Dually Reinforced All-Polyamide Laminate Composites via Microencapsulation Strategy

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A new two-stage strategy is disclosed for the preparation of all-polyamide laminate composites based on polyamide 6 (PA6) matrices reinforced by high volume fractions of polyamide 66 (PA66) textile structures and three different types of nanoclays. In the first stage, PA6 microcapsules (MC) loaded with montmorillonite nanoclays (MMT) are synthesized by activated anionic ring-opening polymerization of ϵ -caprolactam in solution in the presence of three different organically treated MMT brands. In the second stage, the MMT-loaded MC obtained with controlled molecular weight, composition and granulometry are compression molded in the presence of PA66 textile structures to produce the final dually reinforced laminate composites. Mechanical tests in tension, flexion, and impact for selected composites in this study showed up to 73% increase of the Young's modulus, up to 142% increase of the stress at break, and more than a fivefold increase of the notched impact resistance. The mechanical behavior of the dually reinforced composites was discussed in conjunction with the morphology of the samples studied by optical and electron microscopy, and the matrix crystalline structure as revealed by DSC and microfocus synchrotron X-ray diffraction. POLYM. ENG. SCI., 00:000-000, 2016. © 2016 Society of Plastics Engineers

INTRODUCTION

Polymer composites with thermoplastic matrices (TPCs) comprising particulate or fibrous reinforcements are being used in steadily increasing number of applications because of their good material performance and manufacturing flexibility [1]. As compared to their thermoset counterparts, TPCs display higher toughness of the matrix, higher impact resistance, and significantly shorter manufacturing cycles. In addition, TPCs are of light weight, can be welded [2] and relatively easily recycled by reprocessing [3] which is important in view of the rigorous requirements for environmental protection imposed in most industrialized countries.

Most frequently, TPCs are manufactured by melt-processing. In fiber-reinforced systems, matrix material and reinforcements are often combined prior to the manufacturing of the finished article by prepregging [4], film stacking [5], preparation of

powder-impregnated, comingled [6, 7], or braided hybrid yarns [8]. The finished article is prepared by different consolidation techniques including compression molding, pultrusion, autoclave processing, or tape placement. The common shortcoming of these approaches is the elevated costs of both raw materials and manufacturing rendering them feasible only for high performance applications.

An alternative way to produce TPCs is by reactive processing techniques, where the TPC is obtained *in situ*, through polymerization of low-viscosity monomers or oligomers in the presence of the reinforcements. This approach requires monomers able to produce high molecular weight polymers formed at sufficiently high conversions and without generation of byproducts. Among the polymerization types meeting these requirements, the most common is the ring-opening polymerization (ROP) [9]. It is based on anionic or cationic reaction mechanisms, in which ring-shaped monomer molecules are opened and transformed into high molecular weight polymers. Thus, polyamide-6 (PA6) can be produced through activated anionic ROP (AAROP) of the inexpensive ϵ -caprolactam (ECL). The AAROP of lactams to neat polyamides is thoroughly documented and well understood [10, 11]. Strong bases such as metal caprolactamates are most often used as initiators of the process and imide group-containing compounds (e.g., acyl lactams) as activators. They help overcome the induction period and the polymerization process is completed in several minutes.

Numerous studies exist on reactive processing toward materials based on anionic PA6 but only a few of them deal with preparation of composites. Early tests of AAROP for the production of PA6/clay hybrids were made in the late 1980s but the method was abandoned soon due to insufficient control on its rate and on the nanostructure of the final hybrid [12]. Later on, processes related to resin transfer molding (RTM), reactive injection pultrusion (RIP), reactive vacuum infusion (RVI), and reactive rotational molding (RRM) were introduced for the preparation of PA6-based composites. Luisier et al. [13] developed a pilot RIP line for the *in situ* AAROP of lauryllactam to PA12-based, glass fiber-reinforced TPCs. Modeling of all phenomena involved was presented aiming to the development of optimization strategies and engineering tools to control the process. Earlier study reported on a similar RIP process for the preparation of fiber-reinforced PA6 [14]. A series of studies disclosing RVI for manufacturing of PA6 glass fiber composites have demonstrated the potential of this technique for industrial application [15, 16] Harkin-Jones and Crawford [17, 18] explored for the first time the RRM of liquid plastic feedstock comprising a mixture of activated ECL and nylon prepolymer. Neat PA6 and TPCs with glass fibers were prepared and tested with good results for the composite materials.

A new type of TPC based on PA6 matrix and PA66 textile structures was introduced by Gong and Yang under the name

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“all-polyamide” composites. They were produced by either film stacking (FS) of neat PA6 films and PA66 textile plies [19] or by a RTM through bulk AAROP of ECL in the presence of PA66 textile reinforcement [20]. With textile volume fractions close to 0.7, the tensile strengths of the FS samples reached 180 MPa and of those by RTM—155 MPa, the value of the neat PA6 matrix being 68 to 70 MPa. Such significant improvement was attributed to good adhesion and possible chemical bonding at the matrix-fiber interface. It was also pointed out the good recyclability of all-polyamide composites as compared to those reinforced by glass or carbon fibers. It should be noted, however, that so far systematic comparative studies on the mechanical properties of PA6/PA66 TPCs in tension, flexure, and impact are missing.

Recently, PA6-based laminate composites reinforced by glass fiber and PA66 textile structures were obtained by means of reaction injection molding (RIM) via *in situ* AAROP of ECL employing prototype equipment with a mold of constant thickness [21]. The tensile strength and Young modulus values of the glass fiber laminates with volume fractions of reinforcements up to 0.27, as well as the impact strengths were found to be with up to 300% higher than the neat anionic PA6 produced at the same conditions. In the PA6/PA66 textile laminates obtained with volume fractions of 0.10 to 0.13 a similar improvement of the impact resistance was registered, accompanied with a moderate 30 to 60% increase of the tensile strength. The Young modulus of these textile-reinforced samples, however, dropped with 30 to 50% in respect to the neat anionic PA6 matrix. The attempt to use higher PA66 volume fractions in a RIM mold with constant thickness resulted in insufficient wetting and easy delamination of the PA66 plies, as well as in increased void formation.

The reactive *in situ* approach can produce also pulverulent polyamide-based materials that can be used for the preparation of all-polyamide laminate composites by powder impregnation. Previous reports on polyamide powders preparation by AAROP in solution [22–25] disclosed the synthesis of neat PA6 particles with various sizes and topographies. Recent communications on this subject showed the possibility to synthesize loaded PA6 microcapsules (MC) via AAROP in solution [26, 27]. The process was performed in the presence of high concentrations of various solid payloads. These studies showed that the loaded MC can be easily transformed by melt processing into hybrid composites with homogeneous distribution of the reinforcing component within the matrix without any functionalization.

The main objective of this work was to prepare all-polyamide laminate composites with high volume fraction of PA66 textile plies, the PA6 matrix being additionally reinforced by montmorillonite (MMT) nanoclays. This was achieved by impregnation of the textile plies by MMT-loaded PA6 microcapsules and subsequent compression molding. To the best of our knowledge, such dual reinforcement was not considered before in polyamide laminates. The motivation for such an approach is twofold. On the one hand, previous studies have shown that the PA66 textile reinforcement can significantly increase the mechanical properties of PA6, which justifies further systematic research in this field. On the other hand, there exist innumerable reports suggesting that the presence of well-dispersed MMT in the PA6 matrix can strongly enhance all mechanical properties of the composite [28–30]. Consequently, it may be hypothesized

that the dual reinforcement in all-polyamide laminates that became easy to achieve via the microencapsulation strategy may result in some useful synergism in the mechanical behavior. Therefore, this work studies the structure-properties relationship in PA6 clay-loaded microcapsules, PA6-MMT hybrid composites and the final dually reinforced PA6-MMT/PA66 laminates relating data from microscopy, thermal and X-ray techniques with mechanical testing in tension, flexure, and impact.

EXPERIMENTAL PROCEDURES

Materials

The ECL monomer of reduced moisture (AP-Nylon® caprolactam) was delivered from Brüggemann Chemical, Germany. Before use, it was kept under vacuum for 1 h at 50°C. As polymerization activator Brüggolen C20® from Brüggemann Chemical, Germany (C20) was used. According to the manufacturer, it contains 80 wt% of blocked di-isocyanate in ECL. The supposed chemical structure of C20 is presented in Fig. 1. The initiator sodium dicaprolactamato-*bis*-(2-methoxyethoxy)-aluminate (DL) was purchased from Katchem (Czech Republic) and used without further treatment.

Three commercial nanoclay brands based on organically treated natural montmorillonite (MMT) were employed in this study. The Nanomer I.24 TL (NM) is a product of Nanocore (USA) with 12-aminododecanoic acid as surfactant, the typical aspect ratio of the monolayers being of 200 to 400, with a maximum moisture content of 3% and cation exchange capacity (CEC) of 135 meq/100 g. The Cloisite 15A (CL15A) and Cloisite 20A (CL20A) clays were both delivered by Southern Clay Products (USA) and represent MMT modified by dimethyl dihydrogenated tallow quaternary ammonium chloride and contained up to 2% of moisture. The CEC value of CL15A was 125 meq/100 g versus 95 meq/100 g of CL20A, the organic content being 43 and 38%, respectively. The aspect ratio of the monolayers in the CL15A was reported to be in the 75 to 100 range [31] and in average 300 for CL20A [32]. All MMT components were dried for 12 h at 80°C before further use.

The PA66 textile structures were of the plane-weave type with area density of 124 g/m². All they were cut to the shape of the mold and subjected to Soxhlet extraction with acetone for 1 h so as to eliminate any organic coats. After drying for 1 h/100°C they were used for laminate preparation. Toluene, xylene, and all other solvents were purchased from Sigma-Aldrich and used as received.

Sample Preparation

Neat and MMT-Loaded MC by AAROP. The solution-precipitation AAROP of ECL to MC was performed as described previously [26, 27]. The lactam was dissolved in a 1:1 v/v toluene/xylene mixture under nitrogen atmosphere refluxing the reaction mixture for 10 to 15 min. Then, 1 wt% (in respect to ECL) of CL15A, CL20A, or NM were added. In several minutes clear solutions were obtained and the components of the catalytic system DL and C20 were introduced in a molar ratio 1:2. The reaction time was 1 h, keeping the temperature in the 125 to 135°C range at constant stirring. Thus, MC15A, MC20A, and MCNM microcapsules were produced in the form of fine powder, separated from the reaction mixture by vacuum filtration, washed with methanol, and dried. In the same way,

FIG. 1. Chemical reactions occurring during AAROP in solution and schematics of the MC preparation and their transformation into nanoclay hybrid composites. C20, Bruggen C20 (activator) ◆; DL, dicaprolactamato-bis-(2-methoxyethoxy)-aluminate (initiator) with R = OCH₂CH₂OCH₃; ECL, ε-caprolactam ●; PA6, anionic polyamide 6 in the form of microcapsules (MC); MMT platelets —; MP, melt processing (compression molding). [Color figure can be viewed at wileyonlinelibrary.com]

empty MC were prepared without adding during the polymerization any MMT component. The composition and designations of all MC samples are presented in Table 1.

Composites by Compression Molding. The composite materials prepared in this work with the use of microcapsules by compression molding can be classified in two groups: (i) PA6 hybrid plates obtained by direct compression molding of empty and MMT-loaded MC and (ii) dually reinforced laminate composites prepared by compression molding of empty and loaded MC in the presence of PA66 textile plies. Compression molding was performed in a Moore hydraulic hot press (UK) using a mold with dimensions 70 × 70 × 2 mm. The pressure applied was 5 MPa for 10 min at 230°C, i.e., below the melting of PA66, subsequently cooling down to 80°C at a rate of about 15 deg/min. For the preparation of the dually reinforced hybrid laminate composites of k plies, the respective MC were divided into $(k + 1)$ equal portions that were put between the PA66 plies. The molding conditions were the same as above.

The number of textile plies necessary to reach a certain volume fraction of reinforcement was calculated according to the equation:

$$V_f = \frac{A_w \cdot n}{\rho_f \cdot t} \quad (1)$$

where V_f is the volume fraction of reinforcements, A_w the area density of the textile structure used (g/m²), n is the number of plies, ρ_f is the density of the PA66 fibers (g/m³), and t is the laminate thickness. Typical volume fractions of reinforcements in the PA6/PA66 laminate composites produced were 0.3 to 0.6 which corresponded to 6 to 11 PA66 plies, respectively. From each laminates with 9 and 11 plies two types of composites were prepared: anisotropic ones with unidirectional orientation of *warp/weft* and isotropic ones with rotation of consecutive plies: [0/±45/90/0/90/±45/0] or [0/90/±45/90/0/90/±45/90/0]. Standard test samples were cut out of these laminates for mechanical testing.

Measurements and Characterization

Bright field optical microscopy of MC sizes, roundness, and their distributions were performed in an Olympus BH-2 microscope equipped using the Leica Application Suite 4.4 software for image processing. The same equipment was employed in the polarizing light microscopy (PLM) of laminates (L-series) prepared by microtoming. The scanning electron microscopy

TABLE 1. MMT-loaded MC: sample designation, composition, polymerization yield, and granulometry.

MC composition	Load (wt%) ^a	PAMC yield (wt%) ^a	Real load (wt%) ^b	M_v (g/mol)	d_{max} range (μm)	Average roundness (d_{max}/d_{min})
MC00	—	72	—	36,500	35–50	1.2–1.3
MC15A	1	65	1.03	37,900	20–25	1.3–1.4
MC20A	1	62	1.57	34,300	35–40	1.3–1.4
MCNM	1	68	1.38	39,000	20–25; 55–60	1.2–1.3

^aIn respect to the monomer ECL.

^bDerived from TGA data according to Eq. 2.

(SEM) studies were performed in a NanoSEM-200 apparatus of FEI Nova (USA) using mixed secondary electron/back-scattered electron in-lens detection. The microcapsule samples (MC series) were observed after sputter-coating with Au/Pd alloy. The PA66-containing laminates (L-series) and the hybrid plates without PA66 textile reinforcement (P-series) were observed after cryofracture.

The average viscometric molecular weight M_v of the as-prepared MC and molded samples thereof was determined by intrinsic viscosity measurements in 97% sulfuric acid at a concentration of 0.2 g/dL with a suspended level Ubbelohde viscometer thermostatted at 25°C. The Mark-Houwink equation for PA6 was used with $K = 5.066 \times 10^{-4}$ and $\alpha = 0.74$ [33]. Flow times are recorded as an average of at least five runs.

The differential scanning calorimetry (DSC) measurements were carried out in a 200 F3 equipment of Netzsch (Germany) at a heating rate of 10°C/min under nitrogen purge. The typical sample weights were in the 10 to 15 mg range. The crystallinity index x_c of the samples was calculated according to:

$$x_c = \frac{\Delta H_m^i}{V_f \cdot \Delta H_m^0}, [\%] \quad (2)$$

wherein ΔH_m^i is the registered melting enthalpy of the current sample and ΔH_m^0 is the melting enthalpy of a 100% crystalline PA6 (190 J/g) or PA66 (226 J/g)

The real load of MMT in MC or molded composites thereof (R_L) was established by means of thermogravimetric analysis (TGA) in a Q500 gravimetric balance (TA Instruments), heating the samples to 600°C at 10°C/min in nitrogen atmosphere as:

$$R_L = R_i - R_{PA} \quad (3)$$

where R_{PA} is the carbonized residue at 600°C of empty MC and R_i —that of the respective MMT-loaded MC (Table 1). Hybrid composite plates without PA66 were subjected to the same TGA test revealing R_L values close to that of the MC (Table 2). Notably, the carbonized residue at 600°C will reflect correctly only the thermally resistant alumino-silicate content while the more volatile organic surfactants should be lost at this high temperature. Therefore, within each MC or P series, the higher R_L values for the CL20A-containing systems in respect to those with NM and especially with CL15A should be attributed to higher amount and volatility of the organic modifiers in the latter. On this basis and having in mind the MC preparation procedure, equal amounts of organically treated MMT load in all systems was postulated.

Synchrotron wide-angle X-ray scattering measurements were performed in the P03 MINAXS microfocus beamline at PETRA III, the German Synchrotron Source DESY in Hamburg, Germany. A Pilatus 300 two-dimensional detector (DECTRIS Ltd, Switzerland) was used, the sample-to-detector distance being 115 mm, and $\lambda = 0.969$ Å. The X-ray beam dimensions were set to 5×5 µm. Linear XRD profiles were obtained by radial integration of the two-dimensional XRD images by means of the Fit2D software.

The tensile tests were performed in an Instron 4505 testing machine (USA) at $23 \pm 2^\circ\text{C}$ with a standard load cell of 50 kN and at a constant crosshead speed of 50 mm/min. From the different composite plates prepared by compression molding of

TABLE 2. Designation of all composite materials prepared by compression molding of different MC with and without PA66 textile structures.

Sample designation	Type of MMT	Real MMT load (%) (TGA)	No. PA66 plies
P00 ^a	—	—	0
L006			6
L007			7
L009			9
L0011			11
P15A ^b	CL15A	1.34	0
L15A6			6
L15A7			7
L15A9			9
L15A11			11
P20A ^b	CL20A	1.97	0
L20A6			6
L20A7			7
L20A9			9
L20A11			11
PNM ^b	NM	1.54	0
LN6			6
LN7			7
LN9			9
LN11			11

^aHybrid plate of neat anionic PA6 from nonloaded MC.

^bHybrid plate from MMT-containing PAMC without PA66 textile reinforcements.

MC, standard specimens were cut out according to DIN 53504-S3 with a gauge length of 25 mm. At least five specimens of each sample were studied to calculate the average values and their standard deviation. The Young's modulus E was calculated from the stress-strain curves as the tangent at 1% strain.

The flexural properties of the laminate plates were determined in the same Instron 4505 testing machine according to ASTM D 790-03. This test method employs a three-point loading system applied to a simply supported beam using a rate of 2.8 mm/min, a load cell of 1 kN and distance between the points of support of 28 mm. The flexural modulus is calculated according to the following formula:

$$E_f = \frac{L^3 \cdot m}{4bd^3}, [\text{MPa}] \quad (4)$$

with L being the distance between the points of support, m is the slope of the curve of force F as a function of deflection, b and d are the width and the thickness of the sample. Furthermore, the flexural deformation ε_f and the flexural stress σ_f were calculated according to the following expressions:

$$\varepsilon_f = \frac{6Dd}{L^2}, [\%] \quad (5)$$

$$\sigma_f = \frac{3PL}{2bd^2}, [\text{MPa}] \quad (6)$$

where D is the maximum deflection in mm, d is the sample thickness (mm), L is the distance between the points of support (mm), P is the force in Newtons (N), and b is the width of the test sample (mm).

The study of the impact resistance of the composite materials was done by means of Izod pendulum impact test with CEAST Charpy equipment of Instron according to ASTM D 256-04. The notched impact strength (NIS) was calculated as the impact energy absorbed relative to the test bar cross section according to the formulas:

$$\text{NIS} = \frac{E_{\text{comp}} - E_i}{A}, \quad [\text{kJ/m}^2] \quad (7)$$

$$\text{NIS} = \frac{E_{\text{comp}} - E_i}{t}, \quad [\text{J/m}] \quad (8)$$

wherein E_i and E_{comp} are the energies registered in the impact equipment without and with sample bar, respectively, A is the area of the notched sample, and t is the thickness of the sample.

Mechanical characterization is performed with conditioned samples stored for about 30 days at 23°C and 65% relative humidity. The standard samples for each test were cut from one and the same composite plate to ensure reproducibility.

RESULTS AND DISCUSSION

Synthesis of MMT-Loaded Microcapsules

The polymerization of ECL to MC is performed according to the scheme in Fig. 1 using a mixed hydrocarbon solvent able to dissolve all the components of the reaction mixture. As known from detailed earlier studies [10, 11], the initiation and propagation of lactam AAROP require an anionic initiator and an activator comprising imide links $\text{C}(\text{O})\text{—N—C}(\text{O})\text{—}$. It is important that this catalyst system should remain active in the presence of the organically treated MMT and the solvent employed. These requirements determine the selection of the initiator DL and the activator C20, both being commercial products. As indicated in previous studies on AAROP in solution of ECL without any payload [22, 23], the growing PA6 chains form initially viscous, low molecular weight particles that upon additional propagation, coalescence and crystallization produce the final empty MC. It can be hypothesized that the formation of PA6 microcapsules in the presence of soluble nanoclays will follow in a similar way, whereby the MMT platelets will be entrapped into the viscous PA6 particles and will possibly nucleate their crystallization thus forming the loaded MC. The present study showed that the transformation of the viscous particles into MMT loaded MC without formation of lumps requires an optimized stirring rate (600–800 rpm), maintaining the molar ratio $\text{DL/C20} = 2$ and keeping the temperature of AAROP below 135°C.

It was initially intended to work with commercial MMT clays optimized for polar polymer systems such as CL10 and CL11. However, in both cases the AAROP occurred at very slow rates resulting in oligomers. This effect was explained with the presence in these MMT brands of cations blocking the anionic initiator. Such inhibition was not observed in the case of CL15A, CL20A or NM. The AAROP with them yielded 65 to 68% of MMT-loaded MC or 72% of empty MC with a viscosity-averaged molecular weight M_v varying in the 34,000 to 39,000 g/mol range (Table 1). After compression molding to hybrid plates, the M_v values remain unchanged being comparable to the M_v of commercial granulated hydrolytic PA6 with $M_v = 37,200$ g/mol. At the same time, they were significantly lower than of the anionic PA6 produced with the same initiator/

activator system in the bulk at 165°C ($M_v = 88,500$ g/mol) [29]. The higher M_v in the latter case is because the bulk AAROP takes place at higher temperature, in the polar molten ECL and in strongly basic medium. These conditions favor complex side reactions leading to partially cross-linked PA6 characterized by increased molecular inhomogeneity [10].

Microscopy Studies of Microcapsules and Hybrid Plates

The histograms related to the size distribution of equivalent diameters (i.e., the size) and roundness (or the shape) of MC15A and MCNM are represented in Fig. 2. The insets in the graphs of the left-hand side demonstrate the stereoscopic micrograph of MC based on which the size distribution was computed. The insets on the right-hand side display the shape of one single microcapsule of the respective type. Table 1 shows data about the distribution of particles size (maximum diameter) and shape (roundness) for all MC types. The samples display normal distributions of the roundness, the average maximums being in the 1.2 to 1.4 range. The MCNM sample shows a bimodal size distribution with peak values centered at 20 to 25 and 55 to 60 μm , whereas the empty MC (MC00), MC15A, and MC20A possess normal monomodal size distributions centered between 20 and 40 μm . This difference can be due to the fact that NM clay contains 12-aminododecanoic acid as surfactant whose carboxylic end-groups could participate in the ECL ring-opening. As a result, a fraction of the PA6 macromolecules in close vicinity to MMT could be end-tethered to clay platelets. Indeed, Utracki et al. [34] demonstrated end-tethering in hydrolytic PA6/MM hybrids obtained in the 227 to 327°C temperature range. Hence, the presence of normal organically treated platelets and such with end tethering could nucleate differently the crystallization of the growing PA6 chains during AAROP thus causing dual size distribution in MCNM. Partial removal of the amino acid surfactant during AAROP in solution could also result in different nucleation mechanism and be a cause for a more complex size distribution. Anyway, having in mind that all MMT-loaded MC were obtained at the same reaction conditions, it seems logical that it is the MMT brand with its specific surfactant that determines the size and shape distributions of the microcapsules studied.

The morphologies of various MC and molded composites thereof revealed by SEM are presented in Fig. 3. As expected from the light microscopy data in Fig. 2, MC15A, MC20A, and MCNM samples possess almost spherical morphology with average diameters of 25 to 40 μm being equal or close to those of the MC00 (images b, c, d and a, respectively). The bright spots in the 80 to 110 nm range in Fig. 3e show the electron-rich aluminum-silicate domains with their quite homogeneous distribution within the volume of the PA6 shell. Figure 3f obtained with MC20A exemplifies their porosity whose pore sizes vary in the 300 to 800 nm range and is almost the same for all MC samples. These morphological findings are in good agreement with the suggested coalescence-crystallization-precipitation mechanism of AAROP in the presence of the finely dispersed MMT. Figure 3g and h show the homogeneous distribution of the MMT domains within the PA6 matrix in P15A and P20A hybrid composites produced by compression molding of MC15A and MC20A, respectively. Notably, the sizes of these clay domains are of 1 to 3 μm .

FIG. 2. Typical results from bright field transmission microscopy representing the average size and shape distributions for MC15A and MCNM with about 1 wt% of the respective MMT.

Microscopy Studies of the Dually Reinforced Laminate Composites

The light microscopy images of the PA66 textile used in the laminate composites of this study showed that this reinforcement

is anisotropic (Fig. 4a). Vertically (i.e., along the *weft* direction) this plain-weave textile is composed of monofilaments being thicker than those in the horizontal *warp* direction. At the same

FIG. 3. Selected SEM images of MC and molded plates thereof: (a) MC00; (b) MC15A; (c) MC20A; (d) MCNM; (e) sample b in scanning-transmission mode (close-up); (f) sample c (close-up); (g) molded hybrid from MC15A (P15A); (h) molded hybrid P20A from MC20A.

FIG. 4. Selected light microscopy images of PA66 textile and molded laminate composites obtained with MC. (a) stereoscopic image of the neat PA66 textile lamina; (b) PLM image of PA66 textile, normally to the *weft* direction; (c) PLM image of PA66 textile, normally to the *warp* direction; (d) laminate composite L15A6, along the *weft* direction; (e) L20A6, along the *warp* direction; (f) laminate composite LNM6, along the *warp* direction. For sample designation see Table 2.

time, in the *warp* direction there seem to be more filaments per unit area. From Fig. 4b and c the average diameters of the thicker and thinner filaments can be determined as $\sim 20\ \mu\text{m}$ and $\sim 10\ \mu\text{m}$, respectively. Figure 4d–f visualizes representative PLM images of laminate composites with six plies cut along *weft* or *warp* directions. It can be seen (Fig. 4a) that, as expected, the *weft* yarns seem to be less stretched than those in *warp* direction. At the same time, fiber undulation in *weft* direction (Fig. 4d) is different than in *warp* direction (Fig. 4e and f). PLM data allow the conclusion that no fusion of the PA66 occurred during the laminate preparation and that a satisfactory impregnation of the reinforcement by matrix material was achieved with no void formation.

A deeper insight on the morphology of the laminate composites was obtained by SEM of cryofractured samples (Fig. 5). Figure 5a allows a close-up observation of both *weft* and *warp* filaments appearing in this image in horizontal and vertical directions, with thicknesses of about 17 to 18 μm and 11 to 12 μm , respectively. Figure 5b visualizes the fracture of some *warp* PA66 filaments in the L15A6 laminate. Figure 5c–e show the fiber-matrix interface at higher magnifications confirming that in all laminates good impregnation of the textile was achieved, including also the narrow zones between the monofilaments in the bundles. Figure 5f of the LNM6 sample displays the channels in the matrix after pulling-out of some PA66 monofilaments. NM particles of up to 3 μm are clearly seen, just like in Fig. 3g and h that shows P15A and P20A hybrids without PA66. These MMT domains are significantly bigger than in MC15A (Fig. 3e) where the clay particles are smaller than 100 nm. This observation suggests some agglomeration of clay during melt-proceeding of PAMC to plates. To clarify this, X-ray scattering analyzes were performed.

Synchrotron X-Ray Diffraction Studies

To provide information about the microgradients in the fine structure of the MMT-loaded MC, a previously developed methodology involving microfocus synchrotron X-ray diffraction was employed [35]. Monolayers of microcapsules were placed in an appropriate sample holder and attached onto a sliding stage moving consecutively along the *X* (horizontal) and *Z* (vertical) axes and making 11×11 steps of 5 μm (i.e., the microbeam size). In such a way, total sample areas of 3,025 μm^2 were scanned in transmission mode, the irradiation time in each point being 5 s. The two-dimensional diffraction patterns in each of the 121 grid points were analyzed automatically to obtain the intensity maps in two 2θ ranges for MC15A, MCNM, and MC20A (Fig. 6). The images in the left column show the intensity changes of the basal 001 MMT reflection in the 2 to 4° 2θ range as function of the *XZ* position. They provide information about the dispersion of the clay in the scanned area and the effects of exfoliation/intercalation in every grid point. The images in the right column are constructed from the intensity variations of the reflection at $2\theta = 13$ to 14° related to the $\alpha(200)$ plane of the PA6 shell material. These images outline the silhouettes of the loaded microcapsules and help evaluate the packing density in the scanned area.

The visual inspection of the right-hand images in Fig. 6 allows the conclusion that the packing density of the three pulverulent samples was properly chosen. PAMC diameters in the range of 20 to 40 μm can be seen which is in good agreement with the data of granulometry (Table 1). The left-hand images suggest a good distribution of the MMT filler in the three MC samples that roughly follows the microcapsules silhouettes. Only in the case of MCNM, there exist two domains with very high concentration of MMT with coordinates Z9-X10 and Z8-X9.

FIG. 5. Selected SEM micrographs of laminates from loaded MC and PA66 textile. (a) L006; (b) L20A6; (c) – sample b, magnification; (d) L15A6; (e) LNM6; (f) sample e, the matrix after pulling-out of the PA66 fibers. For sample designation see Table 2.

More structural information in MC with MMT can be obtained by analyzing the linear diffraction curves at a certain vertical level Z along the X1-X11 horizontal line of the intensity maps in Fig. 6. The arrow in the images of the MC15A sample indicates the vector of scanning at level Z4. For MCNM and MC20A the selected levels were Z8 and Z3, respectively. The diffraction curves in the two 2θ regions for the three MC samples are presented in Fig. 7. Evidently, in the low 2θ area it is only the NM-containing PAMC that shows clear 001 basal MMT peaks meaning lack of exfoliation in two adjacent 5×5 µm grid points. In MC15A and MC20A no basal MMT peaks are observed suggesting exfoliated nanostructure over the area studied. It should be noted that the 001 peak of neat CL15A appears at $2\theta = 1.97^\circ$ (shown for comparison in Fig. 7) corresponding to a d -spacing of 3.7 nm. The CL20A has lower d -spacing of 3.2 nm. Both of these reflections would have been seen if non-exfoliated domains of them had existed in the respective MC samples. It can be therefore concluded that the AAROP of ECL in solution carried out in the presence of CL15A or CL20A leads to exfoliated clay structure. Some local agglomeration is observed in the case of NM. This observation can be related with its amino acid surfactant that could have been partially removed due to interactions in the process of AAROP.

The curves in the 2θ range of 10 to 20° (Fig. 7, right column) display a clear predominance of the monoclinic α -PA6 polymorph in the three MC samples with MMT. A similar observation was made previously in PA6/MMT hybrids obtained by bulk AAROP [36]. The two characteristic reflections at $2\theta = 13.2^\circ$ and 15.6° correspond to the $\alpha 200$ and $\alpha 002/202$ crystal planes formed between adjacent chains by van der Waals

forces and H-bonds, respectively. It seems that the presence of different MMT in the PA6 microcapsules does not change the position of these two reflections, nor their intensity ratio.

The patterns of the compression molded hybrid plates of the P-series (Fig. 8) show the presence of α -PA6 as major matrix crystalline phase only in the P00 sample representing neat PA6 (curve 1). In the P20A and PNM samples (curves 3, 4), a strong reflection centered at 12.9° appears that corresponds to the $\gamma 001$ plane and proves the coexistence of α - and γ -PA6 polymorphs. Judging from curve 2 in Fig. 8, the PA6 matrix of the P15A hybrid is made almost completely of γ -PA6. The sample displays also a clear reflection at $2\theta = 7^\circ$ belonging to the $\gamma 020$ plane visible in non-oriented PA6 only at high concentrations of the γ -polymorph. All this confirms the previously established by Miri et al. [37] γ -nucleation effect of the MMT in PA6/MMT hybrids after melting and recrystallization of PA6. The reason why P15A is much richer in γ -PA6 than P20A and PNM is not well understood at this point.

In the lower 2θ range of the patterns of all clay hybrids in Fig. 8, weak peaks are observed at $2\theta = 2.5$ to 2.8° best expressed with NM clay (curve 4). They are attributable to the 001 MMT basal reflections, i.e., partial loss of clay exfoliation is observed in all hybrid plates. Since the MMT in the respective microcapsules (especially in MC15A and MC20A) used to be completely exfoliated, the aggregation of the MMT platelets in the molded hybrids must have taken place during the compression molding. Most probably it could be related to loss of surfactant and insufficient compatibility with the matrix PA6.

Comparing the diffraction curves in Figs. 7 and 8 shows that the transition from MC to molded plates results also in an observable shift to lower 2θ angles of the $\alpha 200$ and $\alpha 002/202$

FIG. 6. X-ray microbeam scanning of MMT-loaded MC. The phase contrast in the images of the left column is produced from the WAXS intensity at $2\theta = 2-4^\circ$. The phase contrast in the right column images is based on the intensity at $2\theta = 13-14^\circ$ related to the $\alpha(200)$ plane of the PA6 shell material. The intensity scales in number of counts are given to each image group. For more details see Fig. 7 and the text. [Color figure can be viewed at wileyonlinelibrary.com]

reflections. This means that the respective d -spacing and the unit cell dimensions as a whole increase when MC with MMT undergo melting and recrystallization to plates.

The X-ray diffraction patterns of laminate composites containing PA66 textile structures were also obtained and analyzed (Fig. 9). As seen from the inset of Fig. 9a, the two-dimensional diffraction image of the neat PA66 textile displays point-like reflections in two perpendicular directions. This is related to the geometry of the plain-weave textile whose PA66 filaments are apparently highly oriented. The radial integration of this pattern in three sectors (i.e. the oriented reflection on the meridian (vertical), the one at the equator and the isotropic weak Debye ring in the area between them) produced diffraction curves 2, 3, and 1, respectively. Curves 2 and 3 display the two peaks at $2\theta = 12.3$ and 14.3° typical for PA66 in α -form, whereas curve 1 of the isotropic zone did not show coherent scattering of

ordered phase. Bearing in mind the latter observation, the isotropic Debye rings in the two-dimensional patterns of the L006 and LNM6 (the insets of Fig. 9b) were related to the scattering of the PA6 matrix. Sectoral integration in this area for all dually reinforced laminates produced curves 1 to 4 in Fig. 9b. Curve 1 obtained with the sample L006 not including nanoclay still shows a predominance of the α -PA6 polymorph. However, the PA6 matrix of the laminates (curves 2–4) is almost completely made by γ -PA6. Therefore, it can be concluded that the PA66 textile structure additionally promotes the γ -nucleation in the PA6 matrix during the melt processing of PAMC to laminates.

Thermal Properties of Composites Produced from Microcapsules

Table 3 summarizes some thermal characteristics of the samples from the MC-, P-, and the L-series with nine PA66 plies

FIG. 7. Linear X-ray diffraction profiles of MMT-loaded MC in two 2θ areas. Left, $2\theta = 1\text{--}10^\circ$; right: $2\theta = 10\text{--}20^\circ$. The patterns are taken in the grid points along a horizontal X-axis at certain Z level (the arrow in Fig. 6). [Color figure can be viewed at wileyonlinelibrary.com]

obtained by DSC. Figure 10 shows curves representative for each group of samples. All loaded MC displayed narrow single melting peaks in the 205 to 208°C range, which agrees with the X-ray data indicating predominant α -PA6 polymorph in the microcapsules (Fig. 7, higher 2θ range). The total DSC crystallinity x_c of all MC is similar being in the 41 to 42% range. The T_g values of the loaded MC, however, are with 3 to 8°C higher than those of empty microcapsules. This was expected since the MMT platelets dispersed in the amorphous PA6 will decrease

its mobility. Hence, the higher T_g in the Cloisite-modified microcapsules would mean better clay dispersion than in the Nanomer system, which was confirmed by the microfocus X-ray measurements (Fig. 7, the lower 2θ range).

The hybrids obtained by compression molding of loaded PAMC displayed a dual melting behavior with peaks close to 200°C for the γ -PA6 and around 214°C for the α -PA6 polymorph (Table 3, Fig. 10). This is again in agreement with the diffraction measurements in Fig. 7. The total crystallinity index

FIG. 8. X-ray diffraction profiles of compression molded plates produced from MC. (1) P00; (2) P15A; (3) P20A; (4) PNM. For sample designation see Table 2. [Color figure can be viewed at [wileyonlinelibrary.com](#)]

that includes both α - and γ -PA6 of all three hybrids is similar and varies in the 26 to 27% range, i.e. significantly lower than in MC. This should be attributed to the relatively fast cooling (15 deg/min) during the molding of the plates. The T_g values of all P-samples are close to 47°C indicating similar chain mobility in all composites of this type.

The laminates with nine textile plies displayed two melting peaks. The broad one close to 210°C indicates co-existence of α - and γ -PA6. This peak above the Brill-transition region for PA6 in which intensive conversion of γ - into α -PA6 takes place [38]. The narrow endotherm at 257 to 258°C is the melting of the PA66 textile reinforcement. According to the X-ray patterns in Fig. 9, it should be related to the α -PA66. Table 3 shows very similar T_g values for all laminate composites. Two x_c values of either PA6 matrix or PA66 reinforcements were calculated for these composites. It seems that the x_c of the PA6 matrix is by 4 to 5% lower than in the plates without PA66 not depending on the MMT type. The PA66 crystallinity in the laminates, however, is up to 11% higher than that of the neat textile. This is a result of the isothermal annealing at 230°C during the compression molding. The DSC data in Table 3 allow the conclusion that in all laminate composites with nine plies the x_c values of either PA66 textile or PA6 matrix are very similar, the differences being within the experimental error.

Mechanical Properties of Composites Produced from MC

Tensile Properties. Data about the mechanical properties in tension of the hybrids of the P-series and of the laminates (L-series) are summarized in Table 4. Representative stress–strain curves for samples with different reinforcement and composition in *warp* or *weft* directions are presented in Figs. 11 and 12.

Comparing the curves of P00 (Fig. 11a, curve 1) to those of P15A, P20A and PNM hybrids (curves 2–4), confirms that the reinforcement of PA6 with MMT promotes the brittle failure, the deformation at break ε_{br} of the three hybrids dropping from 25% to about 5%. This is accompanied by a significant growth in the stiffness and strength of the hybrids. Thus, the E -values for P00 of about 1.7 GPa reach 2.81 GPa in PNM, the values for P15A and

FIG. 9. Two-dimensional X-ray patterns of laminate composites and linear profiles obtained by their sectioning. (a) Neat PA66 textile: 1, integration of the isotropic intensity between the oriented reflections; 2, integration of the upper vertical reflection; 3, integration of the horizontal oriented reflection. (b) Laminate composites, sectioning between the oriented reflections: 1, L006; 2, L15A6; 3, L20A6; 4, LNM6. For sample designation see Table 2. [Color figure can be viewed at [wileyonlinelibrary.com](#)]

P20A being in the range of 2.6 to 2.7 GPa (Table 4). The σ_{br} values grow in the following order: P15A > P20A > PNM > P00. Notably, the relative improvement of the E -values in respect to

FIG. 10. Typical DSC curves (first scan) of microcapsules (MC15A), molded plates (P15A) and laminate composites with nine plies (L15A9).

TABLE 3. Results from the DSC experiments.

Sample designation	T_m (°C)	ΔH_f (J/g)	T_g (°C)	x_c (%)
Microcapsules				
MC00	206.8	80.1	32.0	42.2
MC15A	207.4	79.9	40.1	42.0
MC20A	206.8	76.7	39.8	40.4
MCNM	205.4	78.3	35.0	41.2
Hybrid plates				
P00	212.9	49.6	47.5	26.1
	203.6			
P15A	214.1	49.3	46.0	26.0
	202.5			
P20A	212.2	51.9	46.0	27.3
	201.2			
PNM	212.9	50.1	46.5	26.3
	202.5			
Laminate composites with nine plies				
PA66 textile	256.9	73.2	45.3	32.3
L009	211.3	21.3	46.5	22.4
	256.8	44.8		39.6
L15A9	210.8	23.7	46.2	22.4
	257.9	43.6		39.6
L20A9	210.9	22.2	45.0	23.0
	258.5	45.1		40.0
LNM9	208.2	20.5	45.2	21.5
	255.8	49.4		43.7

the P00 reference is of 53 to 63%, and for the σ_{br} —up to 37%. These improvements are larger than in the case of PA6/Cloisite hybrids obtained by conventional melt-mixing, i.e., up to 22% for the E and 13% for the σ_{br} [39]. Apparently, the microencapsulation strategy can produce MMT-reinforced anisotropic PA6 matrices that are stronger and stiffer than the hydrolytic PA6 in the conventional clay hybrids. The predominance of the γ -PA6 polymorph in P15A (Fig. 8) and the good exfoliation of the MMT in MC15A (Fig. 7) can be correlated with the highest strength of the P15A hybrid. Meanwhile, the best E -modulus is found in the PNM hybrid produced from the microcapsules with the less homogeneous distribution of the MMT (Figs. 6 and 7).

Figure 11b displays the stress–strain curves of dually reinforced laminate composites containing PA66 textiles and CL15A. The anisotropic textile plies here are all with parallel alignment of the *weft/warp* directions, the tests samples being cut along the *warp* yarns. The figure shows ductile failure for all laminates at $\varepsilon_{br} > 15\%$ and well-expressed strain-hardening after 2 to 3% of deformation that can be related with additional orientation of the PA66 textile structure along the straining direction. Increasing the number of plies from 6 to 9 ($V_f = 0.3$ – 0.5) results in a growth of E and σ_{br} values compared to the P00 reference, the improvement reaching 66% and 73%, respectively. Further increase of plies to 11 ($V_f = 0.6$) lead to abrupt deterioration of the tensile behavior (Fig. 11b, curve 5, Table 4). These laminates showed signs of incipient rupture of the textiles close to the surface of the sample, accompanied by spontaneous delamination during the mechanical test. The reason for this is most probably related to insufficient impregnation of the PA66 plies by matrix PA6 under the standard conditions of compression molding used in this work. The data in Table 4 allow the generalization of the above observations to all laminate composites tested in *warp* direction. Nine PA66 plies seems

to be the best textile content not only for L15A9 but also for L20A9 and LNM9 presenting the best E and σ_{br} values in the respective sample sets.

Figure 12 compares the stress–strain curves of samples cut along the *warp* and *weft* directions from laminates with nine plies. For comparison, the graphs contain also the curves of the PA6 reference (curve 1) and of the PA66 textile lamina in the respective direction (curve 6). Comparing the data for strength, stiffness and deformation at break for all laminates with 9 and 11 plies in both directions (Table 4), shows that the mechanical characteristics in *weft* direction are significantly larger. Thus, for LNM9 $E_{warp} = 2.37$ GPa versus $E_{weft} = 2.88$ GPa; $\sigma_{br}^{warp} = 87.1$ MPa versus $\sigma_{br}^{weft} = 160$ MPa. For this system the deformation at break ε_{br}^{weft} is with 7% higher than ε_{br}^{warp} . Similar trends are observed in all laminates with 9 and 11 plies, additionally reinforced with CL5A and CL20A with slightly lower values of stiffness and strength in both directions.

The explanation of the large difference of the tensile characteristics in *weft* and *warp* direction should be related to the mechanical properties of the PA66 textile laminae. Their influence grows as the amount of the textile reinforcement becomes predominant at $V_f \geq 0.5$ (9 and 11 plies). As seen from Fig. 12a and b, curves 6, the slope of the strain hardening in the

FIG. 11. Stress–strain curves from the tensile tests of (a) hybrid plates obtained from MC (P series): 1, P00; 2, P15A; 3, P20A; 4, PNM. (b) Laminates L15A with different ply number in *warp* direction: 2, L15A6; 3, L15A7; 4, L15A9; 5, L15A11. Reference: 1, hybrid plate P00. [Color figure can be viewed at wileyonlinelibrary.com]

FIG. 12. Stress-strain curves from the tensile tests of laminates (L-series) with nine textile plies. (a) In *warp* direction; (b) in *weft* direction. 1, P00; 2, L009; 3, L15A9; 4, L20A9; 5, LNM9; 6, PA66 textile lamina. [Color figure can be viewed at wileyonlinelibrary.com]

laminates is similar to that of the single PA66 textile, which in *weft* direction is with more than 50% stronger than in *warp*. This fact should be explained with the finding from Fig. 4a that in the PA66 lamina the *weft* yarns are less stretched than those in *warp* direction. Hence, straining the laminate composite in *weft* direction will first extend the yarns and only then they will start bearing the load and failing. The strain in *warp* direction will result in immediate overstraining of the PA66 yarns, i.e., in shorter strain hardening region of the curve and therefore in lower σ_{br} values.

Comparing the slope of the elastic region in curves 2 to 5 to that of curve 6 in Fig. 12a and b suggests that the E values of the laminate composites should be related to the PA6 matrix and its additional reinforcement by MMT. That is why the stiffness of the laminates is less direction-sensitive than in the region of plastic deformation.

Table 4 contains also the tensile properties of laminate composites with 9 and 11 ply sets (PS9 and PS11) with different orientations of the consecutive PA66 laminae. For PS9 it is $[0/\pm 45/90/0/90/\pm 45/0]$ and for PS11— $[0/90/\pm 45/90/0/90/\pm 45/90/0]$. As expected, in most of the cases such rotation of the PA66 plies results in mechanical properties between those in *weft* and

warp direction, being as a rule closer to the weaker *warp* direction.

Figure 12 and Table 4 include also the mechanical data in tension of laminate composites reinforced only by PA66 textile (L00 series). Comparing these systems to the best performing in tension LNM9 laminate considering the two directions and the ply sets with rotated PA66 lamina shows that the MMT component increases the E -modulus in all laminate types with 27 to 40% and the strength in *weft* direction with up to 25%.

Flexural and Impact Properties. The flexural and notched Izod impact values of all composite materials of this study are presented in Table 5. Within the hybrid plates, the flexural modulus E_{fl} and the flexural strength σ_{fl} are with 6 to 13% higher than that of the neat P00 reference. The best performing sample is P15A, followed by P20A and PNM. In laminates containing MMT with six and seven plies, both E_{fl} and σ_{fl} drop as compared to the respective hybrids and even in respect to the P00 reference. In absolute values the said decrease is different for each MMT brand and should be related to its surfactant amount and type. With nine PA66 plies and $V_f = 0.5$, the E_{fl} remains slightly below that of the P00 and L009 references. The σ_{fl} values of L15A9 and L20A9 become slightly better than P00 but continue similar to that of the L009 laminate without MMT. It can be concluded that in the laminate composites studied the addition of MMT does not enhance the flexural properties.

What the presence of MMT enhances significantly is the impact properties of the laminates. Table 5 displays the notched impact strength (NIS) data. Within the P-series, the best performance was established in the P15A hybrid with $NIS = 105$ J/m i.e., a 115% relative improvement over the P00 reference. The unusually high impact strength of this sample can be related to the crystalline structure of its PA6 matrix. As seen from Fig. 8, curve 2, the matrix of P15A is made of γ -PA6, while in PA20A and PNM the predominant matrix polymorph is α -PA6. As shown in earlier structural studies by synchrotron WAXS, NMR, and Raman spectroscopy [40, 41], γ -PA6 is more ductile than α -PA6. Since a ductile material should have greater fracture energy, the higher impact strength of the P15A sample compared to P20A and PNM seems logical.

The significance of the dual reinforcements is best revealed in the laminates with nine PA66 plies. The L009 sample reaches NIS values of 270 J/m, i.e., a relative improvement of 460% in respect to PA6. The dually reinforced L15A9 and L20A9 samples displayed an additional 15 to 17% improvement of the impact strength in respect to L009 reaching NIS values of 308 to 315 J/m.

To further evaluate the potential of the dual reinforcement in PA6/PA66/MMT laminates in terms of the flexural and impact resistance, a comparison seems to be appropriate between the best performing L15A9 and L20A9 samples and a commercial PA6 special brand reinforced with comparable amount of glass fibers (Table 5). The dry commercial composite possess higher flexural modulus and strength due to the specific properties of the glass fibers. Its two NIS values, however, are considerably lower than those of the conditioned L15A and L20A laminates. This finding could justify further studies dedicated to the microencapsulation approach for the production of MMT/textile reinforced laminate composites.

TABLE 4. Results from the tensile strength experiments.

Matrix composition	No. PA66 plies	Ply orientation	Young's modulus, E (GPa)	Stress at break, σ_{br} (MPa)	Deformation at break, ϵ_{br} (%)
PA66 textile lamina	1	Warp	0.002	59.7 ± 3.0	34.1 ± 0.6
		Weft	0.004	91.4 ± 8.0	32.0 ± 2.0
P00	0	—	1.72 ± 0.05	66.3 ± 4.2	22.5 ± 1.3
L00	6	Warp	1.53 ± 0.07	88.7 ± 4.3	20.3 ± 1.3
	7	Warp	1.75 ± 0.06	76.6 ± 6.0	18.3 ± 7.1
	9	Warp	1.93 ± 0.07	85.7 ± 4.3	20.0 ± 2.5
		Weft	2.37 ± 0.10	128.1 ± 6.3	22.4 ± 1.8
		PS9 ^a	1.98 ± 0.14	109.3 ± 4.1	25.9 ± 1.7
	11	Warp	1.17 ± 0.02	80.3 ± 1.9	24.5 ± 1.9
		Weft	1.41 ± 0.15	144.8 ± 8.0	38.3 ± 3.0
		PS11 ^b	1.11 ± 0.12	83.9 ± 3.0	29.6 ± 1.6
P15A	0	—	2.66 ± 0.07	90.3 ± 3.5	4.9 ± 1.5
L15A	6	Warp	2.31 ± 0.22	93.7 ± 3.7	16.6 ± 4.0
	7	Warp	2.12 ± 0.13	98.6 ± 6.8	17.2 ± 0.3
	9	Warp	2.85 ± 0.11	115.0 ± 3.7	19.5 ± 1.2
		Weft	2.86 ± 0.10	152.2 ± 8.5	24.3 ± 1.9
		PS9	2.80 ± 0.15	121.6 ± 5.5	25.9 ± 1.8
	11	Warp	1.47 ± 0.09	71.5 ± 1.7	16.1 ± 0.6
		Weft	1.65 ± 0.07	134.9 ± 4.0	35.9 ± 3.0
		PS11	1.50 ± 0.14	94.5 ± 4.5	28.6 ± 2.7
P20A	0	—	2.63 ± 0.02	83.3 ± 7.2	5.4 ± 2.1
L20A	6	Warp	1.81 ± 0.14	56.9 ± 2.3	2.7 ± 0.2
	7	Warp	1.89 ± 0.09	61.9 ± 1.9	7.1 ± 1.4
	9	Warp	2.35 ± 0.07	89.5 ± 7.1	15.4 ± 2.8
		Weft	2.70 ± 0.13	139.6 ± 3.7	24.6 ± 0.7
		PS9	2.41 ± 0.10	78.5 ± 2.9	16.3 ± 2.7
	11	Warp	1.33 ± 0.07	67.7 ± 1.2	21.7 ± 0.9
		Weft	1.41 ± 0.05	135.3 ± 4.0	37.0 ± 1.0
		PS11	1.26 ± 0.04	96.7 ± 3.2	31.5 ± 1.4
PNM	0	—	2.81 ± 0.06	76.2 ± 6.7	3.2 ± 0.4
LNM	6	Warp	1.80 ± 0.15	56.8 ± 3.5	9.0 ± 2.1
	7	Warp	2.02 ± 0.11	62.5 ± 1.5	15.8 ± 0.2
	9	Warp	2.37 ± 0.04	87.1 ± 2.9	19.2 ± 2.6
		Weft	2.88 ± 0.10	160.0 ± 6.9	26.1 ± 1.5
		PS9	2.52 ± 0.12	93.4 ± 2.0	21.6 ± 1.4
	11	Warp	1.40 ± 0.03	78.6 ± 1.8	23.7 ± 1.0
		Weft	1.53 ± 0.09	147.5 ± 3.0	37.0 ± 0.6
		PS11	1.44 ± 0.15	98.7 ± 5.8	29.9 ± 2.9

^aPS9, Ply set with 9 PA66 laminae: [0/±45/90/0/90/±45/0].^bPS11, Ply set with 11 PA66 laminae: [0/90/±45/90/0/90/±45/90/0].

TABLE 5. Results from the flexural and Charpy notched impact experiments of conditioned hybrid and laminate composites.

Sample designation	No. PA66 plies	Flexural modulus E_f (GPa)	Flexural strength σ_f (MPa)	Impact strength (J/m)	Impact strength (kJ/m ²)
P00	0	4.69 ± 0.07	75.6 ± 2.5	48.8 ± 8.2	3.8 ± 0.8
L00	6	4.28 ± 0.14	74.0 ± 2.9	230.3 ± 9.2	19.4 ± 0.6
	7	4.34 ± 0.07	72.9 ± 1.4	250.5 ± 9.6	20.0 ± 1.4
	9	4.67 ± 0.03	83.7 ± 0.5	269.6 ± 7.8	22.4 ± 0.6
P15A	0	5.33 ± 0.06	85.3 ± 0.9	105.5 ± 7.6	8.2 ± 1.2
L15A	6	4.21 ± 0.04	70.2 ± 1.3	251.2 ± 8.9	21.2 ± 0.9
	7	4.34 ± 0.08	75.6 ± 1.3	234.2 ± 7.5	19.8 ± 0.6
	9	4.28 ± 0.04	82.3 ± 1.3	315.8 ± 5.6	24.7 ± 0.7
P20A	0	4.96 ± 0.09	80.5 ± 1.9	40.7 ± 3.4	3.4 ± 0.3
L20A	6	3.53 ± 0.04	59.8 ± 1.5	161.8 ± 9.8	13.1 ± 0.8
	7	3.76 ± 0.04	66.6 ± 0.8	176.1 ± 7.0	14.7 ± 0.5
	9	4.23 ± 0.04	80.5 ± 2.0	308.4 ± 9.3	24.4 ± 0.7
PNM	0	4.83 ± 0.04	75.7 ± 1.0	40.5 ± 1.9	3.4 ± 0.2
LNM	6	3.39 ± 0.07	54.9 ± 0.9	212.5 ± 7.2	17.8 ± 0.8
	7	3.70 ± 0.07	60.4 ± 0.9	224.4 ± 3.1	18.9 ± 0.6
	9	4.23 ± 0.04	73.8 ± 1.2	267.1 ± 9.0	22.6 ± 0.8

^aManufacturer's data of Ultramid® 8235G HS BK-102, heat stabilized, pigmented black, 50% glass fiber reinforced PA6, injection molding grade.^b $E_f = 13.2$ MPa; $\sigma_f = 300$ MPa (dry); NIS = 15 kJ/m² or 139 J/m (23°C).

CONCLUSIONS

This work proves possible the preparation of PA6-based composites reinforced by both MMT nanoclays and PA66 textile structures at volume fractions of 0.3 to 0.6 by means of a novel microencapsulation strategy. The *in situ* AAROP in solution in the presence of three different commercial nanoclay brands produced PA6 microcapsules with controlled shapes and average sizes. The process is fast and with high yield of differently loaded microcapsules with high molecular weight. These microcapsules can be transformed into high-modulus and high-strength hybrids by compression molding. If the compression molding of loaded microcapsules is performed in the presence of PA66 textile structures, the resulting dually reinforced, all-polyamide laminates possess good mechanical properties in tension and impact. The microscopy, DSC and X-ray diffraction studies in this work showed the relationship of the mechanical properties to the morphology and nanostructure of matrix, PA66 textiles and MMT.

It should be noted that the microencapsulation strategy toward dually reinforced polymer composites has big potential in combining matrix and reinforcements. Instead of nanoclay and PA66 textile, carbon allotropes, metal or metal oxide powders can be used combined with high-performance textiles. This can open new routes toward advanced composites with tailored properties.

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