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Development of Self-Healing Thermoplastic Composites With Reactive Thermoplastic Agent-Filled Macrocapsules

Eslem Şahin[1,2] | Yalçın Boztoprak[3] | Murat Yazıcı[1]

[1]Applied Mechanics and Advanced Materials Research Group (AMAMRG) Lab., Automotive Eng, Bursa Uludağ University, Bursa, Türkiye | [2]Mudanya University, Bursa, Türkiye | [3]Marmara University, Metallurgical and Materials Eng. Department, Istanbul, Türkiye

Correspondence: Murat Yazıcı (myazici@uludag.edu.tr)

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ABSTRACT

Self-healing materials, which introduce a new approach to innovative materials, can aid in the repair of polymers and composites, leading to the development of more durable and reliable products. In polymer matrix composites, healing micro- or macrocracks helps to eliminate structural defects. A reactive healing agent and curing agent distributed within the thermoplastic matrix can react at the crack site, providing repair without external intervention. Acrylic resin and polypropylene were selected for this study to evaluate the potential of healing in industrial thermoplastics. Capsules filled with a reactive agent containing 3% by weight diethylenetriamine (DETA) were embedded in the matrix. When damaged, these capsules broke, and the liquid agents seeped into the cracks through the filling voids. The reaction released immediate heat, initiated curing, and filled the damaged area. Complete curing occurred after 8 h. The energy absorption of specimens in both damaged and undamaged states was observed through compression testing. The heat generated by the agents flowing from the capsules during the compression test was monitored using a thermal camera. This study offers a new perspective on using reactive thermoplastic resins to develop self-healing composite materials.

1 | Introduction

In recent years, significant advancements have been made in the durability and reliability of structural materials. The development of next-generation composite materials has further enhanced these advancements. Self-healing materials are one of these advancements and represent an important technological area with the potential to extend the lifespan of structures. Repairing polymers and composites constitutes significant research in this field [1–3].

Self-healing materials present an innovative approach to enhancing the durability of materials by autonomously repairing surface cracks [4, 5]. Research in this area aims to provide more effective and efficient solutions than traditional repair techniques. Since the pioneering work by White et al. [4], various methods have contributed to the quality and preparation processes of self-healing polymers [6–9].

Polymer matrix composites (PMCs) consist of at least two phases: a continuous phase and a reinforcement material. The continuous phase is composed of a polymer, while the other phase consists of fibers or additives dispersed throughout the matrix. The polymer continuous phase fills the volume and transmits loads to the reinforcement phase. The reinforcement phase, also known as the dispersed phase, is responsible for enhancing the properties of the matrix, that is, the continuous phase. Due to their lightweight structure, excellent processability, chemical stability under various atmospheric conditions, and superior mechanical properties, polymer matrix composites find wide application in the automotive, construction, aerospace, defense, maritime, and energy sectors. The volume fraction and orientation of the reinforcement material determine the properties of these composites. The reinforcement material significantly impacts the improvement of various properties such as stiffness, strength, durability, and thermal conductivity of the composite [7]. However, the long-term durability of polymeric materials in structural applications remains challenging. Exposure to different environmental conditions can lead to the rapid degradation of polymeric components. Microcracks that develop during service life can cause significant issues and catastrophic material damage, resulting in the failure of structures and can significantly shorten its lifespan [10, 11].

In recent years, research on autonomously self-healing polymer materials has accelerated significantly. Self-healing thermosetting and thermoplastic polymers have significant differences in their mechanical properties, healing mechanisms, and industrial applications. Thermosetting polymers with a high degree of crosslinking cannot remodel when heated. Therefore, autonomous strategies such as microcapsules [12–15], or vascular systems usually realize self-healing in these systems [16–18]. In these structures, the healing agents embedded in the matrix are released when damage occurs and react at the crack sites [19]. In addition, thermoset systems containing dynamic covalent bonds or weak physical interactions have been developed in the literature in recent years; thus, local healing can be achieved, albeit limited [20, 21]. Studies have shown that these systems provide a certain degree of healing while mostly maintaining mechanical integrity. The main advantage of thermoset systems is their high-temperature resistance and excellent structural stability. However, due to the rigid matrix structure, the healing agents cannot sufficiently diffuse into the cracks or integrate into the matrix, limiting the healing efficiency [22].

Since thermoplastic polymers can soften and reform when heated, intrinsic healing mechanisms emerge in self-healing processes. Hybrid systems with low melting temperature thermoplastic additives have made it possible to cure even thermoset matrices by thermal activation [23, 24]. In addition, mechanical properties can be recovered in thermoplastic systems designed with dynamic covalent chemistry or supramolecular interactions, and repeated recovery can be realized [25].

Applicable self-healing strategies for thermoplastic materials, which have an important place in industrial applications, are under development. Although thermoplastic healing systems are effective, they are limited by the need for external activation to melt the thermoplastic material [26]. Unlike thermosets, thermoplastics can be healed through molecular recombination processes [1]. Thermoplastic polymers used as healing agents have been employed in advanced composite structures since 2008 [9]. Early attempts in this direction included manual processes such as heating above the glass transition temperature, welding, or applying solvents [27, 28]. Studies have incorporated encapsulated solvents or plasticizers into thermoplastic polymers to achieve healing at room temperature without manual intervention. One approach developed in these studies involves a matrix filled with monomer-loaded microcapsules as the healing agent and a thermoplastic polymer as the matrix [29]. In this system, the healing agent acts as a solvent and a reactive chemical that can polymerize with the matrix. This application, which involves both physical interaction and chemical bonding, has demonstrated the recovery of mechanical strength. However, these methods present certain challenges when it comes to practical application.

Reactive thermoplastic resins acquire self-healing properties through the presence of reactive monomers dispersed within the thermoplastic polymer matrix. In case of material fracture, these resins can autonomously recombine at the crack site by reacting with the surrounding polymer chains or other reactive agents, thereby restoring the mechanical integrity and preventing further propagation of the crack [15]. The use of reactive thermoplastic acrylic resin, which possesses an independent healing mechanism, is among the innovative methods being explored. Capsules, a successful and versatile approach within autonomous healing methods [30–34], have been developed in macro, micro, and nano sizes containing healing agents [35, 36]. When the material containing these capsules breaks or cracks, the resin within the capsules disperses into the matrix. Remaining in liquid form below the usage temperature, it can quickly fill the void created by the crack. Healing agents that infiltrate microcracks formed due to mechanical damage such as tensile loading, fatigue loading, and impacts play a crucial role in restoring the mechanical properties of the material [37].

The self-healing properties of thermoplastics are typically enhanced using methods such as microcapsule technology, microdroplets, or specialized polymer layers. Materials like polypropylene [38], polyamide [39], polyurethane [40], polyethylene [6, 41], and polymethyl methacrylate (PMMA) [42, 43] form the basis of these studies. Self-healing polymers and composites containing microencapsulated healing agents exhibit high levels of healing efficiency under both static and dynamic loading conditions [44–47].

Polymethyl methacrylate (PMMA), one of the significant industrial polymers, is an amorphous polymer known for its durability, low moisture absorption, and high dimensional stability. PMMA is preferred for its lightweight and impact-resistant structure, easy processability, and high chemical resistance, although it has limited resistance at high temperatures. In some studies where PMMA is used as the matrix, it has served as a liquid healing agent [42, 43]. Additionally, heat and light-sensitive methods have also been employed. Thermal effects on the material surface can trigger automatic repair of cracks [48–52]. Polypropylene (PP), widely used in industrial applications for its high strength and low density, is also a subject of self-healing research. For instance, studies have been conducted on autonomous repair in PP matrix composites incorporating microcapsules and fiber reinforcements [44–47].

The healing of a polymeric material involves the recovery of properties such as fracture toughness, tensile strength, surface smoothness, and molecular weight [53]. Healing efficiency can be determined through mechanical testing [54–58]. Macrocapsules filled with healing agents break upon impact, releasing the agents. The resin, acting as the healing agent, releases into the crack, facilitating the repair of the damage. Healing efficiency can be calculated using Equation (1) [42, 59–61]:

$$\eta = E_{healed} / E_{virgin} \quad (1)$$

where, η represents the healing efficiency, E_{virgin} and E_{healed} show the energies of the undamaged and postdamage healed specimens, respectively (either the energy at peak load or the total absorbed energy) [62–64].

With all these developments, the structural limitations of materials in self-healing composites make the effectiveness of the healing mechanism difficult due to reasons such as restricted chain movements, interfacial incompatibilities [65–67].

Self-healing polymers are attracting attention, particularly for their potential to reduce maintenance requirements and extend the service life of materials. Their ability to self-repair damage without external intervention increases the service life of the material and ensures structural safety in critical sectors such as automotive and aerospace. In the automotive sector, the use of such materials can enable the part to recover its mechanical properties after damage, increasing its lifetime and minimizing repair costs. In the aerospace industry, considering that materials operate under extreme temperature variations and high mechanical stresses, different healing mechanisms can make significant contributions in terms of maintaining structural integrity by repairing microcracks at an early stage. In addition, there are studies on the use of these materials not only in structural applications but also in electronic devices and biomedical applications [18, 68]. Self-healing hydrogels developed especially for flexible electronics and the tissue sector have the potential to increase durability against effects such as abrasion and rupture in daily use and to mimic the healing processes in biological systems [69]. However, there are several challenges that limit the applicability of these technologies on an industrial scale. It therefore highlights the need for further scientific and technological research to integrate self-healing systems into industrial applications.

Ensuring both quality control and economic production in production processes is a significant challenge. The preferred curing strategy needs to be chosen in accordance with the nature of the material. It is important that the curing agents interact effectively with the matrix material, that is, interfacial compatibility. These interfacial interactions need to be designed in a chemically compatible manner in order for the healing efficiency to be high. Otherwise, the repair process may not be realized at the desired level and the recovery of mechanical properties may be limited [70, 71].

In addition, the long-term stability of the material against environmental conditions is another factor that directly affects the remediation performance. In particular, external influences such as humidity, temperature changes, and chemical environments reduce the effectiveness of some curing systems, making it difficult to sustain performance in applications operating in harsh conditions such as aerospace and automotive. Another limitation observed in many systems is the limited number of conditioning cycles. Systems such as capsules or hollow fibers can only be used once and lose the capacity to repair again after the initial retrofit. This limits the system's lifetime, especially in applications where impact, fatigue, and microcracks repeatedly occur [72, 73].

This is crucial, as numerous materials are prone to different types of degradation, resulting in economic losses and safety issues. This study focuses on the development of self-healing composite materials utilizing reactive thermoplastic resins, which are expected to substantially lower maintenance costs and enhance reliability. This field holds significant potential for improving structural durability and reliability, with anticipated critical applications across various industries in the future. This study investigates the impact of curing agent selection on the self-healing performance of composites, aiming to optimize healing efficiency shortly after damage occurs. It will focus on the role and potential of reactive thermoplastic resins in the production of self-healing composite materials.

2 | Materials and Methods

The acrylic resin used as the healing agent was obtained from Izel Kimya, Turkey (IZELCRYL 24T60), diethylenetriamine (DETA) from Sigma-Aldrich, United States (D93856), and methyl ethyl ketone (MEK) from Tekkim, Turkey (TK.050150.02501). Methyl ethyl ketone was used to dilute the acrylic resin with an average molecular weight of $M_w = 72.11\,\mathrm{g\,mol^{-1}}$. The macrocapsules consist of a polypropylene shell structure supplied by Sabic, Netherlands (108MF10).

2.1 | Preparation of Macrocapsules

Macrocapsules, a type of encapsulation method, are typically small spheres ranging in diameter from a few micrometers to a few millimeters, infused with innovative materials that enable them to repair damage in a structure autonomously. The fundamental principle involves the use of encapsulated reactive substances or polymers within these macrocapsules. When damage such as a crack or fracture occurs in a material, these macrocapsules rupture and release healing agents into the affected area, initiating a chemical reaction that repairs the damage.

The shell structure of the macrocapsules, with a diameter of 4 mm, was made of polypropylene. Inside these capsules, the acrylic resin as a healing agent (Figure 1a) and diethylenetriamine, which facilitates curing (Figure 1b), were added. The acrylic resin was diluted with MEK and then encapsulated within the shell. The amine was used as received.

The interiors of the filled PP macrocapsules were melted using a soldering gun, ensuring uniform wall thickness by emptying the spheres. The resulting hollow macrocapsules were filled with the healing agent and curing agent using an injector. The openings in the spheres were sealed by melting the matrix material PP (Figure 2). During the dilution stage of the acrylic resin, a physical mixture was formed. At this stage, MEK was used at a weight ratio of 10%. MEK allows the acrylic resin polymer

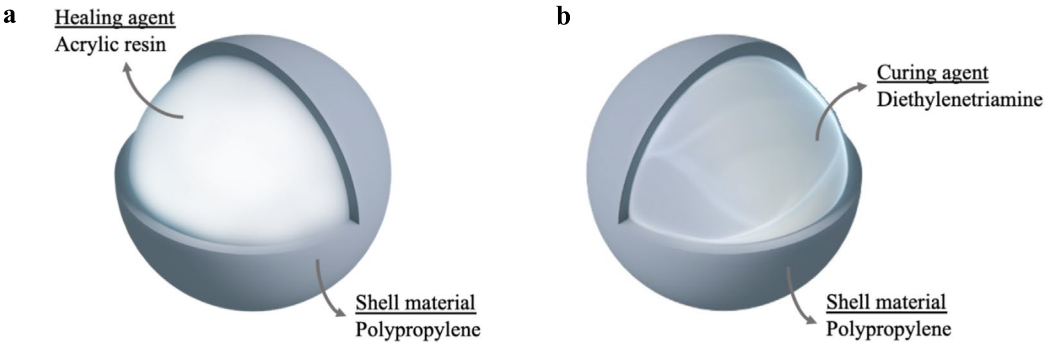
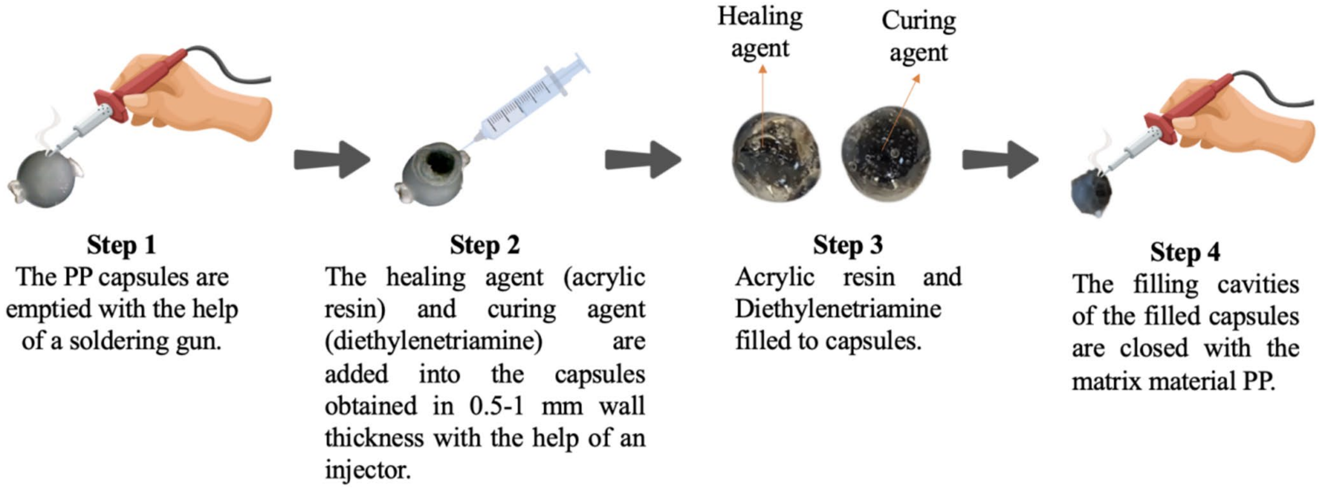


FIGURE 1 | The obtained macrocapsule with a polypropylene shell structure. [Color figure can be viewed at wileyonlinelibrary.com]



Step 1
The PP capsules are emptied with the help of a soldering gun.

Step 2
The healing agent (acrylic resin) and curing agent (diethylenetriamine) are added into the capsules obtained in 0.5-1 mm wall thickness with the help of an injector.

Step 3
Acrylic resin and Diethylenetriamine filled to capsules.

Step 4
The filling cavities of the filled capsules are closed with the matrix material PP.

FIGURE 2 | Macrocapsule production scheme. [Color figure can be viewed at wileyonlinelibrary.com]

chains to dissolve by entering between them, but there is no chemical bonding. Under normal conditions, there is no reactive interaction between the functional groups of MEK (carbonyl group) and the functional groups of the acrylic resin (usually ester and aliphatic hydrocarbons).

Curing times of the acrylic resin were observed physically by manually mixing with DETA at weight ratios of 1%, 2%, 3%, 4%, and 5%. Cure times were observed to be 24, 10, 4, 8, and 18 h, respectively (Table 1). The curing times were observed by manually mixing DETA with acrylic resin at 1%, 2%, 3%, 4%, and 5% weight ratios. The curing times were 24, 10, 4, 8, and 18 h in the tested samples (Table 1). The curing process was found to work well when there was a good balance between the reactive amine groups in DETA and the acrylic groups in the resin. When the DETA ratio was 3% by weight, the optimum ratio between amine groups and acrylic groups was obtained. This combination caused the maximum crosslinking density. Therefore, the fastest curing time was obtained. When DETA was added in larger amounts (4% and 5% by weight), there were too many amine groups compared to the reactive groups in the acrylic matrix. Due to this imbalance, not all amine groups could participate in crosslinking.

The average mass and densities of 5 specimens measured for each macrocapsule are given in Table 2.

TABLE 1 | Effect of DETA on the curing time of acrylic resin.

DETA ratio (%)	Curing time for acrylic resin (Hour)
1	24
2	10
3	4
4	8
5	18

TABLE 2 | Capsule weights and densities according to specimens.

Capsule types	Mass (g)	Density (g/cm^3)
PP capsule	0.7468 ± 0.01	0.0223 ± 0.0008
Empty capsule	0.6358 ± 0.09	0.0217 ± 0.0018
Acrylic resin filled capsule	0.7914 ± 0.06	0.0236 ± 0.0022
DETA filled capsule	0.8894 ± 0.07	0.0265 ± 0.0039

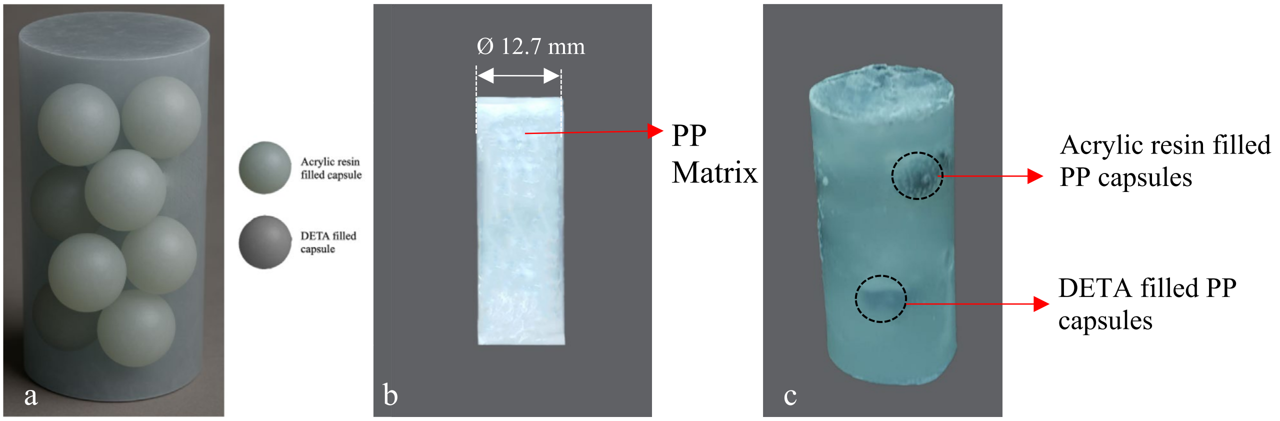


FIGURE 3 | Compression test specimen views: (a) Schematic illustration of capsule placement, (b) Photo of the neat PP matrix, and (c) Photo of the capsule-added PP matrix specimen. [Color figure can be viewed at wileyonlinelibrary.com]

2.2 | Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR (Fourier Transform Infrared Spectroscopy) technique was used to evaluate the effectiveness of the healing and curing agents at different ratios by providing detailed information about their molecular structure. FTIR works by passing infrared light through a specimen, and the molecules in the specimen absorb specific wavelengths of infrared light, corresponding to the vibrational frequencies of the chemical bonds present in the molecules. The chemical composition and repair mechanism of acrylic resin, DETA, and MEK were examined using a Shimadzu instrument. Absorption spectra were recorded in the range of 4000–400 cm^{-1} at room temperature.

2.3 | Compression Test

The specimens were subjected to a compression test according to ASTM D695-15 standard. About 25.4 mm long and 12.7 mm in diameter PP matrix cylindrical specimens (Figure 3) were prepared. To ensure optimum healing performance, macrocapsules were distributed by placing them into the molten PP matrix as groups of three acrylic resin-filled capsules and one DETA-filled capsule. Thus, each specimen contained eight capsules in total: six filled with acrylic resin and two with DETA. During specimen preparation, the capsule shell surface and matrix rise above the melting point of 160°C under the influence of heat. As the temperature increases, the polymer chains in the amorphous regions gain movement, and the molecular chains on the surfaces migrate to the opposite side. These chains' entanglement and physical interlocking allow the two PP surfaces to merge perfectly. Therefore, a strong mechanical interface has been obtained between the capsule and the matrix. This way, the interface compatibility between capsules and matrix was ensured before damage. The perfect interface between the capsule shell and PP is demonstrated in Figure 4. The tests were conducted at a speed of 5 mm/min using a Zwick brand universal testing machine. Five different specimens were tested for each group. The compressive strengths of the PP capsule specimens added into the matrix and the capsule specimens filled with and without healing agents were compared, and the effects of the matrix, capsules, and healing agents on the compression strength were determined. In addition, compression tests were also repeated after healing.

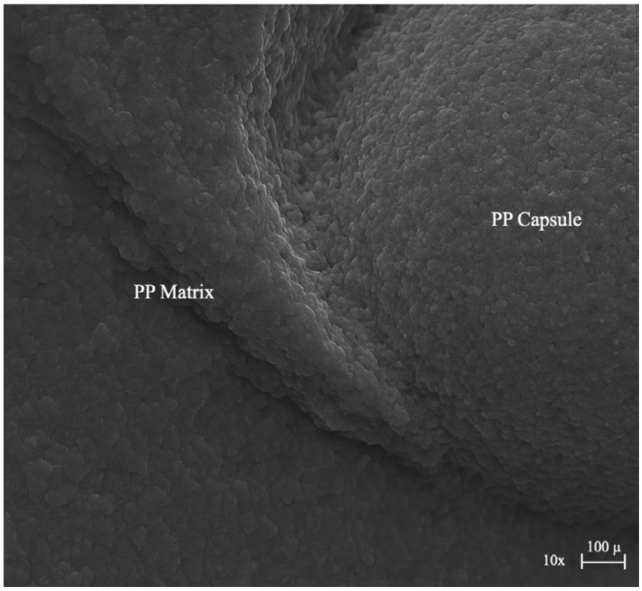


FIGURE 4 | SEM image of the bond formed between PP matrix and PP capsule.

The changing density values of the compression specimens with both empty and filled capsules are given in Figure 5.

3 | Results and Discussion

3.1 | FTIR Analysis Results

The chemical structure of acrylic resin, DETA curing agent, and cured acrylic resin components were investigated by FTIR spectroscopy.

As a result of the experiments with different DETA ratios to determine the optimum curing time of the acrylic resin, it was determined that the study using 3% DETA gave the best curing time. The FTIR spectrum of the acrylic resin cured with 3%

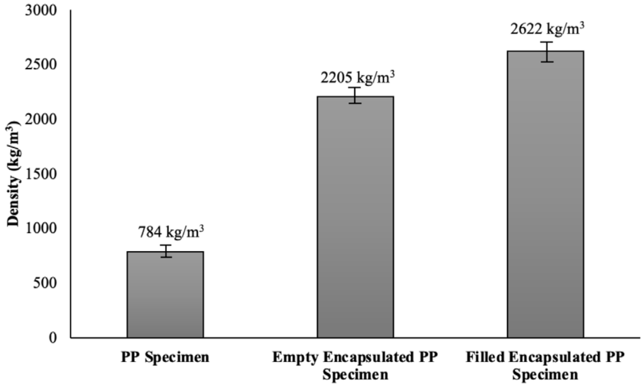


FIGURE 5 | Average density values of specimens prepared for compression test.

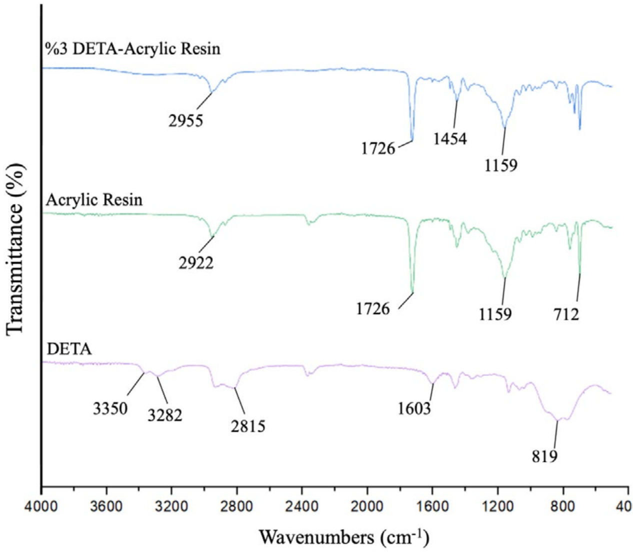


FIGURE 6 | FTIR spectrum of DETA, acrylic resin, and cured acrylic resin. [Color figure can be viewed at wileyonlinelibrary.com]

DETA, where the curing time and curing ratio gave optimum results, is shown in Figure 6.

According to the FTIR spectrum in Figure 6, the characteristic peak at 1726 cm^{-1} corresponds to the carbonyl (C═O) stretching vibration, indicating that the acrylic resin structure is still partially preserved after the reaction. The C—O stretching band, which is characteristic of ester groups, is observed at 1159 cm^{-1}. A new peak appearing at 1454 cm^{-1} can be attributed to N—H bending vibrations, suggesting the incorporation of DETA into the system. The bands at 2815, 2922, and 2955 cm^{-1} correspond to C—H stretching vibrations. A slight shift is observed in the C—H stretching vibration at 2955 cm^{-1} compared to the pure resin, which is likely due to the influence of DETA. N—H stretching bands for primary and secondary amines were observed at 3282 and 3350 cm^{-1}, respectively. The N—H stretching bands of secondary amines are generally weaker and occur at lower frequencies than those of primary amines.

FTIR spectroscopy of MEK, acrylic resin, and acrylic resin diluted with optimum MEK ratio is given in Figure 7. MEK dissolved in toluene was used in the study. The molecular formula of MEK, an organic solvent, is C_4H_8O.

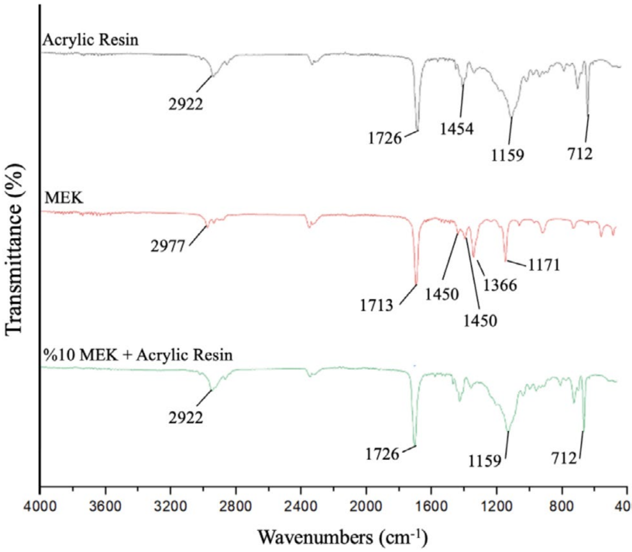


FIGURE 7 | FTIR test results of MEK, acrylic resin, and MEK + acrylic resin. [Color figure can be viewed at wileyonlinelibrary.com]

The 2922 cm^{-1} peak shows an aliphatic C—H stretching vibration. Since the carbonyl peak of ester groups in the resin (1726 cm^{-1}) is more dominant than the carbonyl peak of MEK (1713 cm^{-1}), the peak of MEK overlaps and becomes invisible. The evidence that the acrylic resin has reacted is the reduction or complete disappearance of the C═C bonds in the acrylate structure. However, since the acrylic resin used in the study is dissolved in toluene, the reduction or disappearance of the C═C bonds in the acrylic resin–MEK reaction cannot be observed. Another indication that the reaction has taken place is the occurrence of an exothermic reaction, which releases heat.

In Figure 8, FTIR spectra of pure PP matrix and the interface between the PP matrix and the healing agent are presented for comparison.

In the spectrum of the pure PP matrix, a characteristic band corresponding to the aliphatic C—H stretching vibration is observed at 2915 cm^{-1}. Additionally, bending vibrations of $-CH_2$ and $-CH_3$ groups are identified at 1453 and 1370 cm^{-1}, respectively. A weak peak at 1658 cm^{-1} likely indicates C═C or C═O vibrations, possibly due to environmental moisture or a small amount of unsaturated bond content.

In the spectrum of the PP matrix and the healing agent interface, new peaks are observed. Specifically, a new C—H stretching band at 2855 cm^{-1} suggests the formation of different CH_2 or CH_3 groups in the system. This indicates that the healing agent interacts with the PP matrix. Furthermore, new bands observed at 1413, 1234, and 1088 cm^{-1} suggest the formation of new chemical bonds, such as C—O, C—N, or N—H. These bands support the idea that functional groups present in the healing agent react with the PP matrix, leading to the formation of new bonds.

Additionally, peaks observed at 878 and 629 cm^{-1} can be associated with vibrational modes specific to the structural features of the healing agent. These bands may particularly indicate the presence of ring structures or specific binding motifs.

The obtained FTIR data clearly demonstrate the formation of chemical bonds between the acrylic resin and DETA, the emergence of new functional groups at the interface region, and a strong physical interaction between the healing agent and the PP matrix. These findings provide significant evidence supporting the self-healing potential of the material.

As a result, it can be said that the mixture of MEK and acrylic resin is mainly based on solvent–polymer interaction. The obtained results indicate that the type of solvent and curing agent used contribute to the desired properties of the healing material.

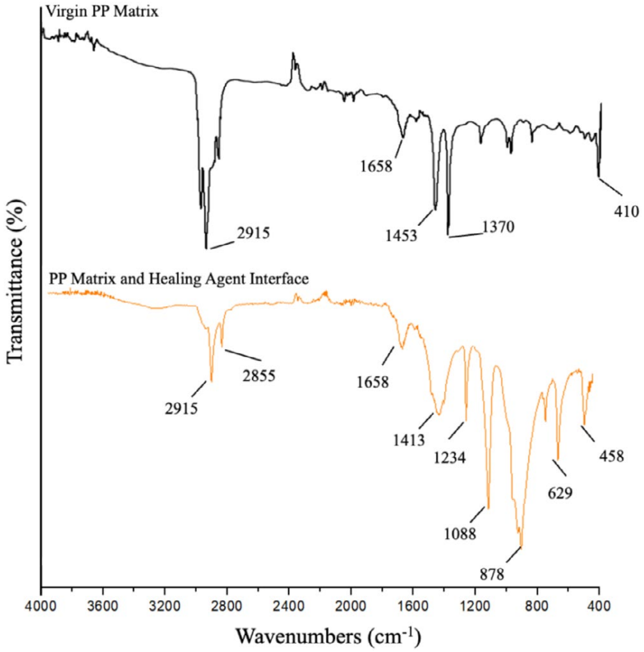


FIGURE 8 | FTIR spectra of PP matrix and healing agent interface. [Color figure can be viewed at wileyonlinelibrary.com]

The desired properties of healing materials made from acrylic resins depend on careful selection of solvents and curing agents that enhance their mechanical strength, biocompatibility, self-healing potential, and thermal stability. By crosslinking with DETA, the resin becomes more stable. The physical bond formed with the PP matrix is based on both Van der Waals forces and microscale interpenetration mechanisms. These improvements increase the applicability of acrylic resin in various fields. In addition, thanks to the optimum proportions of DETA selected as the curing agent, the complete curing time is reduced to 4 h, allowing vital damage to be repaired in a short time.

By obtaining these desired properties, innovative contributions to literature have been presented [49, 74, 75].

3.2 | SEM Microstructure Analysis

SEM images show the microstructural morphology of the polypropylene (PP) composite system containing self-healing agents filled capsules (DETA and acrylic resin). Figure 9a shows the intact PP capsules encapsulating separate core–shell regions of acrylic resin and DETA, separated by a PP wall, within an intact PP matrix. The precise spherical geometry of the capsules and the preservation of the independent structure of the two different capsules despite the indistinguishable combination with each other and the PP matrix material confirm the successful encapsulation of the reactive agents before they were damaged and the reaction started. In contrast, in the second image (Figure 9b), the crushed self-healing capsules were demonstrated within the PP matrix; due to the rupture, the acrylic resin and DETA activator were released toward the crack region and reacted and solidified. In addition, physical adhesion was also established with the crack region surfaces. The exposed fibrous and fractured surfaces indicate the diffusion or leaking of acrylic resin or DETA. The crosslinked acrylic resin filling in the healing regions preserved the structure's integrity by repairing the crack.

3.3 | Compression Test Results

The specimens subjected to the compression tests became plastic deformation. Encapsulated acrylic resin and DETA are in two

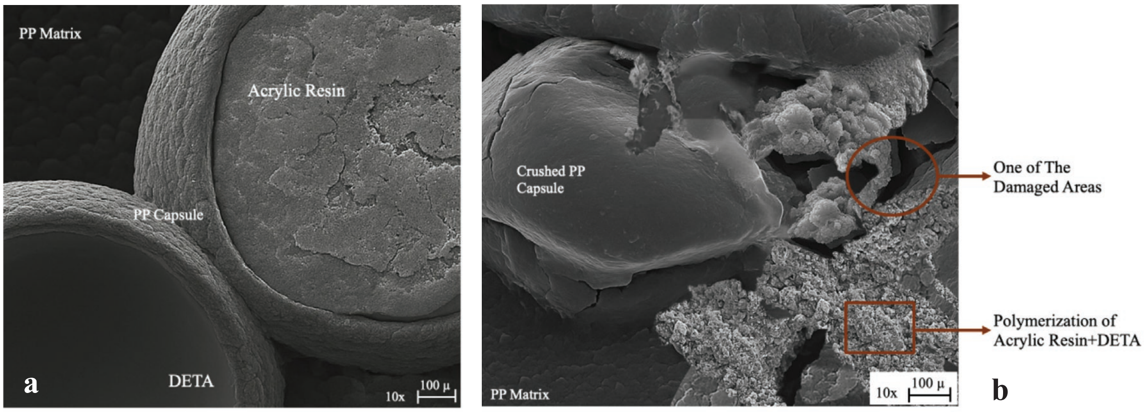
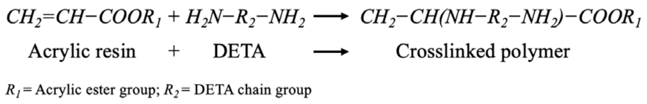


FIGURE 9 | SEM images show (a) The DETA and acrylic resin capsules and the PP matrix and (b) healed crack region. [Color figure can be viewed at wileyonlinelibrary.com]

capsules with a PP shell structure and incorporated in a polypropylene (PP) matrix. During the mechanical loading of this composite structure, cracks initiate, and these cracks encounter these macrocapsules as they travel through the matrix. Acrylic resin and DETA leak into the crack zone through the cracks in the capsules, which are crushed by the compression effect. As the high-viscosity acrylic resin leaks into the cracks, the low-viscosity DETA diffuses along the crack path and penetrates the small volume of a gap formed in the crack zone. Once released, DETA reacts with the surrounding reactive resin, especially with functional groups that can form covalent bonds with amines. This reaction leads to a crosslinked polymer network that bridges the crack and restores the material's structural integrity. The effectiveness of this process depends on several factors, including capsule size and concentration, the rate of diffusion of acrylic resin/DETA, and the kinetics of the reaction between the acrylic resin/DETA and the PP matrix. Optimal distribution of the capsules in high-stress regions ensures that the healing agent reaches the fracture sites efficiently, promoting successful crack closure and mechanical property improvement. Due to this deformation, the capsules filled with curing agents are damaged and crushed. The acrylic resin and DETA encapsulated within the capsule permeate from the sealed area following filling, upon the crushing of the capsule, and infiltrate into the regions where cracks have developed. Self-healing occurs when the acrylic resin and DETA come together; they react in the cracked area and solidify. Methacrylate monomer, one of the main components of acrylic resins, contains double bonds and becomes reactive during polymerization. DETA is a polyamine containing three amine groups. These amine groups exhibit nucleophilic properties and interact with electrophilic centers. It performs addition polymerization. DETA molecules bridge between polymer chains, and a crosslinked network structure is formed (Figure 10).



$$\underset{\text{Acrylic resin}}{CH_2{=}CH{-}COOR_1} + \underset{\text{DETA}}{H_2N{-}R_2{-}NH_2} \longrightarrow \underset{\text{Crosslinked polymer}}{CH_2{-}CH(NH{-}R_2{-}NH_2){-}COOR_1}$$

R_1 = Acrylic ester group; R_2 = DETA chain group

FIGURE 10 | Chemical reaction of acrylic resin and DETA.

Heat is released immediately when the healing agent and the actuator DETA come together. As a result of the reaction in the specimen with an initial temperature of approximately 17°C, the temperature value reached 36.9°C at the end of 45 s. This thermal change was recorded with a thermal camera (Figure 11). Due to the inert structure of PP, a physical bond, the Van der Waals bond, is formed at the interface between the acrylic resin crosslinked by DETA and the matrix crack surface. Thus, the healing in the damaged area was visually observed.

The cross-sectional view before and after damage is shown in Figure 12. To observe the agents leaking into the cracks, acrylic resin colored with red powder paint was added to the capsule. As a result of the reaction of acrylic resin and DETA, a yellow-colored region was formed around the capsule.

The compression strength of the individual capsules crushed during the compression test is given in Figure 13. The maximum forces were obtained as 472.05 ± 0.837 N for the PP capsule, 174.22 ± 1.02 N for the empty capsule, and 355.68 ± 0.943 N for the agent-filled capsule.

The compression test caused a transverse internal expansion in both the capsules and the test specimens. At the end of a certain compression, fractures in the expansion areas and crushing of the capsules started. The internal energy absorption performance of the structure under load is energy absorption. The higher this performance value, the higher the energy absorption.

$$\text{Energy Absorption} = \int_{l_1}^{l_2} F(x)dx \tag{2}$$

$F(x)$ is the instantaneous fracture force due to displacement. l_2 is the defined deformation distance. l_1 is considered as 0 since it represents the change at the first instant [76, 77].

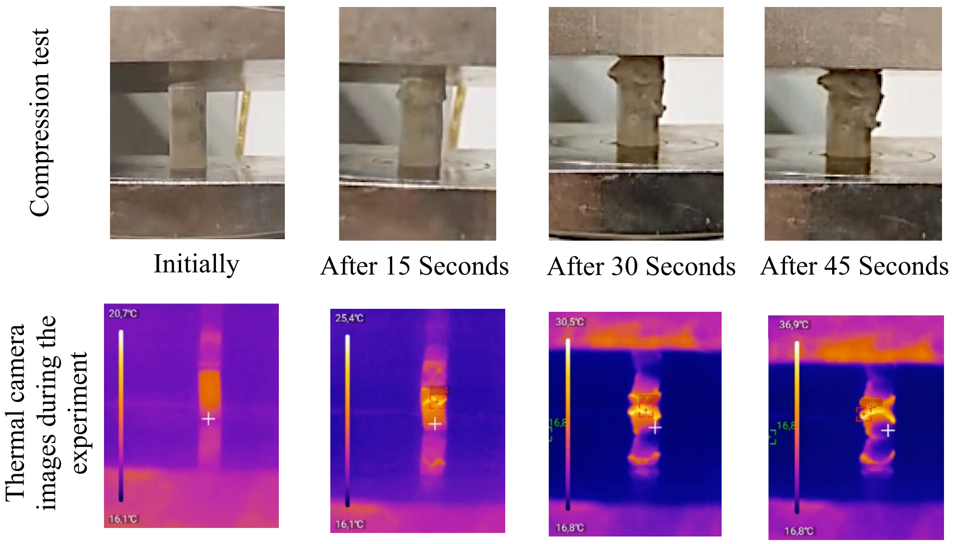


FIGURE 11 | Time-dependent shape and temperature change of the specimen subjected to compression test. [Color figure can be viewed at wileyonlinelibrary.com]

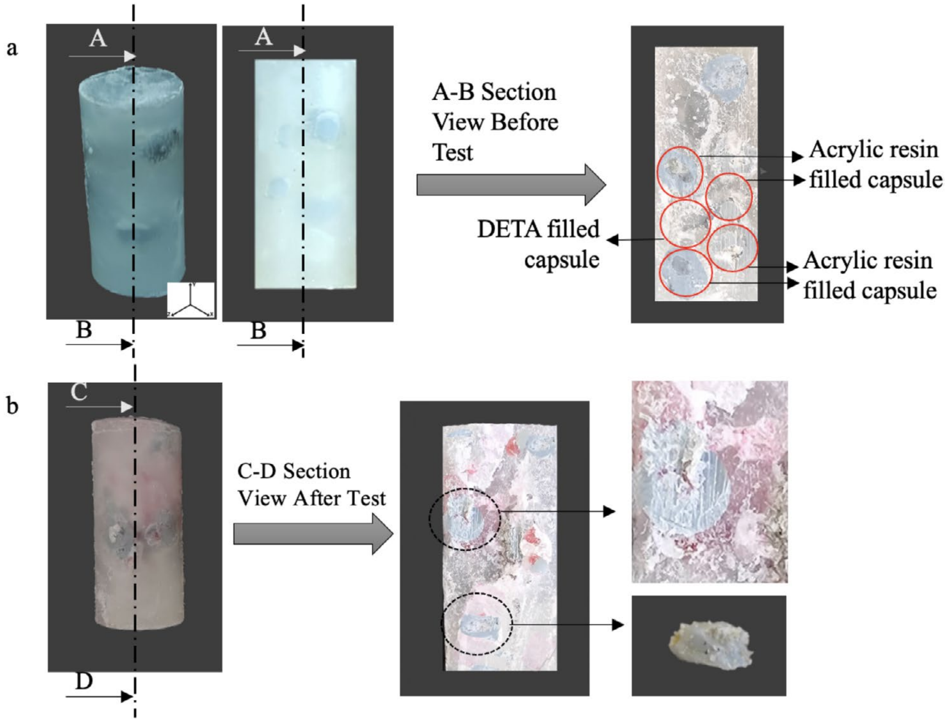


FIGURE 12 | Cross-sectional views of specimens prepared for compression test before and after the test (a) Cross-sectional view of the specimen filled with filled capsule before the test and (b) Cross-sectional view of the specimen subjected to compression test. [Color figure can be viewed at wileyonlinelibrary.com]

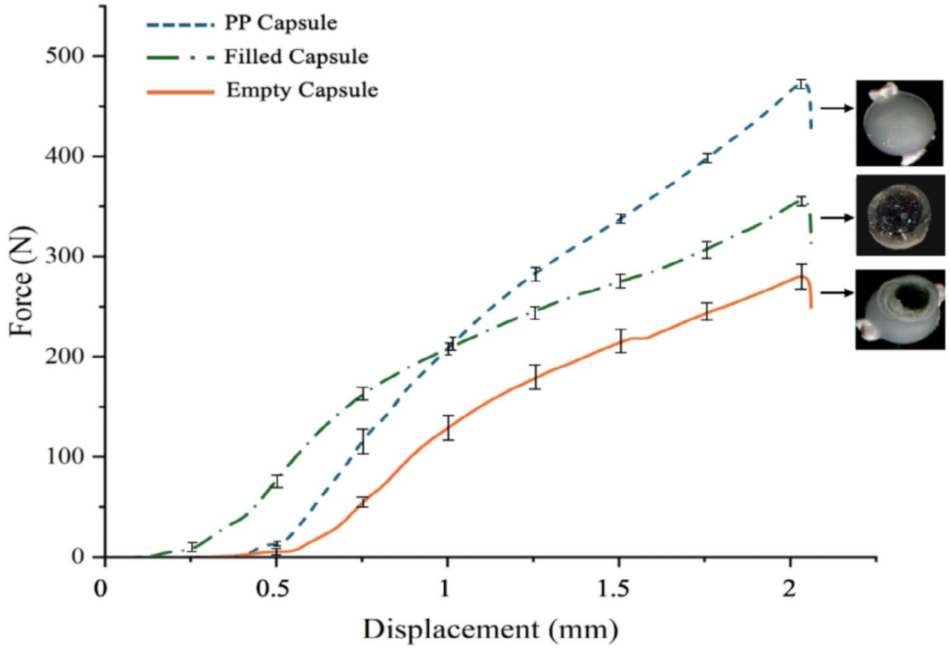


FIGURE 13 | Force–displacement graph obtained because of compression test applied to the capsule. [Color figure can be viewed at wileyonlinelibrary.com]

$$\frac{d}{dx}\left[\frac{1}{F(x)}\int_{0}^{x} F(x)\right]\Bigg|_{x=l_{max}} = 0 \qquad (3)$$

The amount of energy absorption is found by calculating the area under the force–displacement curve. The energy values stored by the capsules are given in Figure 14.

In the first experiment of this test, healing was observed under compression, and elastic and plastic deformations occurred due to the crushing of the capsules and thermoplastic matrix. The substances that perform the healing feature penetrate the deformed areas and eliminate structural defects. In this way, healing occurs. A second test was applied to the damaged specimen to observe the healing performance mechanically.

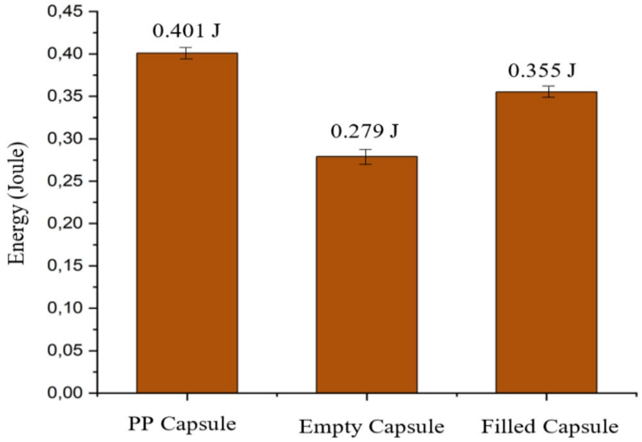


FIGURE 14 | Energy absorption characteristics of individual capsules under compressive loading. [Color figure can be viewed at wileyonlinelibrary.com]

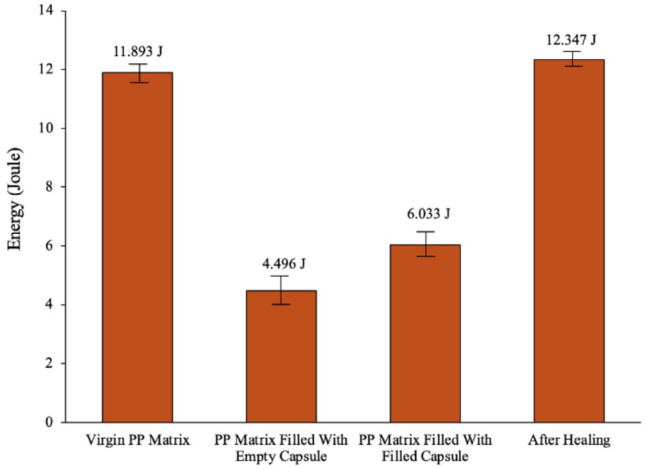


FIGURE 16 | Energy absorption of the compression test specimens. [Color figure can be viewed at wileyonlinelibrary.com]

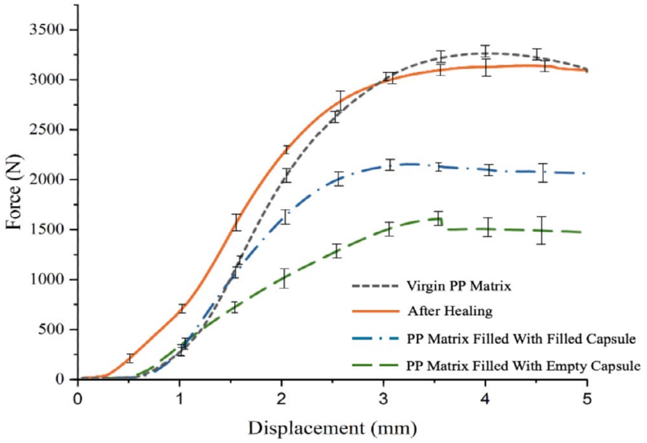


FIGURE 15 | Force–displacement curve of the compression test applied to the damaged specimen after healing. [Color figure can be viewed at wileyonlinelibrary.com]

As seen in the force–displacement curve obtained from this test (Figure 15), the maximum force increased in the second test after healing.

The PP capsules are crushed due to the compression, and the healing agents inside can simultaneously intervene in macro- and microlevel damages. In this way, the energy absorption obtained after healing is higher than the energy absorption of the first compression test specimen (Figure 16). The healing efficiency was determined to be 51% based on the energy values. As a result of the compression tests, a mechanical improvement was observed.

Healing efficiency is calculated according to the ratio of the mechanical properties of the repaired materials to their initial state. In the study, the healing efficiency calculations were based on the healing of the damaged area due to the compression test applied at 2-day intervals, and the healing performance depending on this period was considered.

The material's resistance to deformation was measured through compression tests, and changes in its energy absorption capacity were evaluated. During the initial (unhealed) test, the virgin PP material absorbed 11.893 ± 0.449 J of energy and 4.496 ± 0.597 J for the PP matrix filled with an empty capsule, 6.033 ± 0.996 J for the PP matrix filled with a filled capsule. After healing, this value increased to 12.347 ± 0.321 J. This improvement was achieved through the repair of cracks, enabled by the reaction of acrylic resin and DETA released from the crushed capsules.

4 | Conclusion

In this study, an innovative composite material that is recyclable and capable of self-healing microcracks was developed. The material incorporates polypropylene-shelled capsules containing thermoplastic reactive healing agents, embedded within a polypropylene matrix. Mechanical self-healing ability was observed through static tests. DETA (diethylenetriamine), preferred for its ability to rapidly cure acrylic resin, enhanced the mechanical strength of the structure by forming crosslinks. Additionally, DETA improved the solvent resistance of MEK-soluble acrylic resin. The heat generated by the reaction of the agents leaking into cracks during damage formation was monitored using thermal cameras. This allowed visual detection of both the damaged areas and the healing agents reacting within these regions.

This material, developed with thermoplastic reactive agents, holds significant potential for a wide range of applications in the automotive, marine, aerospace, and energy sectors. Its ability to restore mechanical integrity after damage makes it an ideal choice for demanding environments.

It would be meaningful to investigate the effects of damage and agent release behavior of ductile-walled capsules on self-healing under different loading conditions, such as tensile, bending, or shear loads with smaller sized capsules. In addition, studies on the crack formation behavior under fatigue loading and its self-healing performance for developed materials require additional comprehensive research studies. Moreover, investigations of the life of the developed material's self-healing ability are scientifically significant and have practical importance.

In addition, considering that the production technique of capsules is suitable for industrial-scale mass production and the agent system that provides effective reactive thermoplastic self-healing was developed on a laboratory scale in this study, a production machine that will use the obtained system and produce small-sized capsules can be created. In this respect, it offers a remarkable opportunity for industrial practitioners.

Author Contributions

Eslem Şahin: conceptualization (supporting), data curation (lead), investigation (equal), methodology (equal), visualization (lead), writing – original draft (lead). **Yalçın Boztoprak:** conceptualization (equal), formal analysis (equal), methodology (supporting), validation (equal), writing – review and editing (lead). **Murat Yazıcı:** conceptualization (lead), data curation (lead), formal analysis (lead), funding acquisition (lead), investigation (lead), methodology (lead), project administration (lead), resources (lead), visualization (lead), writing – original draft (supporting), writing – review and editing (lead).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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