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ABSTRACT: The aim of this study was to investigate the scope of the recently developed polymerization molding system for polyamide 12 (PA12), especially with respect to the formation of carbon fiber-reinforced PA12 composites. Initial screening of PA12 composite formation was performed by means of an internal mixer in order to identify the suitable type of surface-treated carbon fiber (CF). The content of residual lauryllactam (LL) monomer reflected the influence of the CF-treatment on the polymerization molding involving anionic *in situ* polymerization of LL. The cryogenic fracture surfaces were analysed by scanning electron microscopy (SEM) in order to evaluate the adhesion quality between the components. Finally, a bench-scale polymerization molding process was established successfully for the fabrication of multi-axial laminates. Macromechanical tests and dynamic mechanical thermo-analysis (DMTA) indicated that the performance of the new polymerization molding process is very similar to that of state-of-the-art PA12/CF composites.

KEY WORDS: polymerization molding, PA12, carbon fiber sizing, liquid impregnation.

INTRODUCTION

HIGH-PERFORMANCE THERMOPLASTIC COMPOSITE materials are attracting more and more interest in the aerospace, automotive and sporting

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goods industries. One of the main advantages of these materials is the possibility of faster cycle times and subsequent high volume applications compared to thermoset composites, but they also exhibit a higher toughness and easier recyclability. The manufacturing processes available to date for thermoplastic matrix composites are, however, limited by the high melt viscosity of these matrices. Due to the latter, the impregnation process of the endless fibers becomes much more difficult, when compared to traditional thermosetting resins. Commonly used techniques include melt, powder or solvent impregnation or the use of commingled yarns. In this field, a lot of work has been done by various authors [1–3].

An alternate way to prepare thermoplastic composite materials is the use of ring-opening polymerization reactions in polymerization molding processes. A current example of a commercially available system to produce thermoplastic composite materials by liquid injection techniques is Cyclics' CBT resin (cyclic butylene terephthalate). When mixed with specific tin or titanium polymerization catalysts, the CBT-rings open and polymerize to form a high-molecular weight polybutyleneterephthalate (PBT) [4].

Another way to prepare thermoplastic composite materials is to use the ring opening polymerization reaction of lactam ring forming polyamides. The activated anionic polymerizations of lactams has been known since the 1940s, and a lot of different activating/initiating systems are described in the literature. Main applications of the anionic polymerization of ε-caprolactam is the reactive extrusion or the reaction injection molding (RIM) process. A commercially available system based on anionic lactam polymerization is the EMS Polymerization Molding System (EPM), consisting of two components, a liquid activator and the molten lactam. The two components are being mixed within a mixing head before entering the mold. The polymerisation starts immediately upon contacting initiator and lactam monomer [5]. Using the EPM system, basic studies on the compatibility of differently treated carbon fiber (CF) and the *in situ* PA12 system have been done by the authors earlier [6]. Moreover, general studies concerning processability [7–9] and first applications in thermo-forming were published by other groups [10].

The objective of this study was to explore the fast anionic LL polymerization from Atofina, using sodium hydride as an initiator and *N*,*N*′-ethylenebisstearmide (EBS) as an activator in liquid injection molding fabrication of high-performance thermoplastic CF composite materials. In contrast to the EPM, this novel initiator system affords stable mixtures of the sodium LL anion together with EBS at 170°C, which can be fed without premature polymerization because the polymerization requires temperatures well above 200°C [11]. The initial low viscosity of the lactam melt should allow an easy and complete impregnation of carbon fiber

fabrics in the mold. Due to the high speed of the polymerization, the reaction should be finished within minutes resulting in a high-molecular weight polyamide. Since anionic lactam polymerization is very sensitive to impurities resulting from CF pretreatment, it is important to carefully select appropriate carbon fibers which do not interfere with polymerization as reflected by build-up of residual lactam monomer.

EXPERIMENTAL

Materials

The Lauryllactam (LL) and EBS were supplied by ATOFINA (France). For further processing, the lactam was used as received and the EBS was dried for 24 h in a vacuum at 60°C. The Sodium Hydride (NaH, Aldrich) was used without further purification. Figure 1 shows the schematic of the anionic LL polymerization; the complete reaction mechanism is described in [12]. For comparison reasons, a second anionic polymerizable laurolactam system from EMS-Chemie AG, Switzerland, was used. It consisted of laurolactam and a novel liquid activator system named Grilonit LA, containing both activator and catalyst. The amount of Grilonit used in this study was 2.5 wt%.

The different CFs and their finishes are listed in Table 1. The PAN-based high-tenacity CFs which received different surface treatments or sizings are: (a) Tenax HTA 5N21 (standard oxidative treatment with PA12 compatible sizing), by Tenax Fibers GmbH & Co. KG (Wuppertal, Germany); (b) Zoltek (surface treated) and Zoltek N-11 (surface treated with PA12 compatible sizing), both delivered from Zoltek Rt. (Nyergesújfalu, Hungary); (c) Sigrafil C40 00B (unsized, untreated) and Sigrafil C40 PAB-1 (surface treated with Polyamide sizing), delivered by SGL Carbon Group (Meitingen, Germany). For producing a laminate by film stacking in an autoclave, a 2/2 twill fabric based on the Tenax HTA 5N21 (6 k) fiber was used. The fabric used in the final injection process was a 2/2 twill fabric made of a standard epoxy sized 3 k-roving. The fabric was thermally desized using radiant heaters. The release agent used in the mold was commercially available Teflon spray.

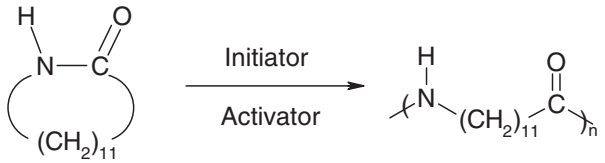

Figure 1. *Schematic of anionic polymerization of PA12.*

Table 1. Differently treated carbon fibers and coding.

Fibre	Fiber code	Fibre finish
Zoltek tr., n.siz.	Zol-oxy	Surface treated
Zoltek, tr., N-11	Zol-PA	Surface treated with PA12 compatible sizing
Tenax HTA 5N21	Ten-PA	Standard oxidative treatment with PA12 compatible sizing
Sigrafil C40 00B	SGL	Unsized, untreated
Sigrafil C40 PAB-1	SGL-PA	Surface treated with PA sizing

Processing

Preliminary experiments on the anionic LL polymerization with the described initiator/activator system were carried out in an internal mixer. The reaction mixtures were prepared in a 250-mL round bottomed flask equipped with a magnetic stirrer and a nitrogen inlet. The polymerization reactions were performed in an Haake Polylab twin-screw internal mixer equipped with a 60-mL mixing chamber. After stirring for about 30 min under an inert atmosphere, the melt was poured into the 270°C hot mixing chamber. Polymerization was performed at a rotational speed of the screws of 60 rpm. When the torque reached a maximum the samples were quickly recovered and quenched between metal plates. In case of producing PA12 with reinforcement, namely the differently treated CFs, the CF were dried (vacuum overnight), chopped and put into the mixer before. Due to the maximum torque of the mixer, a fiber volume content of up to 25% could be realised.

A pilot plant for the liquid injection of lactam was constructed and the setup is shown in Figure 2. The melting of the reaction mixture took place in an electrically heated 10-L flask while being stirred under an atmosphere of nitrogen using a mechanical stirrer. Then the mixture was transported within heated tubes (under the force of a gear pump) into the mold. The mold itself was vented and designed as a negative mold with a linear gate (see Figure 2); it was placed between the heating surfaces of a hydraulic press (Polystat 200T, Schwabenthan). The clamping pressure amounted 10 bar, at a mold temperature of 270°C. After the injection process and a given period of 10 min for polymerization, the mold was cooled with water before the final plates were removed.

Testings

The residual monomer content was determined by means of a thermogravimetric analysis (TGA), using a Netzsch STA 409. All TGA

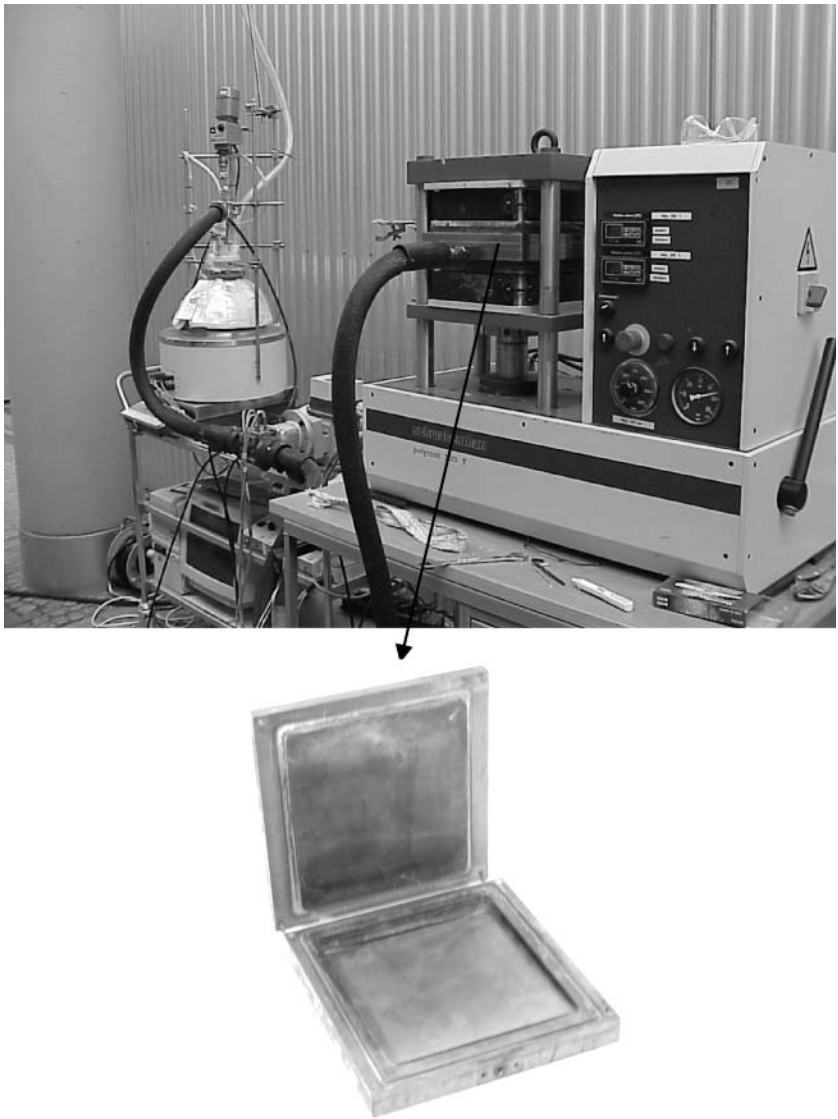

Figure 2. *Experimental setup in laboratory scale, specially designed negative mold.*

measurements were taken under a nitrogen atmosphere. The temperature was increased from 30 to 750°C, and the loss in weight within the temperature range of 185–350°C was attributed to the amount of unreacted LL. Figure 3 shows exemplarily a TGA plot of the pure PA12 system.

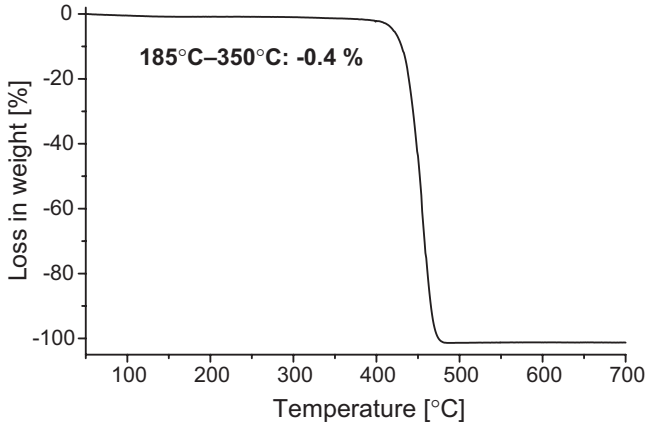

Figure 3. *TGA plot to obtain RMC.*

As unreacted fiber sizing would decompose before 185°C the temperature limits of 185 and 350°C were chosen. Further, comparative measurements were carried out on the monomer itself which exhibits a melting temperature of 151°C. Nevertheless, gel permeation chromatography (GPC) was conducted for a few specimens in order to check the suitability of the TGA measurements. The results were in good agreement with each other.

The laminates underwent both, mechanical testing and determination of density and crystallinity. The latter was obtained by differential scanning calorimetry (DSC) (−100 to 220°C, ramp 10°C/min; Mettler-Toledo DSC 821e). The measurement of the mechanical properties was limited to the flexural strength and modulus. In addition, dynamic mechanical thermal analysis (DMTA) experiments were conducted on an EplexorTM 150 N (Gabo Qualimeter). Viscoelastic material parameters such as mechanical loss factor and complex tensile Young's modulus ($\tan\delta$ and E^*, respectively) were determined in three-point bend loading over a broad temperature range (−100 to +200°C) at a heating rate of 1°C/min and a frequency of 10 Hz.

RESULTS AND DISCUSSION

A typical polymerization sequence for both systems, Atofina and EMS, is shown in Figure 4. In case of the Atofina system (Figure 4(a)), the molten LL containing activator and initiator (160°C) were fed into the preheated internal mixer. After one minute the reaction mixture reached 270°C. The endothermic beginning of the reaction can be identified by the declining temperature. The torque starts increasing after approximately 1.25 min,

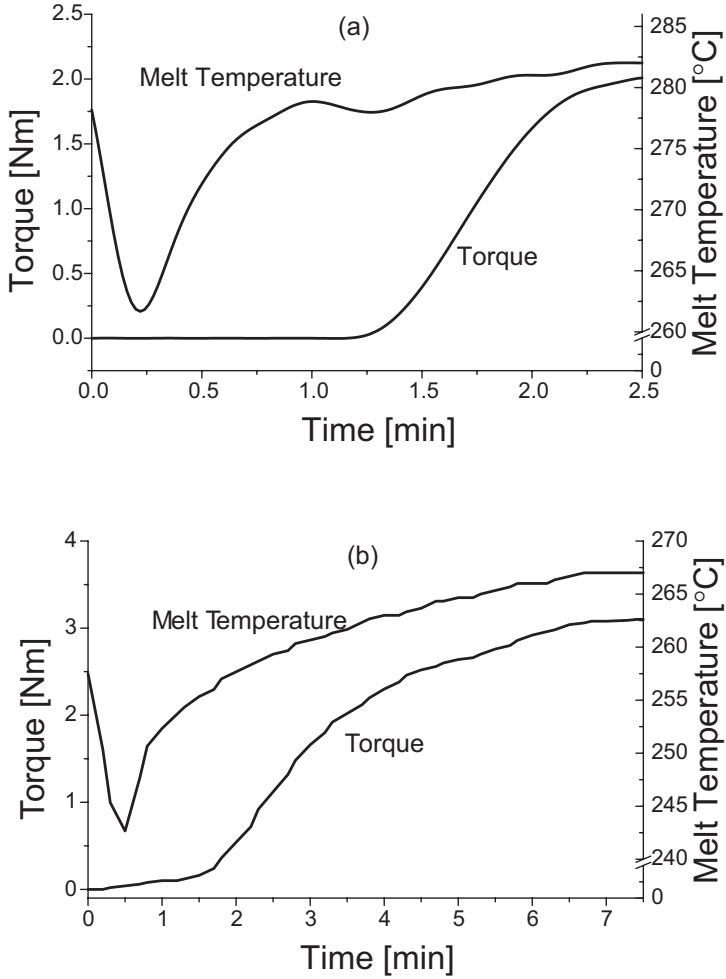

Figure 4. *Data plots from the internal mixer during polymerization process for (a) Atofina system and (b) EMS system.*

reflecting the rising melt viscosity which reaches a maximum after 2.5 min. Then, the polymerization was stopped by turning off the internal mixer. The residual LL monomer content of the resulting pure polyamide 12 was usually less than 0.5%. Having a closer look at the EMS system (Figure 4(b)), it can be explicitly recognised that the polymerization starts almost immediately after feeding the mixer. Then, the viscosity increased continuously, and the polymerization finished after 7 min. A further interesting aspect is the increasing temperature profile parallel to the torque. This could likely be an

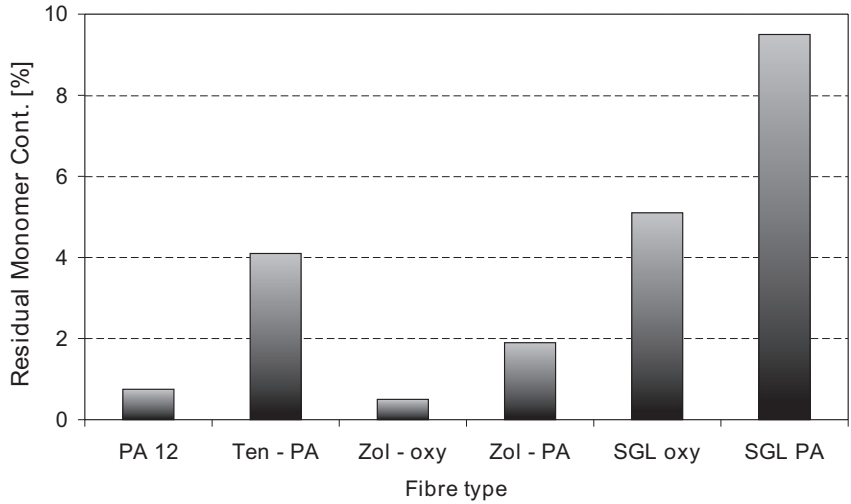

Figure 5. *Results of residual monomer content measurements.*

effect of exothermic reactions due to the activator liquid. Besides, the residual monomer content of the PA12 was around 2.25% in average.

The next step was to (a) add the different CFs and (b) have a look at as to what extent the residual monomer content (RMC) responds. Figure 5 shows the measured RMC values for the differently treated CFs used. Compared to the results in [6], where the EMS system was investigated in the same way, the RMC values for the Ten-PA could be reduced by more than 50%. On the other hand, the SGL-PA shows the reverse effect. Nevertheless, using the Atofina system, we can conclude that for the oxidised fiber types, lower RMC values can be reached than for the sized ones. This fact does not agree with the results measured for the EMS system [6].

With regard to the adhesion between the fibers and the matrix, SEM pictures of flexural loaded cryogenic fracture surfaces were analyzed. Figure 6 shows exemplarily the Zoltek fiber types, oxidized and sized. It is doubtless, that the Zol-oxy fiber exhibits a better adhesion to the PA12 matrix. This behavior could be also observed for the other fiber types. The sizing, however, has a large effect and seems to disturb the polymerization. As a consequence of this result, the standard epoxy sized fiber fabrics, which were used in the injection process, were de-sized before placing them into the mold.

The injection process itself was carried out with the laboratory setup described above, and it was possible to produce laminates using the Atofina system and the thermally desized 2/2 twill CF fabrics. Figure 7 shows cross

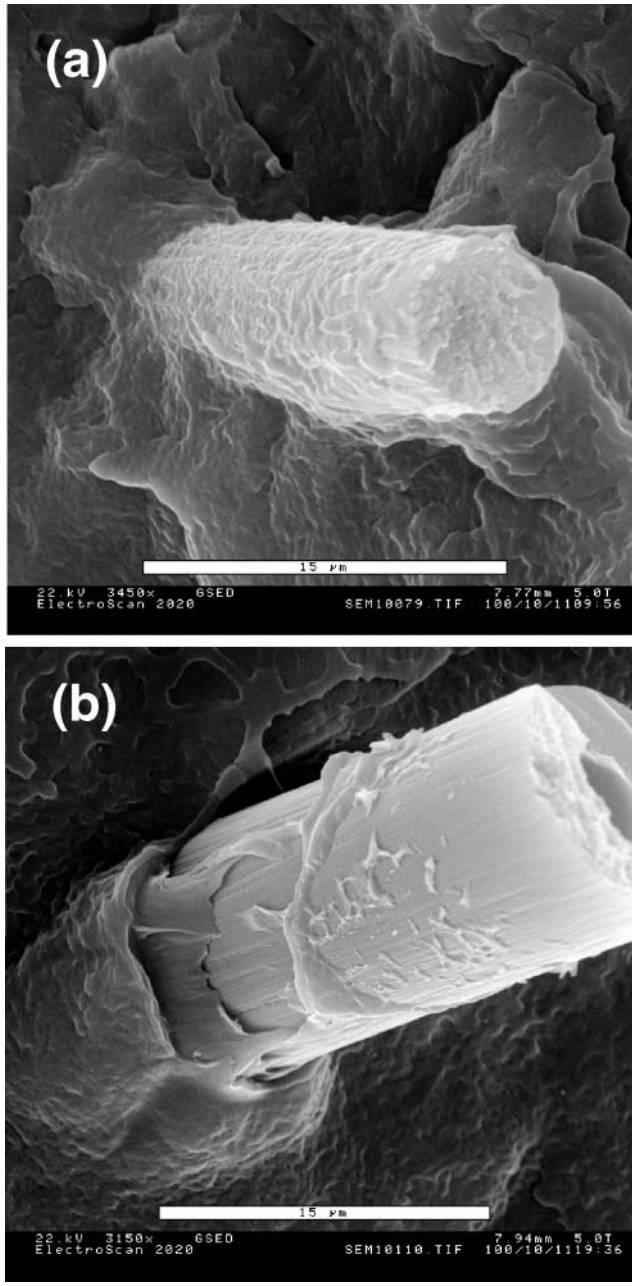

Figure 6. *Scanning electron microscopy pictures of (a) oxidized (Zol-oxy) and (b) sized (Zol-PA) fiber types.*

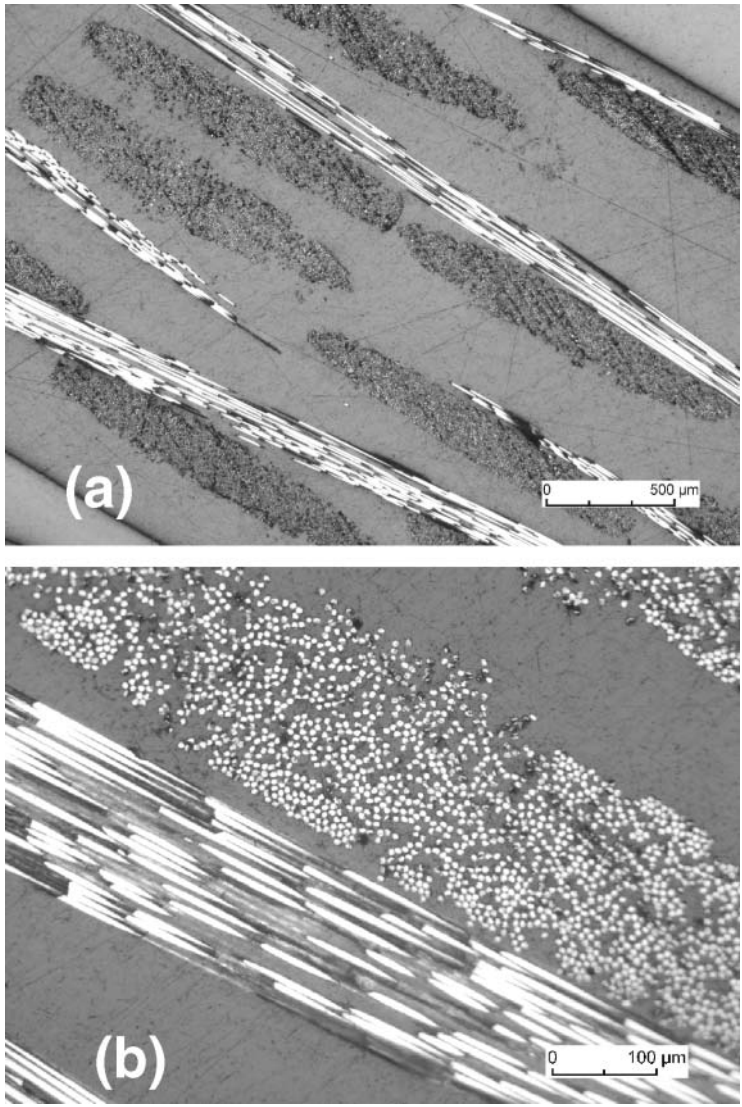

Figure 7. *Light microscopy pictures of cross section of Atofina composite: (a) full laminate; (b) magnification to see fiber bundle.*

sections of the resulting laminates, as recorded by reflected light microscopy. As it can be seen on the laminate with 30% fiber volume content, the global (Figure 7(a)) and local (Figure 7(b)) impregnation quality was excellent; even the very fine (3 k) fiber bundles were very well impregnated due to the

Table 2. Macromechanical properties of different composites.

	EPM	Autoclave	ATOFINA
Fibre volume content (%)	54	54	30
Flexure strength (MPa)	321.2	352.5	311
Flexure modulus (GPa)	37.8	39.1	21.2
Density (g/cm^3)	1.44	1.40	1.21
Crystallinity (DSC) (%)	52	44	29

low viscosity of the melt. Moreover, the RMC of this composite was 0.9% and thus still satisfying.

At this stage, it is also worth mentioning that the polydispersity remained narrow and was independent from the production process, i.e. it was approximately 2 for the internal mixer samples as well as the injected laminates.

The macromechanical properties of the Atofina laminate (as produced by the injection process described before) in comparison with two other laminates is shown in Table 2. On the one hand, the results of a laminate produced by EPM containing a 2/2 twill CF fabric with 54% fiber volume fraction are shown. On the other hand, a laminate produced by PA12-film stacking (conventional PA12 film) in an autoclave, using the same fabric as EPM did and resulting in the same fiber volume content, was chosen as a reference. Comparing the flexural strength data, the Atofina laminate was almost on the same level as the reference material, although it contained 20% less fibers. This fiber minority can, however, be noticed at the flexural modulus values.

In addition, the differences in density and crystallinity are quite remarkable. Apparently, these phenomena do not have a great influence on the damping behavior of the laminates as determined by DMTA measurements (Figure 8). Of course, the higher complex modulus can be again explained due to the higher volume content of the reference composites.

Finally, we like to refer the importance of a good impregnation and its effects on the impact behavior. For this reason, plates were impacted (low velocity) by different energies (1, 2, 4, 5, 10 and 20 J, respectively) so that Barely Visible Impact Damage (BVID) could be generated [13,14]. The impact-induced delaminations can be ascribed to global bending [15]. Moreover, the size of the delamination area is a function of the material properties (especially their elastic constants) and the thereby occurring interlaminar tension distributions [15]. As it is well known that energy transfer in CF–polymer composites is due to the interface, consequently, more energy can be absorbed due to weak interfaces and results in a bigger debonding area. This was studied and verified by fracture mechanics [16].

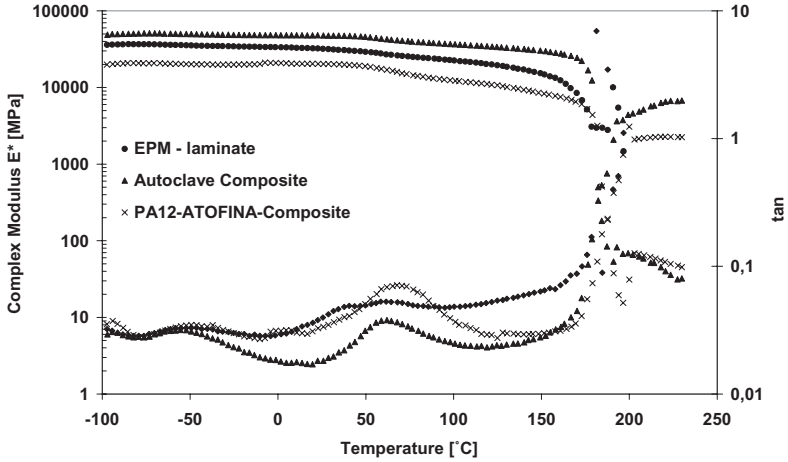

Figure 8. *DMTA results for different composites.*

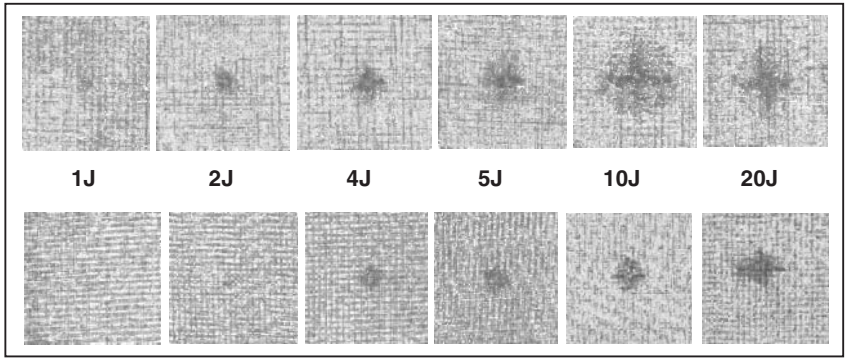

Figure 9. *C-scan of plates impacted with increasing energies: top row – autoclave composite; bottom row – EPM composite.*

Figure 9 illustrates the C-scans of the two different composites with exactly the same fabric and fiber volume content. The failure area of the autoclave composite is bigger than that of the EPM composite at every energy step. This means, that the EPM laminate shows a stronger fiber–matrix interface and thus a better adhesion to the PA12 due to the liquid molding technique. With this example, we would like to point out, that the thermoplastic liquid molding technique opens a new path in order to tailor composites for specific applications.

CONCLUSION

A new polymerization molding technology based upon the anionic LL polymerization by means of the Atofina initiator/activator system was introduced for the fabrication of thermoplastic polyamide 12 (PA12)-based high-performance composite materials with CF reinforcement. The system can be characterized as reliable and with rather good reproducibility. At a polymerization temperature of 270°C, the polymerization reaction is completed within some minutes and the composite materials obtained possess a high molecular weight PA 12 matrix, having only a very small content of residual monomer. Compared to the EMS *in situ* PA 12 systems, an immense advantage is that the polymerization mixture is stable at the melting temperature of the LL for prolonged periods of time. Due to this fact, only one storage tank is sufficent and no mixing devices are needed. Therefore, this system is much more attractive from an engineering point of view because it requires less maintenance and offers an easier handling. A pilot plant for the liquid injection of lactam was constructed and composite materials were produced, showing similar mechanical properties as known from commercially available systems. Moreover, the new PA 12 system is less sensitive to fillers in general, which could be investigated by inspection of the adhesion quality and compatibility to differently sized CFs.

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