1,1,3,3,3-hexafluoro-2-propanol, trifluoroacetic acid, and chlorophenol in their study. Basically, dissolving PAs is difficult due to two reasons: (a) polyamides are highly crystalline, whereas the above treatment holds for amorphous polymers, and (b) solvents for polyamides are believed to act by virtue of strong, highly specific polar forces [6].

Polyamide (PA) is a well-known high-performance engineering plastic (technical thermoplastic [7]) with high strength and good fatigue resistance [8], excellent mechanical and physical properties, increasingly used in industrial machinery [7]. Nylon is the common name of linear aliphatic PAs. Nylons are important commercial polymers, with uses ranging from fibers to cooking bags to coatings [9], carpets, upholstery, and apparel [10].

Coated fabrics are flexible composites, consisting of a fabric substrate and a polymeric coating [10]. The coating could be on one side or on both sides, either with the same or a different polymeric coating per side [10]. Coated woven fabrics are used in a wide range of structural applications to provide lightweight, architecturally striking solutions [11]. The physical properties of a coated-fabric depend on the specific properties of the substrate, coating formulation, coating technique, and processing conditions during coating [10]. There are two

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principal types of coated woven fabric: glass fiber fabric with a PTFE (polytetrafluoroethylene) coating and polyester fabric with PVC (Polyvinyl chloride) coating [12]. Both PTFE- and PVC-coated-fabrics are employed today in different types of tents and architectural membrane structures all over the world [13]. As the fabric is prepared from high crystalline polymer (spun fiber), it can resist environmental loads, as tensile stresses in the plane of the fabric [12]. These fabrics are popular mainly due to their affordable prices, high strength, durability, resistance to wear and tear, various colors, and soft texture [11]. They are often used for wide-span surfaces, membrane-cable structures, and pneumatic constructions [13]. One recent application of coated-fabrics is their application as textile bioreactor which is a vessel to conduct the biological processes (fermentations) [14]. PVC coated-fabric was the first material proposed for this purpose. The recent promising candidate was all-polyamide composite coated-fabric (APCCF) which showed superior properties over the former one [14]. However, using high amount of formic acid as the solvent is still one industrial challenge for scaling-up the production.

The aim of this paper was to introduce a new solvent based on the replacement of FA with urea, calcium chloride (industrially-abundant chemicals) and water to produce an all-polyamide composite coated-fabric from a PA by solvent-casting of only one component to have strong adhesion between the coating and the fabric as well as enhanced recyclability.

Material and Methods

Materials

The formic acid, urea, and calcium chloride used in this work were supplied by Sigma-Aldrich (ACS reagent grade, >98 %). The PA66 plain-woven fabric (70 grams per square meter (gsm))

was provided by FOV Fabrics AB (Borås, Sweden). As a polymer source to produce a solution, PA fiber production waste from the weaving process at FOV Fabrics was used.

Solvent preparation

The solutions were prepared by adding 35 g of PA waste-scraps into 100 g solvent-mixtures, which, in turn, were obtained by mixing different amounts of formic acid (FA), urea (U), calcium chloride (Ca), and distilled water (W) at room temperature, according to the values tabulated in Table 1. For the cases that had more urea and calcium chloride, it took a while (1-3 minutes) to get a clear solution.

Composite preparation

All-polyamide composites were prepared in the form of a flat laminate on the substrate fabric using an isothermal immersion-precipitation method. The solutions of the PA production waste in the formic acid were made by dissolving 35 g of PA in 100 g solvent at room temperature. In low concentrations (less than ≈30 % w/w), PA66 readily dissolves in the formic acid containing the solvent-mixture at room temperature, but for higher concentrations, the solution should be agitated for a longer time. In order to assure the completion of dissolution and have the same agitation condition for all the solutions, the sealed solution flasks were put in a shaker at the speed of 100 rpm for 20 hours at 55 °C to obtain a homogeneous solution [11]. The solutions were cooled to room temperature, and after centrifugation for 10 minutes at the speed of 16,000×g (meaning 16,000 times Earth's gravitational force) to remove the bubbles, the dopes were cast on a PA fabric with the size of 18×24 cm fixed on a glass with adhesive tape, using a ZUA 2000 universal film applicator (Zehntner GmbH Testing Instruments, Sissach, Switzerland) with a gap of 175 μm. Once the casting process was done, after waiting 30

seconds, the glass plate (carrying the fabric and a layer of the PA solution on top of it) was immersed in a distilled water coagulation bath (10 L) at room temperature to induce polymer precipitation (phase separation). After one-hour of coagulation (in the water bath), the composites obtained were first washed three times with distilled water and then held under light press between two sheets of filter papers and dried at 55 °C in a vacuum oven (≈0.1 bar) for 2 hours. The samples were kept in vaccumed zipper storage bag for further analysis. The composites were named according to their corresponding solution ingredients (Table 1). The thickness of the composites varied between 150-200 µm. The reason of variation in the thickness could be the strength of the solvent. In other words, if the solvent is stronger, it will dissolve the surface of th fabric in a greater extent which leads to more reduction of the composite thickness. The thickness of the fabric was 100 µm initially.

Characterization methods

The tensile strength properties were evaluated in accordance with the standard method ISO 527 [15]. Dumbbell shaped test bodies, 75 mm long (with the width of 4 mm), were tested on a MTS 20/M tensile strength tester (MTS Systems Corporation, Eden Prairie, MN, U.S.A.), fitted with a 5 kN load cell and a special grip for films, using a crosshead speed of 5 mm/min. The gauge length, preload force, and first approach speed were 33 mm, 0.5 N, and 2 mm/min, respectively. The thickness of the composites was measured using an Elastocon thickness meter (Elastocon, Sweden). A minimum of five test bodies was tested for each material. The specimens were all cut along the warp direction of the fabric.

To investigate the viscoelastic properties of the composites, dynamic mechanical thermal analysis (DMA Q800, TA Instruments, Waters LLC, U.S.A.) was performed on the prepared composites. The specimens were run with a film tension clamp using the temperature ramp

procedure with a sample dimension of approximately 15×9 mm. The temperature ranged from room temperature to 180 °C with a heating rate of 3 °C/min; the frequency and the amplitude were 2 Hz and 15 % elongation at max, respectively.

Scanning electron microscopy (SEM) was used to monitor the fracture surface morphology of the cross-sections of the composites and to check the adhesion between the coating (the PA film) and the fabric. The specimens were obtained by quenching in liquid nitrogen and breaking by hand. As the samples contained fabric, using only quenching in liquid nitrogen did not take apart the sample completely; therefore, after breaking, the unbroken parts were cut by a sharp blade. The studied surface was sputtered with a layer of gold before the measurements. SEM analysis was performed using AIS2100 (Seron Technology, Korea) operated at an acceleration voltage of 18 kV.

The viscosity measurements were carried out with a Brookfield viscometer (MA, U.S.A.) at 40 °C. The tests were done within 30 seconds for each sample.

Thermogravimetric analysis (TGA) was performed on the composites using the Q500 machine (TA Instruments, MA, U.S.A.). About 8 mg of the material was heated from room temperature to 700 °C at a heating rate of 10 °C/min in a nitrogen purge stream.

The pH measurements were carried out using a Jenway 3505 pH meter (Staffordshire, UK) at room temperature. The pH sensor was placed in the samples for 30 seconds while being stirred at 200 rpm to reach to an equilibrium.

Results and discussion

The most common solvent for polyamides is formic acid (FA), which is neither safe nor easy to handle. To replace a portion of the FA to make it more appropriate, more economical, and safer to handle solvent-mixtures, different amounts of urea, calcium chloride, and water were

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mixed and added to the FA. Thereafter, the polymer was added to the solvent-mixtures to make homogeneous solutions. The solutions were used to make all-polyamide composite coated-fabrics by means of a universal film applicator and consecutively, coagulation in a water bath as a non-solvent in order to induce phase separation (phase inversion). As a result, a composite composed of a thin continuous PA layer (the coating) and a PA fabric out of the most common type of aliphatic PA (PA66) was obtained. The hypothesis in this work was that since each urea molecule contains four hydrogens and can establish strong intermolecular interactions (H-bonding) with the amide groups in the PA, it can disrupt the intermolecular interactions (hydrogen bondings) among the polymer chains, therefore, resulting in an easier dissolution. In general, the dissolution of semi crystalline polymers such as polyamide comprises several steps including solvent penetration [16], de-crystallization of crystalline domains, amorphous polymer swelling, and chain untangling [17]. Formic acid (as the main solvent) has enough penetration power to penetrate into the PA chains [18]. However, the main goal in this paper was to replace a portion of the FA, meaning that the replacement molecule needed to have enough interactions with the PA chains to start penetration. As discussed earlier, urea has four hydrogen bonding per unit of molecule, even if all the four hydrogen cannot engage in hydrogen-bonding, still has high capability of hydrogen-bonding interactions. On the other hand, PA chains contain amide groups which are the strong hydrogen bonding donor/acceptor groups [19], while FA has only one hydrogen bonding per unit of molecule. Therefore, the mixture of FA/urea will have a higher tendency to penetrate into the PA chains. The other steps of dissolution (de-crystallization of crystalline domains, amorphous polymer swelling, and chain untangling) would be done faster and easier if the first step (solvent penetration) occurs faster/easier [20,21]. This process will be enhanced by using calcium chloride as a Lewis acid (to nullify the increased pH due to the addition of urea–an organic base) as well as localizing the paired electrons on the amide groups of PA chains. Different properties were analyzed, and the process parameters were optimized. The selection of different percentages of the solvent's

components (FA, urea, calcium chloride, and water) was done by trying to keep the percentage of the FA as low as possible. Water was added to the solvent mixture, both for imparting hydrogen bonding [22] and also for its well-known effect on the dissolution of polyamides [4,23] when it is used in lower percentages.

Mechanical properties

The maximum force devided by the cross-sectional surface area of the samples needed to break the composite in the tensile strength mode, as well as the elongation at max of the composites are shown in Figure 1. The thickness of the composites were varying between 150-200 µm.

The results from the tensile strength testing (Figure 1) implied an irregular trend. However, a slight trend is evident in terms of the FA content. Four composites had the tensile strength values higher than the one obtained from a solvent out of pure FA. It could be related to the fact that FA partially decomposes the PA chains during the dissolution process [11]. In other composites, which have a FA content that is even less than the FA content of those four good composites, the tensile strength values are not higher than the composite 100-0-0-0 (with pure FA). Although it might seem contradictory with the above proposal for increasing the tensile strength value, it could be the effect of the urea-/calcium chloride-content (and even water content) in the crystallization of the PA chains in the phase-inversion process. Regarding the elongation at max, all the composites prepared from the new proposed solvent-mixtures in this work have lower values compared to the 100-0-0-0 composite. This might be related to the effect of the localization of the paired electron on the amide groups of PA chains, which plays a role like a spacer [24] during the phase-inversion process. We can conclude that the optimized FA content for dissolving PA with the least possible decomposition/degradation is 60 % (the sample 60-7-20-13).

Viscoelastic properties

The loss modulus is a measure of energy dissipation. In the region of the glass transition, molecular segmental motions are activated; however, motions occur with difficulty, described as the molecular friction that dissipates much of the force. Therefore, though the material is less stiff, more force is dissipated as heat, increasing the loss modulus. However, after that region, as the chains are free to move (at the temperature higher than the glass transition temperature), much less energy is stored since the molecules can move with the force, resulting in a rapid decline in the storage modulus. As evident in Figure 2, in the sample prepared from pure FA, the maximum in the curve of the loss modulus decreases with the reduction in the amount of FA in the solution. The solvent 60-7-20-13 contains water and there might be some water molecules left. As the water molecules can act as a plasticizer for polyamide [25], it could plasticise the polymer. Moreso, It might be related to the effect of higher density of hydrogen bonding in a urea-containing solvent (in 60-7-20-13) as well as the localization of the paired electrons of the amide groups from the PA chains. One of the main characteristics of PAs is the strong inter-chain interaction that arises from the hydrogen bonding between the amide groups on adjacent chains [26]. In other words, in the solvation process, the amide groups from the PA chains meet a higher density of hydrogen bonding (offering by urea), leading to weaker intra-interactions among the PA chains, which, in return, decrease the interaction among them. Therefore, they have much more freedom to move in the solvent. This freedom increases the Brownian motion of the chains, which increases their distances from each other [27]. Finally, when they are about to change their phase from solution to solid (coagulation process in the coagulant), they come together in a relatively less-packed structure. Moreover, when they are less-packed in the solid form (having lower-crystallinity), their Tg is slightly lower (Figure 2 for tan delta), and the peak of the loss modulus is seen at a lower temperature for a solution

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with a higher amount of urea. This proposed reason is intensified with the presence of calcium ion as a Lewis acid in a different way. Calcium ion has free orbital to localize the paired electrons of the nitrogen from the amide group of the PA chains; hence, the hydrogen bonding ability of the amide groups of the PA chains also decreases and finally the same effect happens. The same trend is seen in the storage modulus as well as in the tan delta.

Viscosity

The viscosity values are different for various solutions (Figure 3). However, in all solutions, the viscosity value is higher than the one for the solution with only formic acid as a solvent (100-0-0-0). Regarding the merit of the increase in viscosity, during the process of making the APCCF, it was observed several times that when the viscosity of the solution is low, the formed-film (coating) does not have enough coherency. It makes sense as it might be due to the less aggregation of polymer chains on top of the fabric and also letting the solution go through more into the fabric which is not favorable. Because for the application of making the APCCF, only the surface of the fabric must be dissolved partially, not the whole fabric which will decrease the whole tensile strength of the composite. So a solution which has higher viscosity is more favorable for making APCCF as it makes a well-formed coating on top of the PA fabric. When the viscosity of the solution is low, the formed-film does not have enough coherency. Comparatively, when the same percentage of PA solutions in different solvents gives a different viscosity, and on the other hand, the viscosity of around 4000 cP (for the solution 100-0-0-0) is enough to make a proper coating, the solution 75-8-17-0 (which has the highest viscosity value, around 10500 cP) will use less polymer. Additionally, as the APCCF must be waterproof and be as gas-tight as possible, the coating being formed from a higher viscosity solution will be denser and will increase the APCCF's gas-tightness.

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The reason for the difference in the viscosity values in different solutions could be related to the difference in the intermolecular interactions between the solvent's molecules and the PA's molecules. The ones that have a higher amount of urea have higher values in viscosity. This is due to the fact that urea can establish hydrogen bonding in large numbers (up to four units) from two sides, which can make a bridge between two PA chains (two bonds from the one side and two bonds from the other side). By establishing these four bi-directional hydrogen bonds, the fluidity of the PA solution decreases, which, in turn, increases the viscosity.

Morphological properties

According to the scanning electron microscopic images of the cross-section (Figure 4), in almost all the APCCF specimens there is an excellent adhesion between the coating (formed film) and the fabric. In other words, the boundaries between the fiber of the fabric and the coating are not clear because they have faded due to the adhesion of the two components.

It is obvious that a large part of the cross-sectional area of the fabric is dissolved, and the polymer chains are inter-diffused with each other, enabling the APCCF to have a good adhesion between the coating and the fabric, both of which are made out of PA. Although higher surface dissolution helps to create a better adhesion between the fabric and the coating, it also disintegrates the fabric structure and changes the fabric, from being a fibrous form to an amorphous film. Fibers are spun and pose a high crystallinity and thus a good strength while the films are amorphous as they do not have enough time to rearrange their chains in a nice ordered way (fast coagulation in water). Therefore, converting PA from a highly crystalline form to a less crystalline (highly amorphous) form is not favorable from a mechanical point of view. The amount of the surface dissolution should be as low as possible to impart a good adhesion between the fabric and the coating, but a higher dissolution is not favorable [11]. Using this new solvent helps the fabric's surface to be partially dissolved more quickly, due to

the higher hydrogen bond intensity (due to the presence of urea); hence, the adhesion between the fabric and the coating –the coating (formed film) on top of the fabric– would be stronger.

Thermogravimetric analysis (TGA)

The TGA curves showed almost the same values and shape (Figure 5). The only composite that deviates more from the rest is the 75-8-18-0, which tends to decompose slightly earlier than the others, though the difference is not significant. However, it has higher residue percentage compared to the rest of the composites (except the 64-7-14-14). Although PA66 is partially crystalline, all good solvents penetrate the crystallites, disrupting them completely [6]. Calcium ion (which is the acidic ion) is smaller than the urea molecule, resulting in an easier entrance to the crystallites. The final swollen gel is thus amorphous, even though the initial polymer is crystalline [6]. In the composite 75-8-17-0, the ratio of urea to calcium chloride (the source of calcium ion) is 0.5 (Table 2) and the ratio of U/FA is 0.11. These ratios are the same with the composites 69-8-15-8 and 64-7-14-14; however, their Ca/(FA+U+W) and U/(FA+Ca+W) are different. From the last two ratios and the TGA curves, it could be concluded that out of the four ingredients of the new solvent-mixture (U, FA, Ca, and W), the ratio of U and Ca to the other ingredients should be kept as low as possible to have the least disruption of PA crystallites in order not to sacrifice the thermal stability. Noteworthy that the composite 82-9-9-0, which has the same Ca/(FA+U+W) and U/(FA+Ca+W) ration (=10) has the lowest residue in the TGA curve, meaning that the closer the two ratios, the less the thermal stability of the composite.

pH values and observations

From the pH measurements, it is obvious and reasonable that the solutions that have a higher amount of FA have lower pH. The amine group (-NH2) in urea can accept a hydrogen ion, making it a basic substance. However, the carbonyl group (-C=O) offers a significant opportunity for resonance, which will stabilise the amine group, meaning that the paired electrons on N is in resounance. This means, urea is very slightly basic (and very close to neutral). However, in the presence of an acid, the basicity of urea increases (as there is plenty of H+ in the solution, the –NH2 is converted to –NH3+). Hence, in the solution, urea is a base, so the reason for adding calcium chloride (which acts as a Lewis base) was to decrease the pH to make the solution as similar as possible to the pure FA solution. The highest pH is attributed to the solution 75-0-0-25 in which 25 % of the water has increased the pH from -1.74 to -0.30. Basically, polyamides are polymers with a relatively high density of hydrogen bonds [1]. As PA is a weak acid, a solvent with acidic properties can protonate the amide group; consequently, the amide group will have less possibility to establish hydrogen bonding with other chains. Therefore, it will be easier for the solvent to swell into the polymer and dissolve it. In the first six solutions of the solutions tabulated in Table 2, it was observed that the solution 90-0-0-10 was excellent in terms of homogeneity and dissolution power. This might be related to the lower pH they have compared to the others, which have higher pH. However, the pH by itself is not a good criterion to judge the dissolution power of these solutions. For example, in the solution 35-6-48-12, which has the pH value very close to the pH of FA (-1.66 vs. -1.74), the observation showed that the solution does not have a high power of dissolution. This might be related to the calcium chloride content (100*Ca/(FA+Urea+W)), which is 92.59 %, while the value is less than 25 % in those showing "excellent" dissolution. The reason for this might be due to the effect of the counterion, chloride. Chloride is a relatively big ion. In lower numbers, they can help the dissolution; however, when they are increased, they most probably promote some interferences with the interactions of other

ingredients (FA, urea, and water) with polyamide chains. Therefore, it could be concluded that the calcium chloride content should be less than 25 %.

Conclusions

The preparation of all-polyamide composite coated-fabric (APCCF) coated-fabric, a specific form of single-polymer composites, made through a phase inversion method using a new solvent is described. The solvent was obtained by replacing 40 % of the FA with less harmful, cost-effective, more environmentally-friendly, safer to handle, and industrially available chemicals: urea, calcium chloride, and water. The APCCF prepared in this work using the new solvent mixture does not have inferior properties over the one prepared through FA, such as mechanical and thermal properties. The prepared composite has a strong adhesion between the two constituents due to the use of the same polymer (PA66) in the constituents. The composite is fully recyclable since it contains no other materials except PA, which can be melted or dissolved and reused as a PA source. The prepared composite has a broad range of semi-structural applications to provide lightweight, architecturally striking solutions as well as wide-span surfaces, membrane-cable structures, hanging roofs, pneumatic constructions, water-/gas-proof fabric reactors, temporary houses and tents, facade coverings, container linings, tarpaulins, and as material of construction of textile bioreactors.
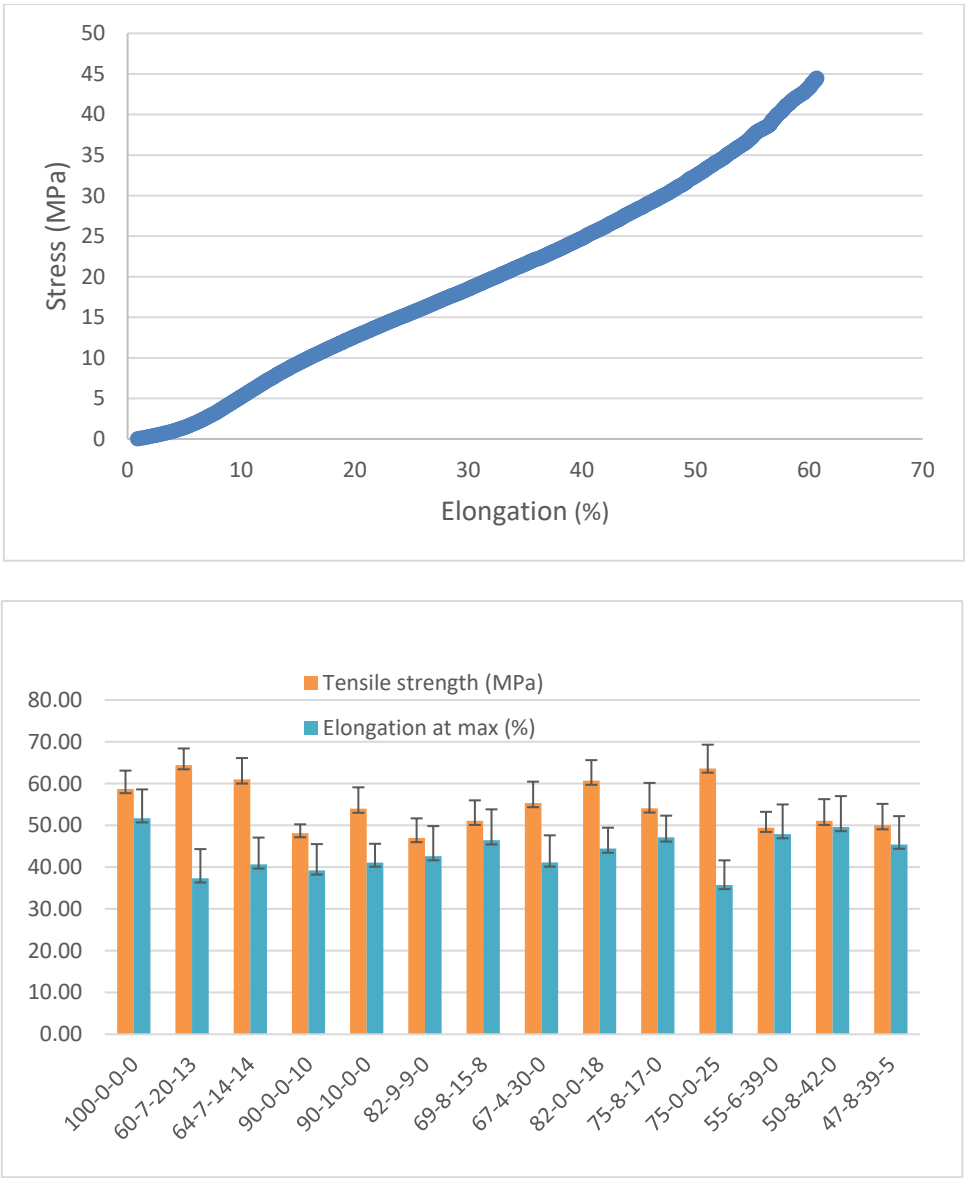
Acknowledgements

Figure 1 An exemplary stress-elongation at max curve for the sample 60-7-20-13 (top), and the tensile strength and the elongation at max values for the composites (down)
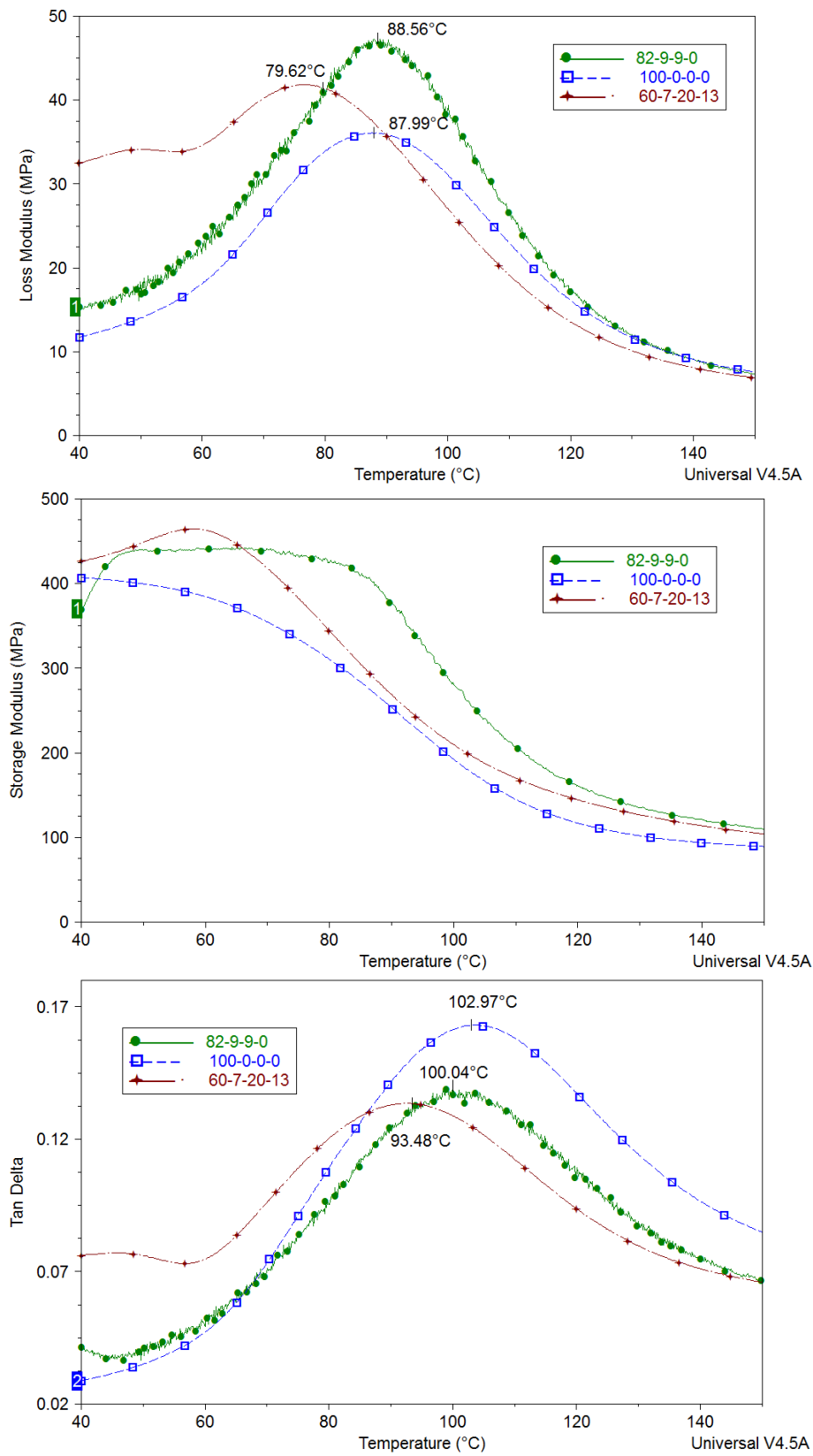
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**Figure 2 Loss modulus, storage modulus, and Tan-delta for the composites prepared
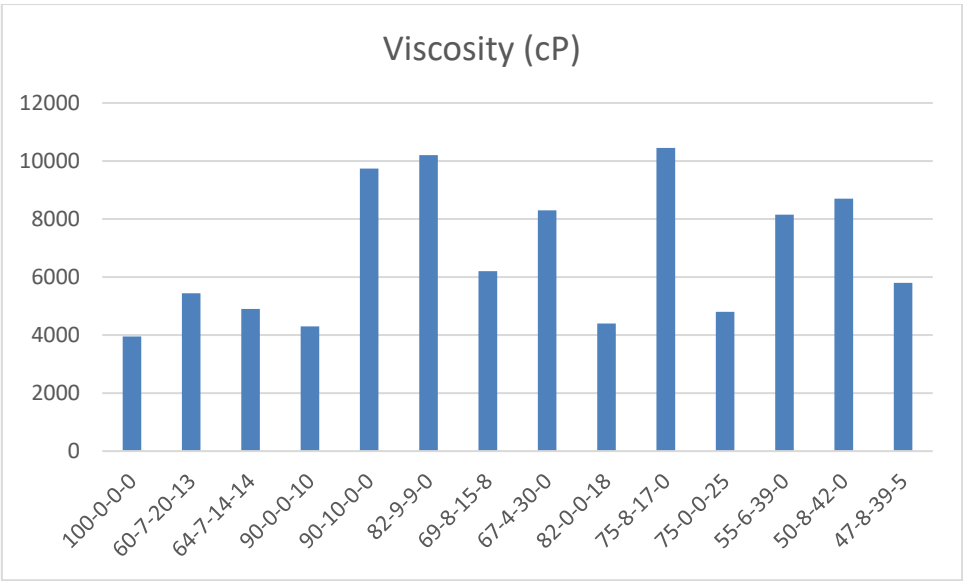from the new solvents**

Figure 3 The viscosity values for the composites. The solution made from the solvent-mixture 75-8-17-0 is the most-viscous solution due to the intermolecular interactions between the ingredients of the solvent-mixture and the polymer
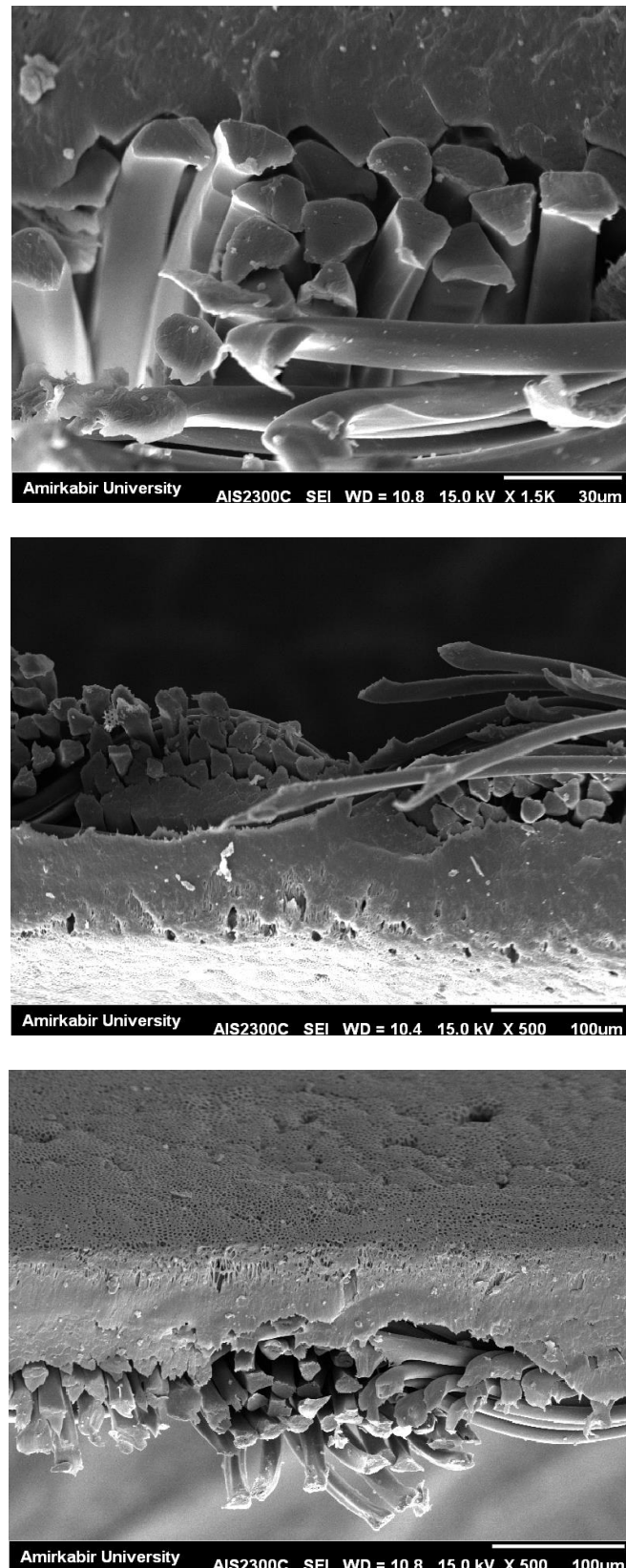
Figure 4 Selected cross-sectional SEM micrographs of the composite 60-7-20-13. Strong adhesion is seen between the coating (the top-film) and the fibers from the fabric. The closer fibrils of the fiber to the coating are fused to each other.
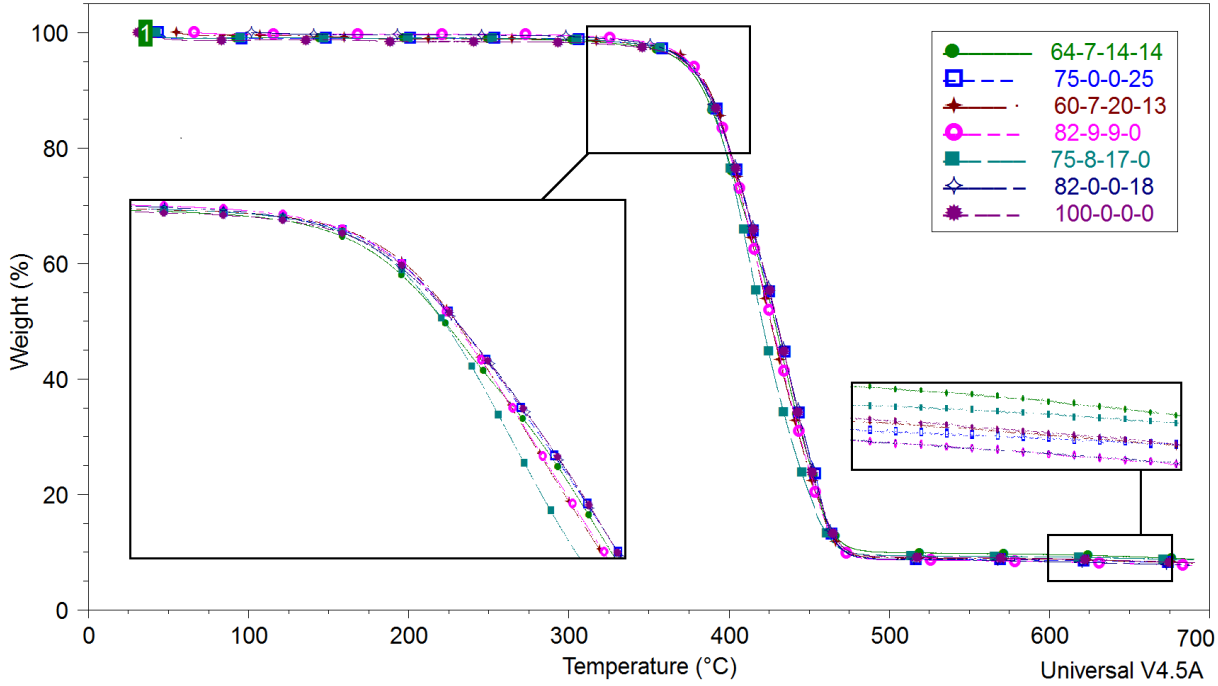
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Figure 5 TGA curves of the composites prepared via the new solvent

Tables

Table 1 Ingredients for the solutions (in some cases, the sum is not 100% –due to the mathematical rounding of the numbers– the names are only for labeling.)

Sample name (FA-U-Ca-W, %)	FA (%)	U (%)	Ca (%)	W (%)
100-0-0-0	100.00	0.00	0.00	0.00
60-7-20-13	60.00	6.67	20.00	13.33
64-7-14-14	64.29	7.14	14.29	14.29
90-0-0-10	90.00	0.00	0.00	10.00
90-10-0-0	90.00	10.00	0.00	0.00
82-9-9-0	81.82	9.09	9.09	0.00
69-8-15-8	69.23	7.69	15.38	7.69
67-4-30-0	66.67	3.70	29.63	0.00
82-0-0-18	81.82	0.00	0.00	18.18
75-8-17-0	75.00	8.33	16.67	0.00
75-0-0-25	75.00	0.00	0.00	25.00
55-6-39-0	54.55	6.06	39.39	0.00
50-8-42-0	50.00	8.33	41.67	0.00
47-8-39-5	47.37	7.89	39.47	5.26
56-6-25-13	56.25	6.25	25.00	12.50
50-6-28-17	50.00	5.56	27.78	16.67
43-7-36-14	42.86	7.14	35.71	14.29
38-6-43-13	38.30	6.38	42.55	12.77
35-6-48-12	34.62	5.77	48.08	11.54

Table 2 Values for the pH and the relative components and also the observations. *The markings were assigned based on the homogeneity of the solutions and the uniformity of the cast-film on the glass.

Sample name	pH	U/Ca	U/FA	100*U/ (FA+Ca+W)	100*Ca/ (FA+U+W)	Observation*
100-0-0-0	-1.74	–	0.00	0.00	0.00	excellent
60-7-20-13	-0.74	0.33	0.11	7.14	25.00	excellent+
64-7-14-14	-0.54	0.50	0.11	7.69	16.67	excellent
90-0-0-10	-1.10	–	0.00	0.00	0.00	excellent
90-10-0-0	-0.18	–	0.11	11.11	0.00	excellent
82-9-9-0	-0.75	1.00	0.11	10.00	10.00	excellent
69-8-15-8	-0.74	0.50	0.11	8.33	18.18	good
67-4-30-0	-1.64	0.13	0.06	3.85	42.11	good
82-0-0-18	-0.56	–	0.00	0.00	0.00	good
75-8-17-0	-0.95	0.50	0.11	9.09	20.00	good
75-0-0-25	-0.30	–	0.00	0.00	0.00	fairly good
55-6-39-0	-1.69	0.15	0.11	6.45	65.00	fairly poor
50-8-42-0	-1.61	0.20	0.17	9.09	71.43	fairly poor
47-8-39-5	-1.50	0.20	0.17	8.57	65.22	fairly poor
56-6-25-13	-0.91	0.25	0.11	6.67	33.33	poor
50-6-28-17	-0.90	0.20	0.11	5.88	38.46	poor
43-7-36-14	-1.08	0.20	0.17	7.69	55.56	bad
38-6-43-13	-1.42	0.15	0.17	6.82	74.07	bad
35-6-48-12	-1.66	0.12	0.17	6.12	92.59	bad

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