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EFFECTS OF CNT ON POLYMER MATRIX: A FOCUSED REVIEW WITH LASERS

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Abstract
In this article, we thoroughly examine the progress of polymer nanocomposites in laser treatment and their properties. The use of CNTs (carbon nanotubes) with polymer materials enhances the properties of polymers, such as mechanical, thermal, and electrical. In this short review, different types of lasers used for the treatment of CNTs polymer nanocomposite are analyzed. Furthermore, this study has extensively investigated the variations in nanocomposites' properties observed by a variety of researchers. The effectiveness of lasers on the surface properties of CNT polymer nanocomposite is also described.

1 Introduction

Polymers and their composites are the most evolving family of structural materials. Its excellent properties, such as low density, corrosion resistance, good mechanical properties, damping ability, etc., come to the fore in a wide variety of applications. A perfect CNT is a seamless cylinder formed by rolling up a graphene sheet with a diameter of only 0.4 nm, a length of several cm at each extremity [1]. Single-wall, double-wall, and multi-wall CNTs are just a few of the various varieties of CNTs. The single sheet of graphene forms a cylinder in single-wall carbon nanotubes (SWCNTs). Whereas multi-wall carbon nanotubes (MWCNTs) are made up of a collection of cylinders spaced 0.35 nm distant from one another, double-wall carbon nanotubes (DWCNTs) are made up of two of these cylinders arranged in a concentric pattern. [2, 3]

Because of their exceptional qualities, CNTs are a viable filler material to magnify the mechanical, thermal, and electrical characteristics of polymer nanocomposites. The important thing is to incorporate CNTs' potential characteristics into polymer composites. Nanotubes have a tendency to aggregate and form ropes or bundles due to the strong, attractive long-range Vander-Walls interaction, often with a highly entangled network topology. Optimizing the chemical bonding between CNTs and solvents and/or polymer matrices may result from this. It is possible that the properties of the functionalized nanotubes will differ from those of the pure ones. [4]

Laser irradiation offers controlled surface treatment with low energy consumption, and it is still widely used for surface changes on metals or polymers. Applications for laser irradiation surface treatment in space, medicine, industry, and other fields have grown due to

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its flexibility and other advantages [5]. A laser is a device that uses optical amplification, based on the stimulated emission of photons, to emit light (electron magnetic radiation). As an abbreviation for Light Amplification by Stimulated Emission of Radiation, the word "laser" first appeared.

For different polymers, the laser welding's process is generally inadequate, and we can say that they cannot weld together due to a lack of compatibility as well as non-identical melting temperatures. For example Polyethylene (PE) and Polyoxymethylene (POM), PE is a non-polar crystalline polymer, while (POM) is a polar (weak) polymer without functional groups in the chain. These are incompatible in the welding process, but for these problems, OPS (oxygen plasma surface) treatment was used to upgrade the welding robustness between PE and POM. [6]

One benefit of laser welding is the ability to quickly and efficiently make deep welds without the heat source coming into contact with the components being connected. If the laser beam can be directed to a distant point, welds can be produced there. Furthermore, "out of position" welds can be produced without significantly depleting the material [7]. Thermoplastic and thermoset combinations must be bonded for specific uses in the aerospace and automotive industries. The aforementioned miscellany of materials is unable to be welded because the components of the thermoset matrix do not melt. [8]

2 Lasers for CNT Polymer Nanocomposite Treatment

Numerous laser sources are frequently used for the treatment of CNT polymer nanocomposite materials. These include ns pulsed Nd:YAG lasers, which are usually used at the second harmonic of 532 nm wavelength; high power infrared continuous CO_2 lasers operating at 9.4 and 10.6 µm wavelengths; and small-sized, high power semiconductor diode lasers, which are usually used in the visible emission range. A wide range of thermoplastic polymers, such as acrylonitrile butadiene styrene (ABS), PE, polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polymethylmethacrylate (PMMA), can be bonded together using laser sources [9]. To regulate their absorption coefficient in relation to the laser wavelength being used, these polymers are frequently filled or coated with nanostructures.

2.1 Solid State Laser

Nd:YAG laser operating at 532 nm (visible light), the effectiveness of plastic laser welding was tested on a few transparent or adsorbing polymers based on pristine PE and PE with CNTs (Table 1). In order to make the bottom layer laser absorbent, CNTs, or carbon black (CB), are traditionally used as pigments. [10]

Rasool W. I.et. al., comprising a pulsed Nd:YAG laser with a wavelength of 1064 nm, a single pulse capacity of up to 70 J/10 ms, a pulse length of 1–50 ms, and a frequency range of 1-100 Hz. The device was converted to a manipulator via a 400 µm diameter optical wire. To determine which type of CNTs achieved greater cohesiveness with the base material and to confirm the results from the EDS test, SEM images of the work pieces covered with MWCNTs and DWCNTs, respectively, were taken. The images showed that the DWCNTs were distributed more evenly throughout the work piece's surface. The heat conductivity of the PMMA surface was boosted by the DWCNTs by 8 times and by the MWCNTs by 5 times over its initial value. [11]

Comparably, A.M. Visco et al. investigated the impact of CNTs on PE generated by solid-state lasers; they categorized polymeric batch of PE as immaculate and filled them with CNTs in amounts ranging from 0.1 to 10 wt%. In order to absorb laser energy and restrict the interface among two polymeric batches, one of which is adsorbent and the other laser-transparent filler must be present. The findings of the experiment showed that the CNT filler could effectively absorb laser light. The Nd:YAG laser source modifies the polymer in the contact region, causing an energetic process that produces radical species, heat, ions, and new chemical rearrangements. [9]

Table 1. Different laser sources for polymer-CNTs nanocomposites

Laser	Polymer Matrix	Filler	References
Solid state	PMMA, PE, PC	MWCTs, DWCNTs	9, 10, 11
CO_2	PA12, PVA, PP	MWCNTs, CNTs	12, 13, 14, 15
Diode	PC, PE	MWCNTs, GF	17, 18

2.2 CO_2 Laser

By using melt blending, a master batch of polypropylene (PP) with 15 wt% of MWCNTs was created. One CO_2 laser makes up the laser apparatus (Table 1). Depending on the parameters used, radiation causes distinct lengths, widths, and geometries of tracks to form on the injection-molded, rectangular polymeric plates [12, 13]. A unique technique for laser printing metal-free conductive tracks on polymeric nanocomposites reinforced with 2% MWCNTs was developed. Numerous studies have examined how laser processing affects the final characteristics of nanocomposites, such as the thermal behavior of the materials, the electrical resistance of the tracks produced after laser irradiation, and modifications brought about by laser action on the microstructure. The outcomes unequivocally demonstrate that utilizing MWCNTs to create conductive pathways on polymer surfaces via laser printing is an easy, quick, adaptable, and reasonably inexpensive process. [14]

Furthermore, polyvinyl alcohol (PVA) CNT composites with varying CNT concentration (prior to volume fraction 0.038) were produced and irradiated with different CO_2 laser levels (prior to 200 joules), and their microwave absorption and dielectric characteristics were calculated. SDS (sodium dodecyl sulfate) was used as a dispersing agent to produce uniform, steady distribution and well oriented CNT inside the PVA matrix. [15]

2.3 Diode Laser

Diode lasers are well recognized for their uses in information technology and communication, as well as consumer electronics. Diode lasers could be ramped up to a power level that made them appealing for material preparation at the start of the previous decade. However, mostly due to advancements in cooling, mounting, and beam shaping technologies, this was made possible by unique semiconductor technology. [16]

MWCNTs can accelerate thermal breakdown and removal of the polymer from the composite surface due to the photothermal conversion phenomenon caused by semiconductor laser light. It was discovered that, in pure PE/MWCNTs nanocomposites, only a very small percentage of MWCNTs are directly on the film surface. This is due to the surface tension forces of the polymer matrix melt and the high work of polymer attachment to the nanotube surface. They demonstrate the removal of the polymer matrix with its entire structure from the near-surface layer, together with the appearance of a minor amount of amorphous carbon material in surface contacts caused by laser light. [17]

PC as a transparent material and PA66GF (polyamide 66 glass fiber) as a black material to absorb the laser energy were used to explain the parameters of the diode laser for strong welding (Table 1). The strength of joints grew first, then declined as line energy and spot diameter increased. The laser parameter plays an important role in laser transmission welding [18]. Furthermore, PP and low density polyethylene (LDPE) or high density polyethylene (HDPE) thin films are welded with high speed spot welding. The line spot has considerable significance not only because it permits better arrangement of optical beams and welding material but also because diode lasers are innately astigmatic. [19]

3 Properties of CNT Polymer Nanocomposite

3.1 Mechanical properties

The tensile strength of polycarbonate (PC) and MWCNT nanocomposites after the ablation of lasers was found to exhibit an increase in tensile strength from 67 to 74 MPa when the MWCNT component reaches 2.5 wt%. The tensile strength of PC/MWCNT composites is shown to decline from 74 to 62 MPa when the MWCNT component exceeds 2.5 wt% [20].With increasing MWCNT loading, the tensile modulus, tensile strength, and stress at break all gradually rise. The effect of reinforcement becomes more pronounced at 1% of MWCNTs. Moreover, when MWCNT loading increases, the elongation at break considerably reduces. [21]

Due to the very tiny wire shape and high surface/volume ratio of MWCNTs, the nanocomposite structure has a high elastic elasticity, low density, and high tensile strength. MWCNTs contribute to reducing hardness change in laser cutting and heat, while CNTs exhibit thermal resistance and are held together by Van der Waals forces. [22]

The micromechanical properties of PMMA/PBT (polybutylene terephthalate) laser welding's were enhanced with the PC as an intermediate material, but the bubble formation increased. Results show that PMMA, PC, and PBT were four times stronger than PMMA and PBT. These bubbles actually support the welding's strengths [23]. Polyether ether ketone (PEEK) and CNT/MMT (montmorillonite) nanocomposites were fabricated to solve the agglomeration problems as well. The nanocomposite is produced by melt mixing, and the mechanical properties of the nanocomposite were increased due to the strong reinforcement of CNTs and MMT into the PEEK matrix [24]. The newly developed family of colored PA6-based polymers that can be used for laser welding technologies has increased mechanical and technological properties [25]. PA6 was welded in two different ways: scarf and lap joints. The tensile strength of the lap joint welds was 55% that of the base materials. [26]

3.2 Electrical Properties

Near-infrared (NIR) laser annealing is used to produce conductive stripes on the surface of PP/MWCNT plates. Prior to irradiation, the nanocomposite is nonconductive due to poor alignment of the MWCNT throughout injection molding. In the results, they found that NIR laser irradiation significantly reduces the surface sheet resistance, which they attribute to the randomization of MWCNT orientation in the PP matrix melt. The sheet resistance of PP/MWCNTs, annealed with a laser at a power density of 7 W/cm^2, drops from 100 M/sq to 1 k/sq after just 5 seconds of exposure, a decrease of more than 4 times [27]. The electrical conductivity of the PC/MWCNT composites at 0.5 wt% MWCNT content is approximately 10^{-10} S/cm. The electrical conductivity of the PC/MWCNT composites increases significantly to approximately 10^{-3} and 10^{-2} S/cm for 1.5 and 2.5 wt% MWCNT content, respectively. [20]

Furthermore, with the laser used for the electrical properties of DWCNTs and MWCNTs polymer nanocomposites, the PMMA's surface condition was transformed from an insulator with an electrical conductivity of 10^{-15} S/m to a conductor with 0.813×10^3 S/m and 0.14×10^3 S/m, respectively. As a result, the DWCNTs outperformed the MWCNTs by about six times [11]. The creation of a percolating network was indicated by a dramatic increase in conductivity observed when the MWCNT loading level rose from 1.25 to 2.5 wt%. The conductivity of the produced nanocomposites containing 5 and 15 wt% MWCNTs is a function of mechanical deformation. [28]

3.3 Thermal Properties

Thermal properties are the most significant properties of polymers in laser welding. The differences in heat conductivity between polymers and polymers with fillers are a crucial distinction. The fiber has a stronger heat conductivity than the polymer matrixes around it. The results show that absorption occurs predominantly at the fibers in both natural polymer matrix and fiber reinforcements. This means that a larger volume must be melted before the connecting partner's upper layer achieves joining temperature. The feeding rates that may be achieved are significantly less than with traditional transmission welding, which uses PA6 loaded with carbon black as the laser absorber connecting partner. This is because the technique is time-consuming. Modifying the optical characteristics of the matrix polymer by adding carbon black as absorbent particles is one technique to increase heat dispersion and hence achievable weld strengths while reducing the needed energy per unit. As a result, the surface absorption of the incident laser light becomes easier to manage, and the heat distribution becomes more uniform [29]. In the analysis of thermal studies on PP with MWCNTs, the curves clearly show the formation of defected crystals in the presence of MWCNTs, which start melting at low temperatures. [30]

CB concentration in the PP polymer matrix has potent effects on welding's qualities. With the increase in CB concentration, the weld temperature increases, which is higher than the degradation temperature. Good welding's quality was achieved by increasing the weld speed, which eventually decreased the weld depth. According to the results, the PP contains more than 1% CB and is difficult to weld with high speed and low line energy. [31]

Additionally, ABS and ABS/CNTs with different ratios were welded through laser. The DSC curves show that the thermal response of ABS/CNT to laser radiation does not change significantly with the concentration of CNTs. ABS with a high concentration of CNTs was more sensitive to laser radiation. [32]

4 Surface Morphology

A regeneratively amplified Ti:Sapphire laser with a 800 nm center wavelength, and 150 fs pulse duration was used to ablate surface features in the polymer substrates. Microchannels with a rectangular cross-section were created by conducting many parallel scans at the same depth with a 4 μm lateral separation. The SEM image demonstrates the excellent quality of the created microchannels, which had low roughness and crisp edges. Spectroscopic studies proved that the chemistry of the polymeric substrates was unaffected by the laser irradiation. It was found that femtosecond laser ablation changed PMMA's wettability. Specifically, independent of the above-threshold laser fluence, the PMMA wetting behavior changes from moderately hydrophilic to hydrophobic following laser ablation. Found that the porous morphology created at the submicroscale following laser processing is mostly responsible for the altered wettability. [33]

Furthermore, 160 fs laser pulses with a center wavelength of 780 nm and a maximum pulse energy (Ep) of 1 mJ using a commercially available amplified Ti:sapphire laser system. The laser beam was Gaussian in shape and had a diameter of 6 mm. By graphing the diameter of the ablated patches versus the pulse energy and extrapolating to zero, one can determine the ablation threshold fluences of the Gaussian laser beam [34]. It was discovered that the polycarbonate ablation thresholds for fs laser ablation were Fth = 1.52 J/cm^2, which was quite near to the measured value. The craters are measured after they have formed under different numbers and intensities of laser pulses. A contact-mode profilometer and the ablated crater's section profiles were used to determine the ablated crater's depth. SEM images and the crater profiles laser-ablated at Ep = 6.57 μJ and Ep = 241 μJ. The incubation effect caused the ablation threshold to fall as the number of laser pulses increased. The pace of ablation is determined by the pulse energy. The rate at which ablating occurs rises with decreasing pulse energy and falls with increasing pulse energy. [35]

The surface roughness also contributes to the scattering of light. The scattering and absorbance of the PP, PC, and PP increased with the amount of filler. Scattering and absorbance play important roles in laser welding [36]. For PMMA welding, laser transmission spot welding (LTSW) was used. During this process, bubbles were created at a high frequency with the passage of time. The weld pool diameter is higher at high frequencies, which leads to the strong welding of PMMA. [37]

5 Conclusions

After incorporating an adequate proportion of CNTs, polymers and their properties undergo considerable changes. Pristine possesses exceptional mechanical, electrical, and thermal properties. As a result, the use of CNTs improves the characteristics of the polymer matrix. However, a specific concentration of CNTs in the polymer matrix is required to attain the desired properties. In the treatment of polymers and polymer nanocomposites, several lasers are used, such as solid-state, CO_2, and diode lasers. After laser welding, the mechanical properties of CNT polymer nanocomposites were found to be greater than before. Laser ablation of CNT polymer nanocomposites transforms them from nonconductive to conductive nanocomposites with MWCTs or DWCNTs. Lasers have little influence on the thermal response of CNT polymer nanocomposites.

The surface properties of CNT polymer nanocomposites are crucial in laser treatment. The surface characteristics of polymers influence laser light transmission and absorption. The wettability of CNT polymer nanocomposites changes after laser treatment. For the welding of transparent polymers, a few substances, such as dyes, pigments, coatings, and solutions, have been discovered. Research is needed in the welding and treatment of thermoplastic-based CNT polymer nanocomposites. Despite the abundance of research articles about laser welding and the treatment of CNT polymer nanocomposites, there is a future scope for the compatibility of transparent and opaque polymer nanocomposites.

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