

THE BIODEGRADATION BEHAVIOR OF THE SILOXANE/POLYCAPROLACTONE COMPOSITE

Fortună Maria Emiliana¹, Ignat Maria^{1,2}, Ungureanu Elena², Bogdan-Marian Tofanica³, Rotaru Razvan¹, Harabagiu Valeria¹

¹, „Petru Poni” Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, Iasi 700487, Romania

²“Alexandru Ioan Cuza” University of Iași, Faculty of Chemistry, 11 Bd. Carol I, 700506 Iași, Romania

³“Ion Ionescu de la Brad” Iasi University of Life Sciences, 3 Mihail Sadoveanu Alley, 700490 Iasi, Romania

Introduction and Aim

To obtain composite materials using epoxy-functional siloxanes, direct amine addition to epoxy groups is thought to be a particularly useful approach for crosslinking epoxy, and they are used as the most popular curing agents.

In this study, we have focused on an epoxy–siloxane amine composite obtained by the reaction between 1,3-Bis(3-glycidyloxypropyl)tetramethyldisiloxane (DS-PMO) and an aromatic amino compound, p-Phenylenediamine (PPDA). Two stages were involved in the preparation of the epoxy–siloxane amine composites. In the first stage, the hydrosilylation reaction between allyl glycidyl ether (AGE) and 1,1,3,3-tetramethyldisiloxane (TM-DS) was performed in the presence of a Karstedt catalyst, resulting in the glycidoxypolydisiloxane (GP-DS) intermediary compound. In the second stage, the GP-DS derivative was modified with PPDA to obtain the epoxy–siloxane amine composites (PP-DDS).

The polymers' structures were confirmed by FTIR, ¹H-NMR, MS spectroscopy. The morphology and surface chemical compositions were highlighted using scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX). The samples were subjected to thermal investigations using thermogravimetric analysis (TGA) as well as advanced thermogravimetric analysis, namely TGA/FT-IR/MS. In addition, the optical properties and static contact angle of precursors and synthesized sample have been investigated. The results showed that modifying epoxy-siloxane with p-Phenylenediamine allows for the production of hybrid materials with very good thermal stability, and it can also be recommended to use the PPD-DS composite material for UV-based applications.

Methods

FT-IR spectra of the PP-DDS composite and of the DS-PMO and PPDA precursors were obtained using a Nicolet 60 SX (Thermo Scientific) Fourier transform spectrophotometer equipped under dry air, at room temperature, on KBr pellets. Mass spectrometry analysis was carried out on a Bruker UltrafleXtreme MALDI-TOF/TOF mass spectrometer equipped with a Nitrogen laser and operated in the positive ion mode.

¹H-NMR spectra were recorded using a Bruker Avance NEO 400 MHz spectrometer, equipped with a 5 mm inverse detection, z-gradient, multinuclear probe. The morphology and content of materials were investigated with scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX). Thermogravimetric analysis (TGA) coupled with FTIR spectroscopy was made using a STA 449 F1 Jupiter apparatus (Netzsch-Germany) coupled to a Vertex 70 spectrophotometer (Bruker) and Aeolos QMS 403C mass spectrometer (TG/DTA/FT-IR/MS).

Results and Discussion

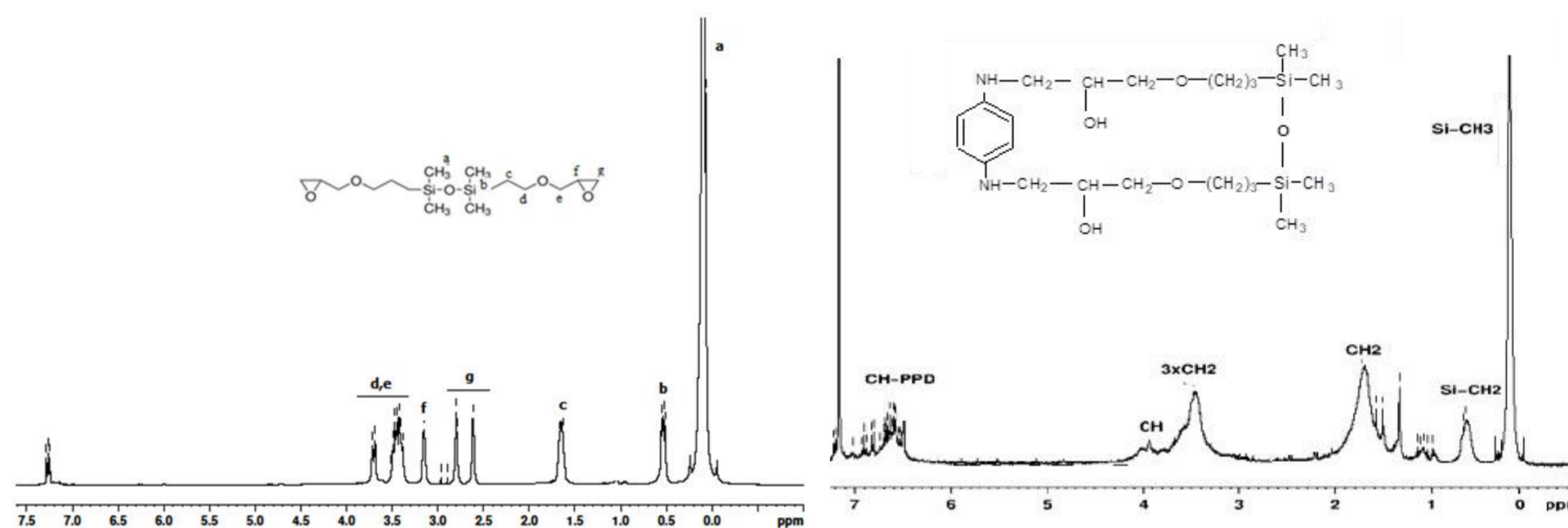


Figure 2. ¹H-NMR spectrum for DS-PMO and PP-DDS composite at 400 MHz, in CDCl₃

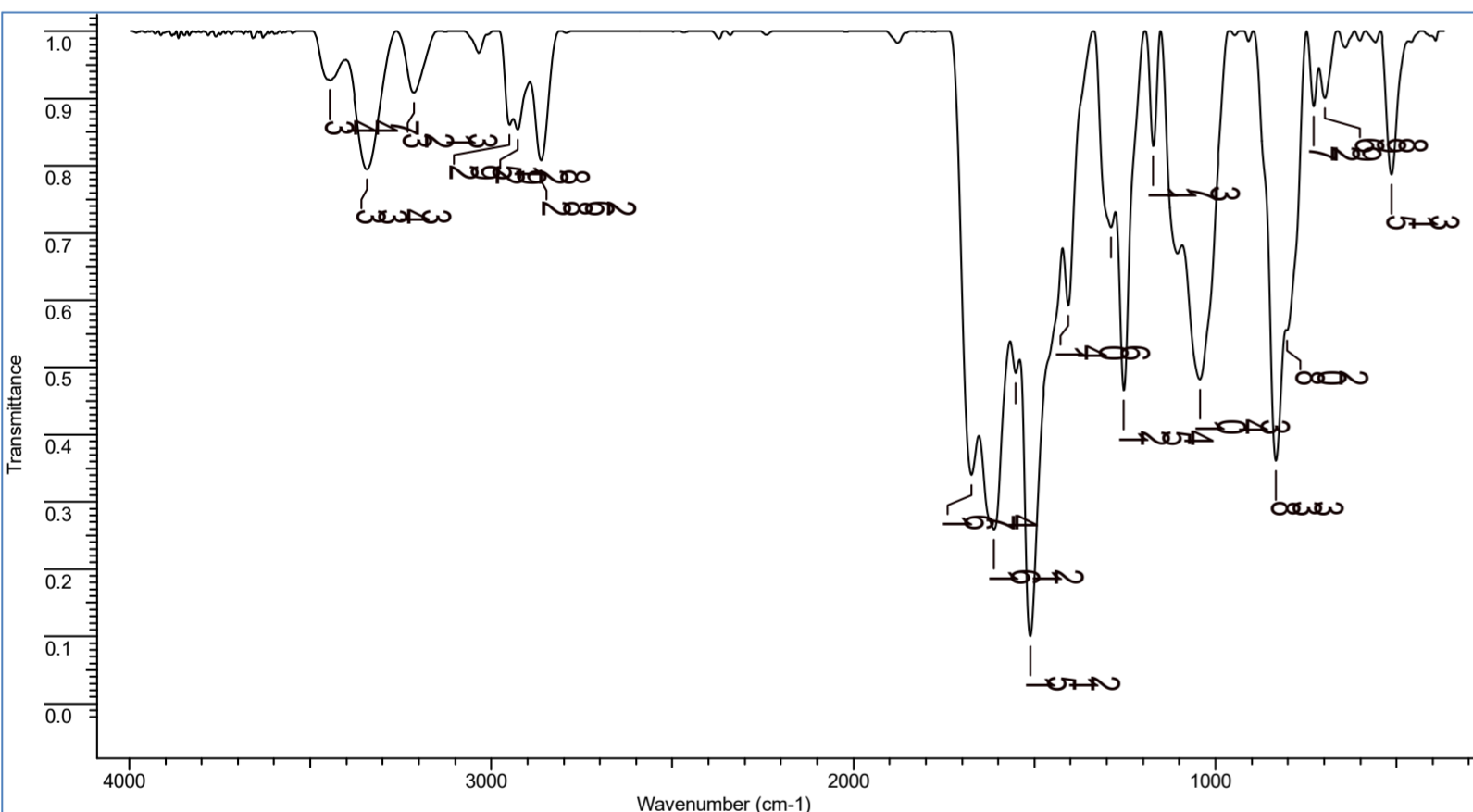


Figure 1. IR spectrum for PP-DDS composite

PP-DDS composite presents characteristic bands (asymmetric Si–O–Si stretching vibration overlapped with C–O–C vibration at 1043 cm⁻¹, symmetric deformation/rocking vibrations of the Si–CH₃ group at 1254 cm⁻¹ and Si–CH₃ stretching vibration at 833 cm⁻¹). Aromatic C–H stretching vibration is seen at 3213 in PP-DDS. The N–H stretches of amines (3447 cm⁻¹ and 3343 cm⁻¹) and N–H bending vibrations of primary amines (1674 cm⁻¹) indicate a strengthening of the N–H bond. The –NH₂ deformation mode is observed at 1612 cm⁻¹. Epoxy characteristic band of DS-PMO at 910 cm⁻¹ disappeared in the FT-IR spectrum of PP-DDS composite, which means the epoxy-ring opening in the synthesis reaction of the hybrid siloxane material.

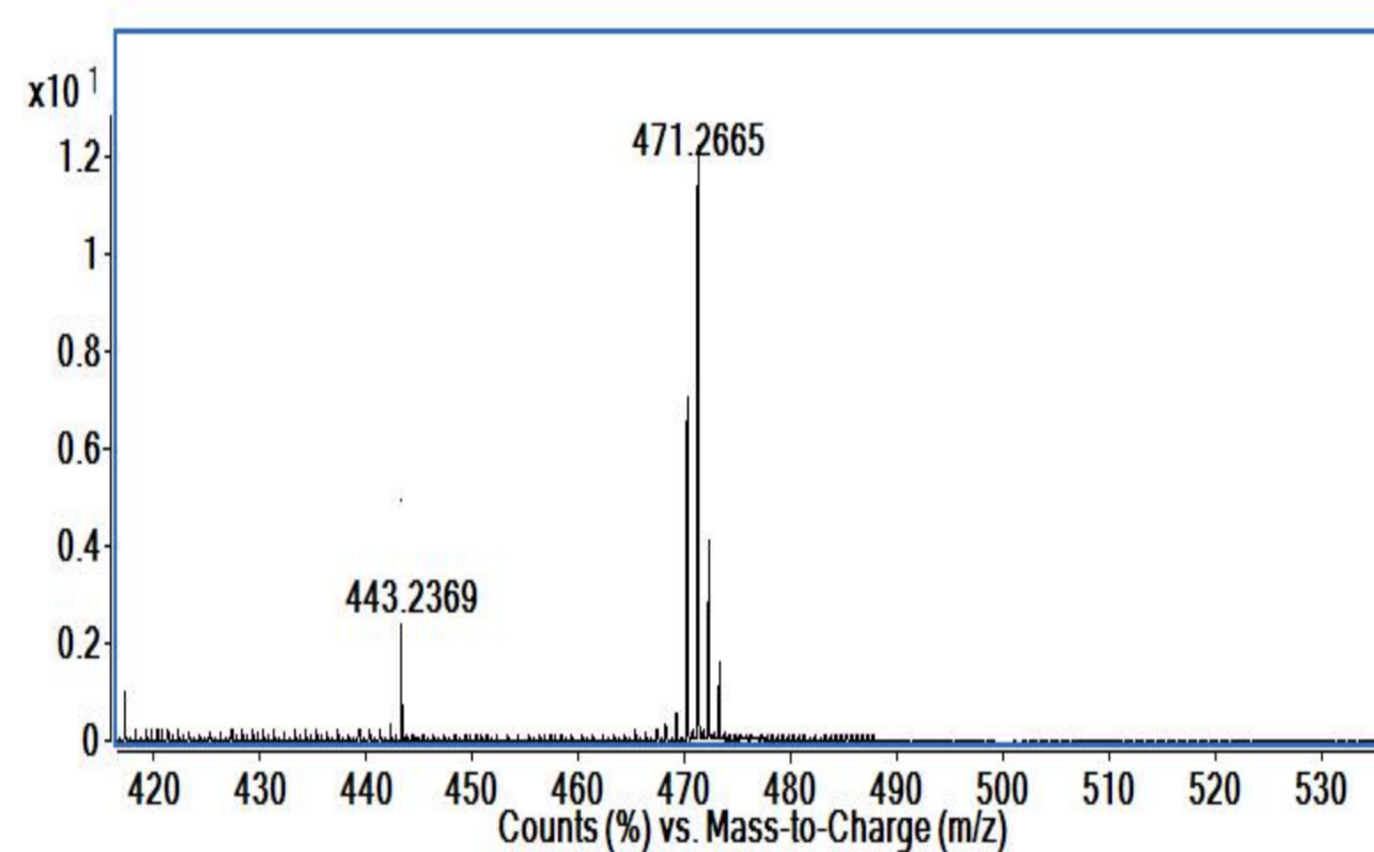


Figure 3. ESI-MS spectrum of the PP-DDS

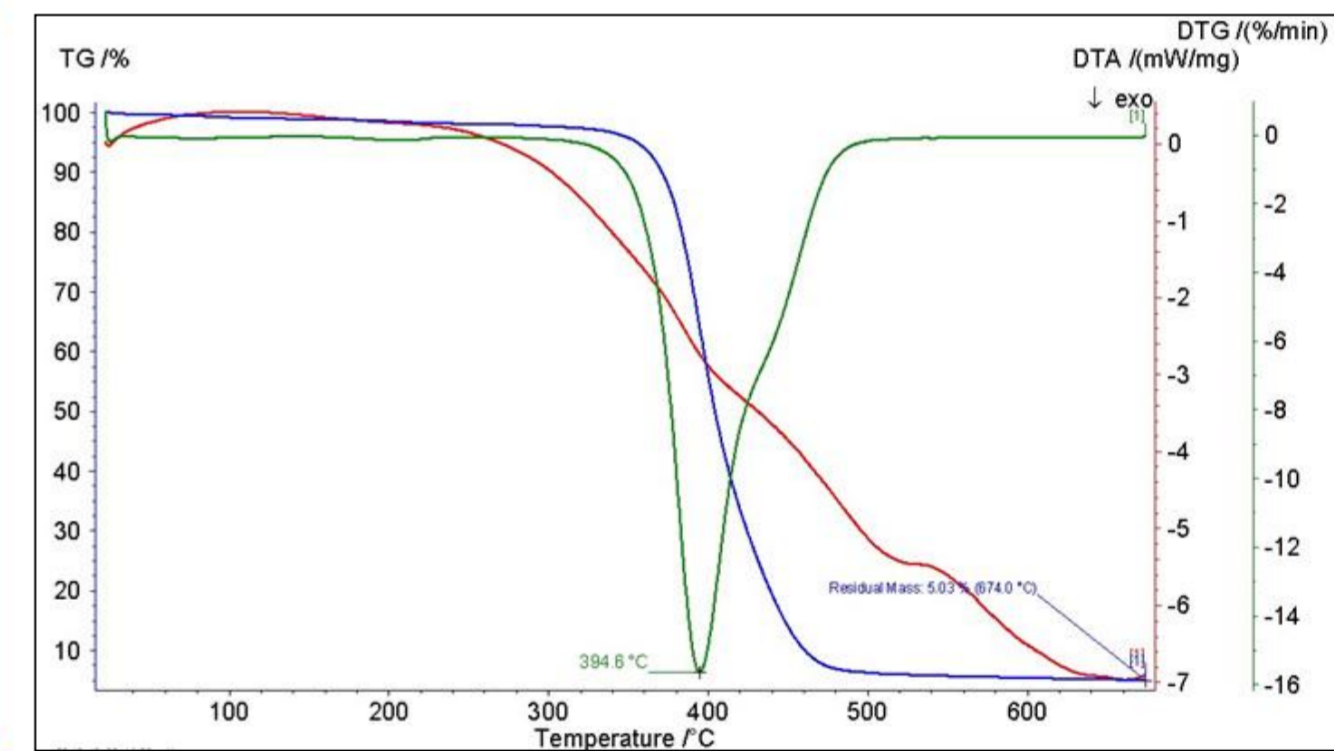


Figure 4. TG, DTA and corresponding DTG curves for PP-DDS

Table 1. Thermal parameters

Sample	Heating rate °C/min	Degradation stage	T _{onset} DTG °C	T _{peak} °C	W %	T ₁₀ °C	T ₂₀ °C	GS °C
PP-DDS	10	I II residue	- 363	- 395	1.23 93.74 5.03	371	383	390
DS-PMO	10	I residue	287	337	99.88 0.12	270	292	-
PPD	10	I residue	204	237	98.82 1.18	187	203	-

Tonset – the temperature at which the thermal degradation starts; Tpeak – the temperature at which the degradation rate is maximum; T10, T20, - the temperatures corresponding to 10 % and 20 % mass losses;

CONCLUSION

Using the NIST database, it was possible to assign the following chemical structures: water (H₂O⁺, m/z = 18, 17, 16); carbon dioxide (CO₂⁺, m/z = 44, 28, 16, 12); carbon monoxide (CO⁺, m/z = 28, 16, 12); aliphatic derivative, as methane (CH₄⁺, m/z = 16, 15, 14, 13, 12); ethane (C₂H₆⁺, m/z = 30, 29, 28, 27, 26, 25, 15); propane (C₃H₈⁺, m/z = 44, 43, 41, 39, 29, 28, 27, 26, 15); propanal (C₃H₆O⁺, m/z = 58, 57, 39, 29, 28, 27, 26); benzene (C₆H₆⁺, m/z = 78, 77, 74, 52, 51, 50, 49, 39, 38); propyl amine (C₃H₉N⁺, m/z = 59, 41, 30, 28); methyl propyl ether (C₄H₁₀O⁺, m/z = 74, 45, 41, 29, 27, 15); ethyl ether (C₄H₁₀O⁺, m/z = 74, 59, 45, 31, 29, 28, 27, 15); 1,1,3,3-tetramethyl disiloxane (C₄H₁₄OSi₂⁺, m/z = 134, 133, 120, 119, 103, 73, 59, 45); dimethylethyl silane (C₄H₁₂Si⁺, m/z = 88, 87, 73, 59, 58, 45, 43, 31, 29).

Amine functional siloxanes were synthesized from 1,3-bis(glycidoxypoly) tetramethyldisiloxane and para-phenylenediamine. The structure was determined by FTIR, ¹H-NMR, MS spectroscopy. Determination of the chemical structure of the products resulting from the thermal degradation was based on the molecular weight of ionic fragments identified from the MS spectra. The results of the MS spectra are in good agreement with the FT-IR data. The TG curves of PPDA and DS-PMO show a sudden and rapid degradation while the PPD-DS presents a wide thermal degradation process at high temperature and lower speed which makes them more thermally stable.

1. Fortuna Maria Emiliana, Nita Tudorache, Rotaru Razvan, Nicolescu Alina, Harabagiu Valeria

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