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Bäcklund Transformations: Some Old and New Perspectives

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Abstract. Bäcklund transformations (BTs) are traditionally regarded as a tool for integrating nonlinear partial differential equations (PDEs). Their use has been recently extended, however, to problems such as the construction of recursion operators for symmetries of PDEs, as well as the solution of linear systems of PDEs. In this article, the concept and some applications of BTs are reviewed. As an example of an integrable linear system of PDEs, the Maxwell equations of electromagnetism are shown to constitute a BT connecting the wave equations for the electric and the magnetic field; plane-wave solutions of the Maxwell system are constructed in detail. The connection between BTs and recursion operators is also discussed.

Keywords: Bäcklund transformations, integrable systems, Maxwell equations, electromagnetic waves

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1. INTRODUCTION

Bäcklund transformations (BTs) were originally devised as a tool for obtaining solutions of nonlinear partial differential equations (PDEs) (see, e.g., [1] and the references therein). They were later also proven useful as *recursion operators* for constructing infinite sequences of nonlocal symmetries and conservation laws of certain PDEs [2–6].

In simple terms, a BT is a system of PDEs connecting two fields that are required to independently satisfy two respective PDEs [say, (*a*) and (*b*)] in order for the system to be integrable for either field. If a solution of PDE (*a*) is known, then a solution of PDE (*b*) is obtained simply by integrating the BT, without having to actually solve the latter PDE (which, presumably, would be a much harder task). In the case where the PDEs (*a*) and (*b*) are identical, the *auto-BT* produces new solutions of PDE (*a*) from old ones.

As described above, a BT is an auxiliary tool for finding solutions of a given (usually nonlinear) PDE, using known solutions of the same or another PDE. But, what if the BT itself is the differential system whose solutions we are looking for? As it turns out, to solve the problem we need to have parameter-dependent solutions of *both* PDEs (*a*) and (*b*) at hand. By properly matching the parameters (provided this is possible) a solution of the given system is obtained.

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The above method is particularly effective in *linear* problems, given that parametric solutions of linear PDEs are generally not hard to find. An important paradigm of a BT associated with a linear problem is offered by the Maxwell system of equations of electromagnetism [7,8]. As is well known, the consistency of this system demands that both the electric and the magnetic field independently satisfy a respective wave equation. These equations have known, parameter-dependent solutions; namely, monochromatic plane waves with arbitrary amplitudes, frequencies and wave vectors (the “parameters” of the problem). By inserting these solutions into the Maxwell system, one may find the appropriate expressions for the “parameters” in order for the plane waves to also be solutions of Maxwell’s equations; that is, in order to represent an actual electromagnetic field.

This article, written for educational purposes, is an introduction to the concept of a BT and its application to the solution of PDEs or systems of PDEs. Both “classical” and novel views of a BT are discussed, the former view predominantly concerning integration of nonlinear PDEs while the latter one being applicable mostly to linear systems of PDEs. The article is organized as follows:

In Section 2 we review the classical concept of a BT. The solution-generating process by using a BT is demonstrated in a number of examples.

In Sec. 3 a different perception of a BT is presented, according to which it is the BT itself whose solutions are sought. The concept of *conjugate solutions* is introduced.

As an example, in Secs. 4 and 5 the Maxwell equations in empty space and in a linear conducting medium, respectively, are shown to constitute a BT connecting the wave equations for the electric and the magnetic field. Following [7], the process of constructing plane-wave solutions of this BT is presented in detail. This process is, of course, a familiar problem of electrodynamics but is seen here under a new perspective by employing the concept of a BT.

Finally, in Sec. 6 we briefly review the connection between BTs and recursion operators for generating infinite sequences of nonlocal symmetries of PDEs.

2. BÄCKLUND TRANSFORMATIONS: CLASSICAL VIEWPOINT

Consider two PDEs $P[u]=0$ and $Q[v]=0$ for the unknown functions u and v, respectively. The expressions $P[u]$ and $Q[v]$ may contain the corresponding variables u and v, as well as partial derivatives of u and v with respect to the independent variables. For simplicity, we assume that u and v are functions of only two variables x, t. Partial derivatives with respect to these variables will be denoted by using subscripts: u_x, u_t, u_{xx}, u_{tt}, u_{xt}, etc.

Independently, for the moment, also consider a pair of coupled PDEs for u and v:

$$B_1[u,v]=0 \quad (a) \qquad B_2[u,v]=0 \quad (b) \tag{1}$$

where the expressions $B_i[u,v]$ (i=1,2) may contain u, v as well as partial derivatives of u and v with respect to x and t. We note that u appears in both equations (a) and (b). The question then is: if we find an expression for u by integrating (a) for a given v, will it match the corresponding expression for u found by integrating (b) for the same v? The answer is that, in order that (a) and (b) be consistent with each other for solution for u, the function v must be properly chosen so as to satisfy a certain *consistency condition* (or *integrability condition* or *compatibility condition*).

By a similar reasoning, in order that (a) and (b) in (1) be mutually consistent for solution for v, for some given u, the function u must now itself satisfy a corresponding integrability condition.

If it happens that the two consistency conditions for integrability of the system (1) are precisely the PDEs $P[u]=0$ and $Q[v]=0$, we say that the above system constitutes a *Bäcklund* *transformation* (BT) connecting solutions of $P[u]=0$ with solutions of $Q[v]=0$. In the special case where $P\equiv Q$, i.e., when u and v satisfy *the same* PDE, the system (1) is called an *auto-Bäcklund* transformation (auto-BT) for this PDE.

Suppose now that we seek solutions of the PDE $P[u]=0$. Assume that we are able to find a BT connecting solutions u of this equation with solutions v of the PDE $Q[v]=0$ (if $P\equiv Q$, the auto-BT connects solutions u and v of the same PDE) and let $v=v_0(x,t)$ be some known solution of $Q[v]=0$. The BT is then a system of PDEs for the unknown u,

$$B_i[u,v_0]=0\ , \quad i=1,2 \tag{2}$$

The system (2) is integrable for u, given that the function v_0 satisfies *a priori* the required integrability condition $Q[v]=0$. The solution u then of the system satisfies the PDE $P[u]=0$. Thus a solution $u(x,t)$ of the latter PDE is found without actually solving the equation itself, simply by integrating the BT (2) with respect to u. Of course, this method will be useful provided that integrating the system (2) for u is simpler than integrating the PDE $P[u]=0$ itself. If the transformation (2) is an auto-BT for the PDE $P[u]=0$, then, starting with a known solution $v_0(x,t)$ of this equation and integrating the system (2), we find another solution $u(x,t)$ of the same equation.

Let us see some examples of the use of a BT to generate solutions of a PDE:

1. The *Cauchy-Riemann relations* of Complex Analysis,

$$u_x=v_y \quad (a) \qquad u_y=-v_x \quad (b) \tag{3}$$

(here, the variable t has been renamed y) constitute an auto-BT for the *Laplace equation*,

$$P[w]\equiv w_{xx}+w_{yy}=0 \tag{4}$$

Let us explain this: Suppose we want to solve the system (3) for u, for a given choice of the function $v(x,y)$. To see if the PDEs (a) and (b) match for solution for u, we must compare them in some way. We thus differentiate (a) with respect to y and (b) with respect to x, and equate the mixed derivatives of u. That is, we apply the integrability condition $(u_x)_y=(u_y)_x$. In this way we eliminate the variable u and find the condition that must be obeyed by $v(x,y)$:

$$P[v]\equiv v_{xx}+v_{yy}=0\ .$$

Similarly, by using the integrability condition $(v_x)_y=(v_y)_x$ to eliminate v from the system (3), we find the necessary condition in order that this system be integrable for v, for a given function $u(x,y)$:

$$P[u]\equiv u_{xx}+u_{yy}=0\ .$$

In conclusion, the integrability of system (3) with respect to either variable requires that the other variable must satisfy the Laplace equation (4).

Let now $v_0(x,y)$ be a known solution of the Laplace equation (4). Substituting $v=v_0$ in the system (3), we can integrate this system with respect to u. It is not hard to show (by eliminating v_0 from the system) that the solution u will also satisfy the Laplace equation (4). As an example, by choosing the solution $v_0(x,y)=xy$, we find a new solution $u(x,y)=(x^2-y^2)/2+C$.

2. The *Liouville equation* is written

$$P[u] \equiv u_{xt} - e^u = 0 \quad \Leftrightarrow \quad u_{xt} = e^u \tag{5}$$

Due to its nonlinearity, this PDE is hard to integrate directly. A solution is thus sought by means of a BT. We consider an auxiliary function $v(x,t)$ and an associated PDE,

$$Q[v] \equiv v_{xt} = 0 \tag{6}$$

We also consider the system of first-order PDEs,

$$u_x + v_x = \sqrt{2}\; e^{(u-v)/2} \quad (a) \qquad u_t - v_t = \sqrt{2}\; e^{(u+v)/2} \quad (b) \tag{7}$$

Differentiating the PDE (*a*) with respect to *t* and the PDE (*b*) with respect to *x*, and eliminating ($u_t - v_t$) and ($u_x + v_x$) in the ensuing equations with the aid of (*a*) and (*b*), we find that *u* and *v* satisfy the PDEs (5) and (6), respectively. Thus, the system (7) is a BT connecting solutions of (5) and (6). Starting with the trivial solution v=0 of (6), and integrating the system

$$u_x = \sqrt{2}\; e^{u/2} \;, \qquad u_t = \sqrt{2}\; e^{u/2} \;,$$

we find a nontrivial solution of (5):

$$u(x,t) = -2\ln\left(C - \frac{x+t}{\sqrt{2}} \right) .$$

3. The "*sine-Gordon" equation* has applications in various areas of Physics, e.g., in the study of crystalline solids, in the transmission of elastic waves, in magnetism, in elementary-particle models, etc. The equation (whose name is a pun on the related linear Klein-Gordon equation) is written

$$P[u] \equiv u_{xt} - \sin u = 0 \quad \Leftrightarrow \quad u_{xt} = \sin u \tag{8}$$

The following system of equations is an auto-BT for the nonlinear PDE (8):

$$\frac{1}{2}(u+v)_x = a\,\sin\left(\frac{u-v}{2}\right) \;, \qquad \frac{1}{2}(u-v)_t = \frac{1}{a}\,\sin\left(\frac{u+v}{2}\right) \tag{9}$$

where a (≠0) is an arbitrary real constant. [Because of the presence of *a*, the system (9) is called a *parametric* BT.] When *u* is a solution of (8) the BT (9) is integrable for *v*, which, in turn, also is a solution of (8): $P[v]$=0; and vice versa. Starting with the trivial solution v=0 of $v_{xt}= \sin v$, and integrating the system

$$u_x = 2a\,\sin\frac{u}{2} \;, \qquad u_t = \frac{2}{a}\,\sin\frac{u}{2} \;,$$

we obtain a new solution of (8):

$$u(x,t) = 4\arctan\left\{ C\exp\left(ax + \frac{t}{a} \right) \right\} .$$

3. CONJUGATE SOLUTIONS AND ANOTHER VIEW OF A BT

As presented in the previous section, a BT is an auxiliary device for constructing solutions of a (usually nonlinear) PDE from known solutions of the same or another PDE. The converse problem, where solutions of the differential system representing the BT itself are sought, is also of interest, however, and has been recently suggested [7,8] in connection with the Maxwell equations (see subsequent sections).

To be specific, assume that we need to integrate a given system of PDEs connecting two functions *u* and *v*:

$$B_i[u,v]=0\ , \quad i=1,2 \tag{10}$$

Suppose that the integrability of the system for both functions requires that *u* and *v* separately satisfy the respective PDEs

$$P[u]=0 \quad (a) \qquad Q[v]=0 \quad (b) \tag{11}$$

That is, the system (10) is a BT connecting solutions of the PDEs (11). Assume, now, that these PDEs possess known (or, in any case, easy to find) *parameter-dependent solutions* of the form

$$u=f(x,y;\alpha,\beta,\ldots)\ , \qquad v=g(x,y;\kappa,\lambda,\ldots) \tag{12}$$

where *α*, *β*, *κ*, *λ*, etc., are (real or complex) parameters. If values of these parameters can be determined for which *u* and *v* jointly satisfy the system (10), we say that the solutions *u* and *v* of the PDEs (11*a*) and (11*b*), respectively, are *conjugate through the BT* (10) (or *BT-conjugate*, for short). By finding a pair of BT-conjugate solutions one thus automatically obtains a solution of the system (10).

Note that solutions of *both* integrability conditions *P*[*u*]=0 and *Q*[*v*]=0 must now be known in advance! From the practical point of view the method is thus most applicable in *linear* problems, since it is much easier to find parameter-dependent solutions of the PDEs (11) in this case.

Let us see an example: Going back to the Cauchy-Riemann relations (3), we try the following parametric solutions of the Laplace equation (4):

$$u(x,y)=\alpha(x^2-y^2)+\beta x+\gamma y\ ,$$
$$v(x,y)=\kappa xy+\lambda x+\mu y\ .$$

Substituting these into the BT (3), we find that $\kappa=2\alpha$, $\mu=\beta$ and $\lambda=-\gamma$. Therefore, the solutions

$$u(x,y)=\alpha(x^2-y^2)+\beta x+\gamma y\ ,$$
$$v(x,y)=2\alpha xy-\gamma x+\beta y$$

of the Laplace equation are BT-conjugate through the Cauchy-Riemann relations.

As a counter-example, let us try a different combination:

$$u(x,y)=\alpha xy\ , \quad v(x,y)=\beta xy\ .$$

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Inserting these into the system (3) and taking into account the independence of *x* and *y*, we find that the only possible values of the parameters *α* and *β* are *α*=*β*=0, so that *u*(*x*,*y*)= *v*(*x*,*y*)=0. Thus, no non-trivial BT-conjugate solutions exist in this case.

4. EXAMPLE: THE MAXWELL EQUATIONS IN EMPTY SPACE

An example of an integrable linear system whose solutions are of physical interest is furnished by the *Maxwell equations* of electrodynamics. Interestingly, as noted recently [7], the Maxwell system has the property of a BT whose integrability conditions are the electromagnetic (e/m) wave equations that are separately valid for the electric and the magnetic field. These equations possess parameter-dependent solutions that, by a proper choice of the parameters, can be made BT-conjugate through the Maxwell system. In this and the following section we discuss the BT property of the Maxwell equations in vacuum and in a conducting medium, respectively.

In *empty space*, where no charges or currents (whether free or bound) exist, the Maxwell equations are written (in S.I. units) [9]

$$\begin{aligned} &(a)\quad \vec{\nabla}\cdot\vec{E}=0 &&(c)\quad \vec{\nabla}\times\vec{E}=-\frac{\partial\vec{B}}{\partial t} \\ &(b)\quad \vec{\nabla}\cdot\vec{B}=0 &&(d)\quad \vec{\nabla}\times\vec{B}=\varepsilon_0\mu_0\frac{\partial\vec{E}}{\partial t} \end{aligned} \qquad (13)$$

where $\vec{E}$ and $\vec{B}$ are the electric and the magnetic field, respectively. Here we have a system of four PDEs for two fields. The question is: what are the necessary conditions that each of these fields must satisfy in order for the system (13) to be self-consistent? In other words, what are the *consistency conditions* (or *integrability conditions*) for this system?

Guided by our experience from Sec. 2, to find these conditions we perform various differentiations of the equations of system (13) and require that certain differential identities be satisfied. Our aim is, of course, to eliminate one field (electric or magnetic) in favor of the other and find some higher-order PDE that the latter field must obey.

As can be checked, two differential identities are satisfied automatically in the system (13):

$$\vec{\nabla}\cdot(\vec{\nabla}\times\vec{E})=0\ ,\quad \vec{\nabla}\cdot(\vec{\nabla}\times\vec{B})=0\ ,$$

$$(\vec{\nabla}\cdot\vec{E})_t=\vec{\nabla}\cdot\vec{E}_t\ ,\quad (\vec{\nabla}\cdot\vec{B})_t=\vec{\nabla}\cdot\vec{B}_t\ .$$

Two others read

$$\vec{\nabla}\times(\vec{\nabla}\times\vec{E})=\vec{\nabla}(\vec{\nabla}\cdot\vec{E})-\nabla^2\vec{E} \qquad (14)$$

$$\vec{\nabla}\times(\vec{\nabla}\times\vec{B})=\vec{\nabla}(\vec{\nabla}\cdot\vec{B})-\nabla^2\vec{B} \qquad (15)$$

Taking the *rot* of (13*c*) and using (14), (13*a*) and (13*d*), we find

$$\nabla^2 \vec{E} - \varepsilon_0 \mu_0 \frac{\partial^2 \vec{E}}{\partial t^2} = 0 \qquad (16)$$

Similarly, taking the *rot* of (13*d*) and using (15), (13*b*) and (13*c*), we get

$$\nabla^2 \vec{B} - \varepsilon_0 \mu_0 \frac{\partial^2 \vec{B}}{\partial t^2} = 0 \qquad (17)$$

No new information is furnished by the remaining two integrability conditions,

$$(\vec{\nabla} \times \vec{E})_t = \vec{\nabla} \times \vec{E}_t \;\;, \quad (\vec{\nabla} \times \vec{B})_t = \vec{\nabla} \times \vec{B}_t \;\; .$$

Note that we have *uncoupled* the equations for the two fields in the system (13), deriving separate second-order PDEs for each field. Putting

$$\varepsilon_0 \mu_0 \equiv \frac{1}{c^2} \;\; \Leftrightarrow \;\; c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \qquad (18)$$

(where *c* is the speed of light in vacuum) we rewrite (16) and (17) in wave-equation form:

$$\nabla^2 \vec{E} - \frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} = 0 \qquad (19)$$

$$\nabla^2 \vec{B} - \frac{1}{c^2} \frac{\partial^2 \vec{B}}{\partial t^2} = 0 \qquad (20)$$

We conclude that the Maxwell system (13) is a BT relating solutions of the e/m wave equations (19) and (20), these equations representing the integrability conditions of the BT. It should be noted that this BT is *not* an *auto*-BT! Indeed, although the PDEs (19) and (20) are of similar form, they concern *different* fields with different physical dimensions and physical properties.

The e/m wave equations admit plane-wave solutions of the form $\vec{F}(\vec{k} \cdot \vec{r} - \omega t)$, with

$$\frac{\omega}{k} = c \quad \text{where} \quad k = |\vec{k}| \qquad (21)$$

The simplest such solutions are *monochromatic plane waves* of angular frequency *ω*, propagating in the direction of the wave vector $\vec{k}$:

$$\begin{aligned} \vec{E}(\vec{r},t) &= \vec{E}_0 \exp\{ i (\vec{k} \cdot \vec{r} - \omega t)\} \quad (a) \\ \vec{B}(\vec{r},t) &= \vec{B}_0 \exp\{ i (\vec{k} \cdot \vec{r} - \omega t)\} \quad (b) \end{aligned} \qquad (22)$$

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where $\vec{E}_0$ and $\vec{B}_0$ are constant complex amplitudes. The constants appearing in the above equations (amplitudes, frequency and wave vector) can be chosen arbitrarily; thus they can be regarded as *parameters* on which the plane waves (22) depend.

We must note carefully that, although every pair of fields $(\vec{E}, \vec{B})$ satisfying the Maxwell equations (13) also satisfies the wave equations (19) and (20), the converse is not true. Thus, the plane-wave solutions (22) are not *a priori* solutions of the Maxwell system (i.e., do not represent actual e/m fields). This problem can be taken care of, however, by a proper choice of the parameters in (22). To this end, we substitute the general solutions (22) into the BT (13) to find the extra conditions the latter system demands. By fixing the wave parameters, the two wave solutions in (22) will become *BT-conjugate* through the Maxwell system (13).

Substituting (22*a*) and (22*b*) into (13*a*) and (13*b*), respectively, and taking into account that $\vec{\nabla} e^{i\vec{k}\cdot\vec{r}} = i\vec{k}\, e^{i\vec{k}\cdot\vec{r}}$, we have

$$(\vec{E}_0\, e^{-i\omega t})\cdot\vec{\nabla} e^{i\vec{k}\cdot\vec{r}} = 0 \;\Rightarrow\; (\vec{k}\cdot\vec{E}_0)\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} = 0\,,$$
$$(\vec{B}_0\, e^{-i\omega t})\cdot\vec{\nabla} e^{i\vec{k}\cdot\vec{r}} = 0 \;\Rightarrow\; (\vec{k}\cdot\vec{B}_0)\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} = 0\,,$$

so that

$$\vec{k}\cdot\vec{E}_0 = 0\,, \quad \vec{k}\cdot\vec{B}_0 = 0\,. \tag{23}$$

Relations (23) reflect the fact that that the monochromatic plane e/m wave is a *transverse wave*.

Next, substituting (22*a*) and (22*b*) into (13*c*) and (13*d*), we find

$$e^{-i\omega t}(\vec{\nabla} e^{i\vec{k}\cdot\vec{r}})\times\vec{E}_0 = i\,\omega\,\vec{B}_0\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} \Rightarrow$$
$$(\vec{k}\times\vec{E}_0)\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} = \omega\,\vec{B}_0\, e^{i(\vec{k}\cdot\vec{r}-\omega t)}\,,$$

$$e^{-i\omega t}(\vec{\nabla} e^{i\vec{k}\cdot\vec{r}})\times\vec{B}_0 = -i\,\omega\,\varepsilon_0\mu_0\vec{E}_0\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} \Rightarrow$$
$$(\vec{k}\times\vec{B}_0)\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} = -\frac{\omega}{c^2}\,\vec{E}_0\, e^{i(\vec{k}\cdot\vec{r}-\omega t)}\,,$$

so that

$$\vec{k}\times\vec{E}_0 = \omega\,\vec{B}_0\,, \quad \vec{k}\times\vec{B}_0 = -\frac{\omega}{c^2}\,\vec{E}_0 \tag{24}$$

We note that the fields $\vec{E}$ and $\vec{B}$ are normal to each other, as well as normal to the direction of propagation of the wave. We also remark that the two vector equations in (24) are not independent of each other, since, by cross-multiplying the first relation by $\vec{k}$, we get the second relation.

Introducing a unit vector $\hat{\tau}$ in the direction of the wave vector $\vec{k}$,

$$\hat{\tau} = \vec{k}/k \quad (k = |\vec{k}| = \omega/c)\,,$$

we rewrite the first of equations (24) as

$$\vec{B}_0 = \frac{k}{\omega}(\hat{\tau}\times\vec{E}_0) = \frac{1}{c}(\hat{\tau}\times\vec{E}_0) \ .$$

The BT-conjugate solutions in (22) are now written

$$\begin{aligned} &\vec{E}(\vec{r},t) = \vec{E}_0 \exp\{\, i(\vec{k}\cdot\vec{r} - \omega t)\} \ , \\ &\vec{B}(\vec{r},t) = \frac{1}{c}(\hat{\tau}\times\vec{E}_0)\exp\{\, i(\vec{k}\cdot\vec{r} - \omega t)\} = \frac{1}{c}\,\hat{\tau}\times\vec{E} \end{aligned} \tag{25}$$

As constructed, the complex vector fields in (25) satisfy the Maxwell system (13). Since this system is homogeneous linear with real coefficients, the real parts of the fields (25) also satisfy it. To find the expressions for the real solutions (which, after all, carry the physics of the situation) we take the simplest case of *linear polarization* and write

$$\vec{E}_0 = \vec{E}_{0,R}\, e^{\,i\alpha} \tag{26}$$

where the vector $\vec{E}_{0,R}$ as well as the number α are real. The *real* versions of the fields (25), then, read

$$\begin{aligned} &\vec{E} = \vec{E}_{0,R} \cos(\vec{k}\cdot\vec{r} - \omega\, t + \alpha) \ , \\ &\vec{B} = \frac{1}{c}(\hat{\tau}\times\vec{E}_{0,R})\cos(\vec{k}\cdot\vec{r} - \omega\, t + \alpha) = \frac{1}{c}\,\hat{\tau}\times\vec{E} \end{aligned} \tag{27}$$

We note, in particular, that the fields $\vec{E}$ and $\vec{B}$ “oscillate” in phase.

Our results for the Maxwell equations in vacuum can be extended to the case of a *linear non-conducting medium* upon replacement of ε_0 and μ_0 with ε and μ, respectively. The speed of propagation of the e/m wave is, in this case,

$$\upsilon = \frac{\omega}{k} = \frac{1}{\sqrt{\varepsilon\mu}} \ .$$

In the next section we study the more complex case of a linear medium having a finite conductivity.

5. EXAMPLE: THE MAXWELL SYSTEM FOR A LINEAR CONDUCTING MEDIUM

Consider a linear conducting medium of conductivity σ. In such a medium, Ohm’s law is satisfied: $\vec{J}_f = \sigma\vec{E}$, where $\vec{J}_f$ is the free current density. The Maxwell equations take on the form [9]

$$(a) \quad \vec{\nabla}\cdot\vec{E}=0 \qquad (c) \quad \vec{\nabla}\times\vec{E}=-\frac{\partial\vec{B}}{\partial t}$$
$$(b) \quad \vec{\nabla}\cdot\vec{B}=0 \qquad (d) \quad \vec{\nabla}\times\vec{B}=\mu\sigma\vec{E}+\varepsilon\mu\frac{\partial\vec{E}}{\partial t} \tag{28}$$

By requiring satisfaction of the integrability conditions

$$\vec{\nabla}\times(\vec{\nabla}\times\vec{E})=\vec{\nabla}(\vec{\nabla}\cdot\vec{E})-\nabla^2\vec{E} \;,$$
$$\vec{\nabla}\times(\vec{\nabla}\times\vec{B})=\vec{\nabla}(\vec{\nabla}\cdot\vec{B})-\nabla^2\vec{B} \;,$$

we obtain the *modified wave equations*

$$\nabla^2\vec{E}-\varepsilon\mu\frac{\partial^2\vec{E}}{\partial t^2}-\mu\sigma\frac{\partial\vec{E}}{\partial t}=0$$
$$\nabla^2\vec{B}-\varepsilon\mu\frac{\partial^2\vec{B}}{\partial t^2}-\mu\sigma\frac{\partial\vec{B}}{\partial t}=0 \tag{29}$$

which must be separately satisfied by each field. As in Sec. 4, no further information is furnished by the remaining integrability conditions.

The linear differential system (28) is a BT relating solutions of the wave equations (29). As in the vacuum case, this BT is *not* an auto-BT. We now seek BT-conjugate solutions. As can be verified by direct substitution into equations (29), these PDEs admit parameter-dependent solutions of the form

$$\begin{aligned}\vec{E}(\vec{r},t)&=\vec{E}_0\exp\{-s\,\hat{\tau}\cdot\vec{r}+i\,(\vec{k}\cdot\vec{r}-\omega t)\}\\&=\vec{E}_0\exp\left\{\left(i-\frac{s}{k}\right)\vec{k}\cdot\vec{r}\right\}\exp(-i\omega t)\;,\\\vec{B}(\vec{r},t)&=\vec{B}_0\exp\{-s\,\hat{\tau}\cdot\vec{r}+i\,(\vec{k}\cdot\vec{r}-\omega t)\}\\&=\vec{B}_0\exp\left\{\left(i-\frac{s}{k}\right)\vec{k}\cdot\vec{r}\right\}\exp(-i\omega t)\end{aligned} \tag{30}$$

where $\hat{\tau}$ is the unit vector in the direction of the wave vector $\vec{k}$:

$$\hat{\tau}=\vec{k}/k \quad (k=|\vec{k}|=\omega/\upsilon)$$

(υ is the speed of propagation of the wave inside the conducting medium) and where, for given physical characteristics ε, μ, σ of the medium, the parameters s, k and ω satisfy the algebraic system

$$s^2-k^2+\varepsilon\mu\omega^2=0\;, \quad \mu\sigma\omega-2sk=0 \tag{31}$$

We note that, for arbitrary choices of the amplitudes $\vec{E}_0$ and $\vec{B}_0$, the vector fields (30) are not *a priori* solutions of the Maxwell system (28), thus are not BT-conjugate solutions. To obtain such solutions we substitute expressions (30) into the system (28). With the aid of the relation

$$\vec{\nabla} e^{\left(i-\frac{s}{k}\right)\vec{k}\cdot\vec{r}} = \left(i-\frac{s}{k}\right)\vec{k}\, e^{\left(i-\frac{s}{k}\right)\vec{k}\cdot\vec{r}}$$

one can show that (28*a*) and (28*b*) impose the conditions

$$\vec{k}\cdot\vec{E}_0 = 0\,, \quad \vec{k}\cdot\vec{B}_0 = 0 \tag{32}$$

As in the vacuum case, the e/m wave in a conducting medium is a *transverse* wave.

By substituting (30) into (28*c*) and (28*d*), two more conditions are found:

$$(k+is)\,\hat{\tau}\times\vec{E}_0 = \omega\vec{B}_0 \tag{33}$$

$$(k+is)\,\hat{\tau}\times\vec{B}_0 = -(\varepsilon\mu\omega + i\mu\sigma)\vec{E}_0 \tag{34}$$

Note, however, that (34) is not an independent equation since it can be reproduced by cross-multiplying (33) by $\hat{\tau}$, taking into account the algebraic relations (31).

The BT-conjugate solutions of the wave equations (29) are now written

$$\begin{aligned} \vec{E}(\vec{r},t) &= \vec{E}_0\, e^{-s\hat{\tau}\cdot\vec{r}} e^{i(\vec{k}\cdot\vec{r}-\omega t)}\,, \\ \vec{B}(\vec{r},t) &= \frac{k+is}{\omega}\,(\hat{\tau}\times\vec{E}_0)\, e^{-s\hat{\tau}\cdot\vec{r}} e^{i(\vec{k}\cdot\vec{r}-\omega t)} \end{aligned} \tag{35}$$

To find the corresponding real solutions, we assume linear polarization of the wave, as before, and set

$$\vec{E}_0 = \vec{E}_{0,R}\, e^{i\alpha}\,.$$

We also put

$$k + i\,s = |\,k + i\,s\,| e^{i\varphi} = \sqrt{k^2+s^2}\; e^{i\varphi} \;\;;\;\; \tan\varphi = s/k\,.$$

Taking the real parts of equations (35), we finally have:

$$\begin{aligned} \vec{E}(\vec{r},t) &= \vec{E}_{0,R}\, e^{-s\hat{\tau}\cdot\vec{r}} \cos(\vec{k}\cdot\vec{r}-\omega t+\alpha)\,, \\ \vec{B}(\vec{r},t) &= \frac{\sqrt{k^2+s^2}}{\omega}\,(\hat{\tau}\times\vec{E}_{0,R})\, e^{-s\hat{\tau}\cdot\vec{r}} \cos(\vec{k}\cdot\vec{r}-\omega t+\alpha+\varphi)\,. \end{aligned}$$

As an exercise, the student may show that these results reduce to those for a linear non-conducting medium (cf. Sec. 4) in the limit $\sigma\to 0$.

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6. BTS AS RECURSION OPERATORS

The concept of symmetries of PDEs was discussed in [1]. Let us review the main facts:

Consider a PDE $F[u]=0$, where, for simplicity, $u=u(x,t)$. A transformation

$$u(x,t) \rightarrow u'(x,t)$$

from the function u to a new function u' represents a *symmetry* of the given PDE if the following condition is satisfied: $u'(x,t)$ is a solution of $F[u]=0$ *if* $u(x,t)$ is a solution. That is,

$$F[u']=0 \quad \textit{when} \quad F[u]=0 \tag{36}$$

An *infinitesimal symmetry transformation* is written

$$u' = u + \delta u = u + \alpha Q[u] \tag{37}$$

where α is an infinitesimal parameter. The function $Q[u] \equiv Q(x, t, u, u_x, u_t, \ldots)$ is called the *symmetry characteristic* of the transformation (37).

In order that a function $Q[u]$ be a symmetry characteristic for the PDE $F[u]=0$, it must satisfy a certain PDE that expresses the *symmetry condition* for $F[u]=0$. We write, symbolically,

$$S(Q;u)=0 \quad \textit{when} \quad F[u]=0 \tag{38}$$

where the expression S depends *linearly* on Q and its partial derivatives. Thus, (38) is a linear PDE for Q, in which equation the variable u enters as a sort of parametric function that is required to satisfy the PDE $F[u]=0$.

A *recursion operator* $\hat{R}$ [10] is a linear operator which, acting on a symmetry characteristic Q, produces a new symmetry characteristic $Q' = \hat{R}Q$. That is,

$$S(\hat{R}Q;u)=0 \quad \textit{when} \quad S(Q;u)=0 \tag{39}$$

It is not too difficult to show that *any power of a recursion operator also is a recursion operator*. This means that, starting with any symmetry characteristic Q, one may in principle obtain an infinite set of characteristics (thus, an infinite number of symmetries) by repeated application of the recursion operator.

A new approach to recursion operators was suggested in the early 1990s [2,3] (see also [4-6]). According to this view, a recursion operator is an auto-BT for the linear PDE (38) expressing the symmetry condition of the problem; that is, a BT producing new solutions Q' of (38) from old ones, Q. Typically, this type of BT produces *nonlocal* symmetries, i.e., symmetry characteristics depending on *integrals* (rather than derivatives) of u.

As an example, consider the *chiral field equation*

$$F[g] \equiv (g^{-1}g_x)_x + (g^{-1}g_t)_t = 0 \tag{40}$$

(as usual, subscripts denote partial differentiations) where g is a $GL(n,C)$-valued function of x and t (i.e., an invertible complex $n\times n$ matrix, differentiable for all x, t).

Let $Q[g]$ be a symmetry characteristic of the PDE (40). It is convenient to put

$$Q[g] = g\,\Phi[g]$$

and write the corresponding infinitesimal symmetry transformation in the form

$$g' = g + \delta g = g + \alpha g\,\Phi[g] \tag{41}$$

The symmetry condition that Q must satisfy will be a PDE linear in Q, thus in Φ also. As can be shown [4], this PDE is

$$S(\Phi; g) \equiv \Phi_{xx} + \Phi_{tt} + [g^{-1}g_x\,,\,\Phi_x] + [g^{-1}g_t\,,\,\Phi_t] = 0 \tag{42}$$

which must be valid when $F[g]=0$ (where, in general, $[A, B] \equiv AB-BA$ denotes the *commutator* of two matrices A and B).

For a given g satisfying $F[g]=0$, consider now the following system of PDEs for the matrix functions Φ and Φ':

$$\begin{aligned} \Phi'_x &= \Phi_t + [g^{-1}g_t\,,\,\Phi] \\ -\Phi'_t &= \Phi_x + [g^{-1}g_x\,,\,\Phi] \end{aligned} \tag{43}$$

The integrability condition $(\Phi'_x)_t = (\Phi'_t)_x$, together with the equation $F[g]=0$, require that Φ be a solution of (42): $S(\Phi\,; g) = 0$. Similarly, by the integrability condition $(\Phi_t)_x = (\Phi_x)_t$ one finds, after a lengthy calculation: $S(\Phi'; g) = 0$.

In conclusion, for any g satisfying the PDE (40), the system (43) is a BT relating solutions Φ and Φ' of the symmetry condition (42) of this PDE; that is, relating different symmetries of the chiral field equation (40). Thus, if a symmetry characteristic $Q=g\Phi$ of (40) is known, a new characteristic $Q'=g\Phi'$ may be found by integrating the BT (43); the converse is also true. Since the BT (43) produces new symmetries from old ones, it may be regarded as a *recursion operator* for the PDE (40).

As an example, for any constant matrix M the choice $\Phi=M$ clearly satisfies the symmetry condition (42). This corresponds to the symmetry characteristic $Q=gM$. By integrating the BT (43) for Φ', we get $\Phi'=[X, M]$ and $Q'=g[X, M]$, where X is the “potential” of the PDE (40), defined by the system of PDEs

$$X_x = g^{-1}g_t \;, \quad -X_t = g^{-1}g_x \tag{44}$$

Note the *nonlocal* character of the BT-produced symmetry Q', due to the presence of the potential X. Indeed, as seen from (44), in order to find X one has to *integrate* the chiral field g with respect to the independent variables x and t. The above process can be continued indefinitely by repeated application of the recursion operator (43), leading to an infinite sequence of increasingly nonlocal symmetries.

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7. SUMMARY

Classically, Bäcklund transformations (BTs) have been developed as a useful tool for finding solutions of nonlinear PDEs, given that these equations are usually hard to solve by direct methods. By means of examples we saw that, starting with even the most trivial solution of a PDE, one may produce a highly nontrivial solution of this (or another) PDE by integrating the BT, without solving the original, nonlinear PDE directly (which, in most cases, is a much harder task).

A different use of BTs, that was recently proposed [7,8], concerns predominantly the solution of linear systems of PDEs. This method relies on the existence of parameter-dependent solutions of the linear PDEs expressing the integrability conditions of the BT. This time it is the BT itself (rather than its associated integrability conditions) whose solutions are sought.

An appropriate example for demonstrating this approach to the concept of a BT is furnished by the Maxwell equations of electromagnetism. We showed that this system of PDEs can be treated as a BT whose integrability conditions are the wave equations for the electric and the magnetic field. These wave equations have known, parameter-dependent solutions – monochromatic plane waves – with arbitrary amplitudes, frequencies and wave vectors playing the roles of the "parameters". By substituting these solutions into the BT, one may determine the required relations among the parameters in order that these plane waves also represent electromagnetic fields (i.e., in order that they be solutions of the Maxwell system). The results arrived at by this method are, of course, well known in advanced electrodynamics. The process of deriving them, however, is seen here in a new light by employing the concept of a BT.

BTs have also proven useful as *recursion operators* for deriving infinite sets of nonlocal symmetries and conservation laws of PDEs [2-6] (see also [11] and the references therein). Specifically, the BT produces an increasingly nonlocal sequence of symmetry characteristics, i.e., solutions of the linear equation expressing the symmetry condition (or "linearization") of a given PDE.

An interesting conclusion is that the concept of a BT, which has been proven useful for integrating nonlinear PDEs, may also have important applications in linear problems. Research on these matters is in progress.

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Impedance Spectroscopy and Equivalent Circuit Modelling of Carbon Nanotube Dispersion in Thermosetting Blends

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Abstract. The dispersion of carbon nanotubes (CNTs) in a typical epoxy resin was monitored on line via the employment of impedance spectroscopy. The use of interdigital sensors has the advantage for in situ process monitoring during the dispersion process which is significant for the effective use of CNTs in modern technological products such as those used in marine applications. Monitoring the dispersion process ensures high quality of products and facilitates optimal material selection in the product formulation. The real and imaginary parts of the impedance were recorded during frequency scans at regular intervals in the course of the sonication of the mixture. The equivalent circuit analysis of the sensor signal assisted in the detection of the gradual progress of the process and also the indication of time of completion.

Keywords: carbon nanotubes, dispersion, impedance spectroscopy, interdigital sensors, equivalent circuit analysis

PACS: 82.35.Np Nanoparticles in polymers, 82.70.-y Disperse systems; complex fluid, 62.23.Pq Composites (nanosystems embedded in a larger structure), 61.46.Fg Nanotubes

INTRODUCTION

Carbon Nanotubes (CNTs) were found to improve electrical, thermal and mechanical properties of polymer matrices when they used as fillers, similar to Carbon Black (CB) particles with the advantage that for building up the conductive percolation network, much lower weight content of CNTs is needed [1]. For the application of using CNTs in the matrix of smart tooling, the electrical as well as thermal properties enhancement is considered. In order to obtain conductive polymer/CNT composites, the CNTs are incorporated into the polymer matrix, where they form a three dimensional conductive network above a critical volume called the percolation threshold (p_c) [2] inversely dependent on the aspect ratio (the ratio of the long dimension over the short dimension) of the inclusions. Therefore, the high aspect ratio of CNTs provides conductive carbon fibre reinforced polymers (CFRPs) with the inclusion of low filler concentration [3, 4].

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The first major step of CNT reinforced CFRPs production depends on the homogeneous dispersion of the CNTs in the polymer matrix. Therefore depending on the desirable target properties, the processing parameters like the viscosity of the matrix, the size and geometry of the particles and the machine parameters like rotation speed, mixing time and temperature, the optimum filler content and manufacturing process can vary for each filler-matrix combination. One basic challenge consists in finding the best technology for the energy input to disperse the fibres without damaging them and the epoxy matrix. There are significant challenges and peculiarities when dispersing CNTs in thermoset resin systems.

On the other hand the CNT-reinforced resin systems are used as matrix material in CFRPs. This is usually achieved by prepregging, Resin Transfer Moulding (RTM), wet laminating or autoclave technologies. Critical parameters are amongst others the viscosity of the matrix, the dispersion quality and the particle size.

Dispersion and percolation behaviour depend on many factors. Shape and size of the dispersed particles, shear rate, viscosity and chemical functionalization; all of these parameters influence the dispersion result. However, once dispersed, the system is not in the state of equilibrium. The particles dispersed in a viscous material are subject to Brownian motion and hydrodynamic forces and the particles interact due to different attractive and repulsive forces.

While curing the epoxy/CNT composites, two processes counteract each other. Viscosity decreases with increasing temperature but once the curing reaction is initiated, cross-linking between the molecules will result progressively increment in viscosity with time. This leads to an accelerated re-agglomeration. It is well known that carbon nanotubes re-agglomerate during the curing process. There are methods to achieve a stable dispersion**,** either by modifying the potential curve or by stabilising the suspension via the existence of a potential barrier.

All the above demonstrate the significance for nanotube-reinforced polymers of the effective dispersion of the CNTs in the matrix system. Nano-scaled particles exhibit an enormous surface area (more than 1000 m^2/g), which is several orders of magnitude larger than the surface of conventional fillers. This surface area acts as interface for a stress transfer, but is also responsible for the strong tendency of the CNTs to form agglomerates. An efficient exploitation of the CNT properties in polymers is therefore related to their homogeneous dispersion in the matrix or an exfoliation of the agglomerates and a good wetting with the polymer.

The precise characterisation of the dispersion quality is a complex issue. There are different, partly multistage procedures, interpreting the results of specific testing methods. The validation does not generate absolute values but has a relative, describing character. Low resolution analysis can be used to search for significant agglomerates inside a bigger area, while high resolution methods are able to evidence (or not) the existence of single dispersed CNTs.

METHODOLOGY

Dielectric analysis, or dielectrometry, is a technique that can be used to investigate the processing characteristics and chemical structure of polymers and other organic materials by measuring their dielectric properties. Dielectric measurements are usually implemented as an electrical admittance measurement. This measurement can be accomplished by placing a sample of the material of interest between two electrically conducting plates (electrodes), applying a time-varying voltage, $v(t)$, between the two electrodes and measuring the resulting time-varying current, $i(t)$ [5,6].

Impedance spectroscopy coupled with equivalent circuit modelling can be used in order to investigate the on-line monitoring of thermoset cure [7]. One limitation of using equivalent circuits is the non-uniqueness of the model because the material response can be represented by a variety of combinations of electrical components. Recent work has shown that when the addition of CNTs induces a conductive response, impedance generally increases as crosslinking advances [8]. In the case of neat epoxy resin, this behaviour can be attributed to mobility limitations imposed on the charge carriers by the process of cure [9], while in the case where the epoxy matrix has been reinforced with SWNTs the frequency corresponding to the conductive mechanisms of the system increases with the process of cure [10].

Changes in a material's degree of electrical dipole alignment and/or its ion mobility can be used to infer information concerning its bulk material properties, such as its viscosity, rigidity, reaction rate, cure state, etc. Fundamental to the methodology of actually accomplishing dielectric (admittance) measurements is the critical assumption that the electrical response of the sample is linear and time-invariant [11].

A typical epoxy resin (Huntsman XU3508) was used for the dispersion of 0.1 %w/w multi-wall carbon nanotubes (MWCNTs) of more than 98% carbon basis, with outside diameter 6-13 nm and length 2.5-20 μm from Sigma-Aldrich. Impedance measurements were performed using an Advanced Dielectric Thermal Analysis System (DETA-SCOPE by ADVISE) and commercially available GIA microsensors supplied at the site of the CNT mixing. The amplitude of the excitation voltage applied to the sensors was 10 V. A sweep of 12 frequencies between 10 Hz and 100 kHz was made. A control thermocouple was placed inside the resin tank in order to measure the temperature during the frequency cycles. The commercial dielectric sensor used (GIA sensors, Pearson Panke) comprise an assembly of interdigital copper electrodes, printed at a spacing of 300 μm on a polymeric substrate film. The sensors were dipped into the resin/CNT dispersion and measurement were taken at regular intervals during the mixing process.

DEVELOPMENT OF EQUIVALENT CIRCUIT MODEL

The application of the flat interdigital sensors allows for the in-process monitoring of the dispersion of carbon nanotubes in the epoxy matrix, as the transformation from the parallel plate capacitor to coplanar electrodes. These electrodes create fringing electric field lines which interact with the material. In this way, measurements may be one or two sided allowing for easy, non invasive measurements in most systems (Figure 1). The distance between the electrodes is proportional to the penetration depth in the material. In this way, the choice of sensor defines the representative volume that is interrogated with the method.

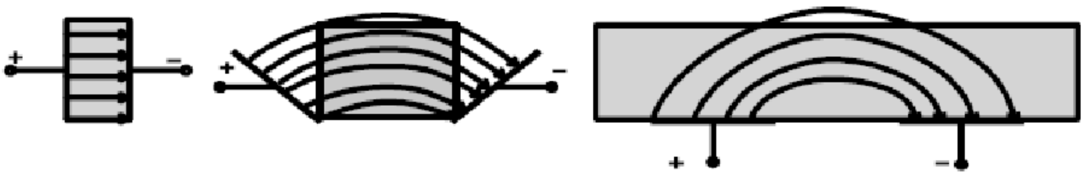

FIGURE 1. From the parallel to the coplanar capacitor configuration: the interdigital sensor and the resulting electric field.

The impedance response of the mixture is dominated by the behaviour of the conductive loose aggregates of nanotubes and the resin-rich areas acting as interfaces among them. The dielectric response of typical epoxy systems depends on the complex dielectric permittivity ε* which involves contribution from both dipoles and ion mobility:

$$\varepsilon^* = \varepsilon^*_{dipolar} + \varepsilon^*_{ionic} \quad (1)$$

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When the electric field is interacting with the dielectric material, contributions from polarization of dipoles and ionic species take place at the vicinity of the capacitor plates or at randomly created interfaces in the material volume. Although the aforementioned contribution constitute an equivalent circuit where separate branches have to be accounted for in all distinct species, typically, in plain epoxy configurations the equivalent circuit is simplified, which directly relates to the resin viscosity and the degree of cure. In this case, the equivalent circuit is formed as a capacitor and a resistance in parallel (Figure 2), where the ionic contribution is characterized by the resistance R, and the mobility of the branches of the molecular network is represented by the capacitor C.

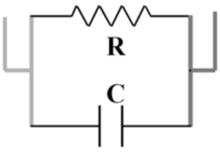


FIGURE 2. Simplified equivalent circuit for a typical epoxy cure reaction

In the case of the inclusion of the CNT phase, the equivalent circuit becomes more complicated. Previous works [12], [13] have revealed inductive contributions to electrical signal from the presence of CNT inclusions. In these studies a three branch circuit for the modelling of CNTs dispersion in the resin and of the curing process with the addition of hardener was used. The circuit representation was overall satisfactory for both mixing and curing of the resin, however an indication of the end of the dispersion process was not clearly observed. Therefore this circuit model needs to be improved. To this end, the three branch circuit of these studies [12], [13] is modified by shifting the branch corresponding to the contribution of the nanophase (a typical inertia element, i.e. a coil, and a resistance) to a new position in series to the other branches. In this way, it is believed that the equivalent circuit shown in Figure 3 has the inertia element (the inductance L) in a more prominent role to represent accurately the dispersion of the nanophase (movement and structural changes of the CNTs). At the same time, the resistance R2 should be directly related to the conductivity of the mixture as dispersion stops percolation effects.

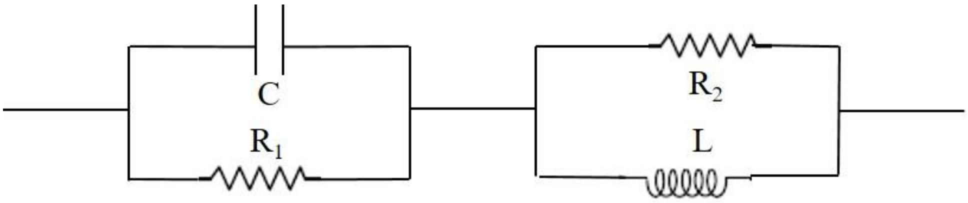


FIGURE 3: Equivalent circuit for the neat epoxy resin with CNT inclusions.

ANALYSIS OF EXPERIMENTAL RESULTS

The temperature changes during the dispersion process were measure with a control thermocouple and the results are shown in Figure 4. It is observed that temperature is increasing at the initial stages of the dispersion and after 60 min it stabilises around 35^{o}C.

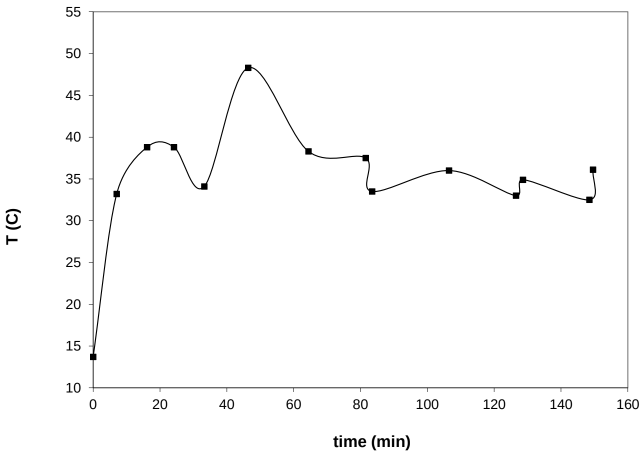


FIGURE 4. Values of T(t), the temperature T vs. dispersion time.

The acquired impedance values during selected times at the course of CNT dispersion in the epoxy resin matrix were analysed and fitted to the circuit of Figure 3 by employing a complex non linear least square immitance fitting program developed by Ross Macdonald in 1999 and since then upgraded with additional features. The circuit of Figure 3 is adapted to standard circuit models embedded in the fitting software, where each circuit model consists of 40 elements. Out of the 40 parameters (P1, P2, …, P40) of the circuit model, only those related to the elements of the circuit of Figure 3 (P1, P6, P7, P8 and P9) are variable, while all others are fixed to 0. Further details of the fitting method and the fitting software tool are provided in [13]. The main interface of the fitting software with the key settings used for the data treatment is shown in Figure 5.

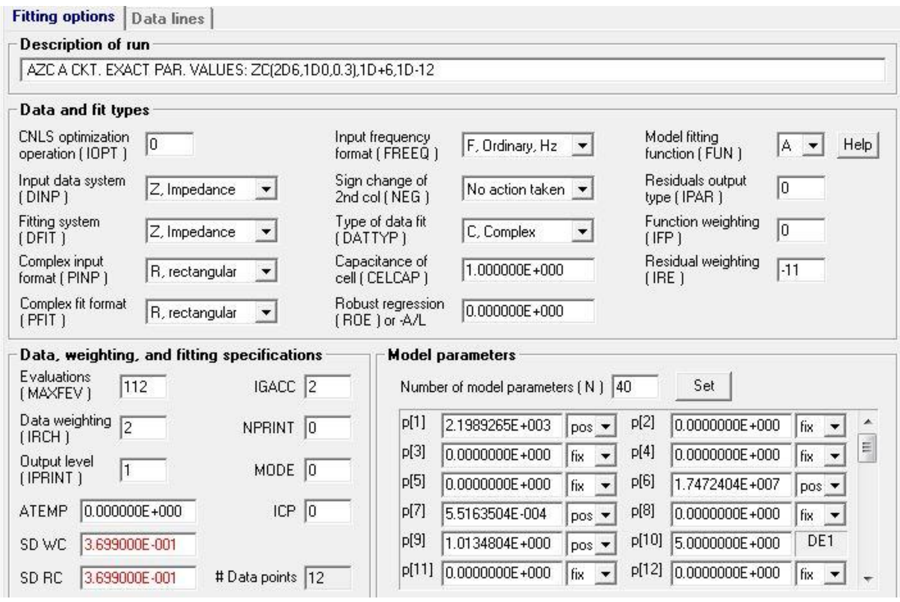


FIGURE 5. User interface of the complex non-linear least square impedance fitting software for the analysis of the data obtained during CNT dispersion in epoxy resin matrix.

A typical fitting involved loading the measurement data from the specific impedance spectrum (real and imaginary impedance vs. test frequency) and running the fitting software with the above described model and settings of parameters. The predicted values of real and imaginary impedance (model = continuous line) was compared with the measurement data (points = measurements) to assess the fitness of the model, as shown in Figure 6.

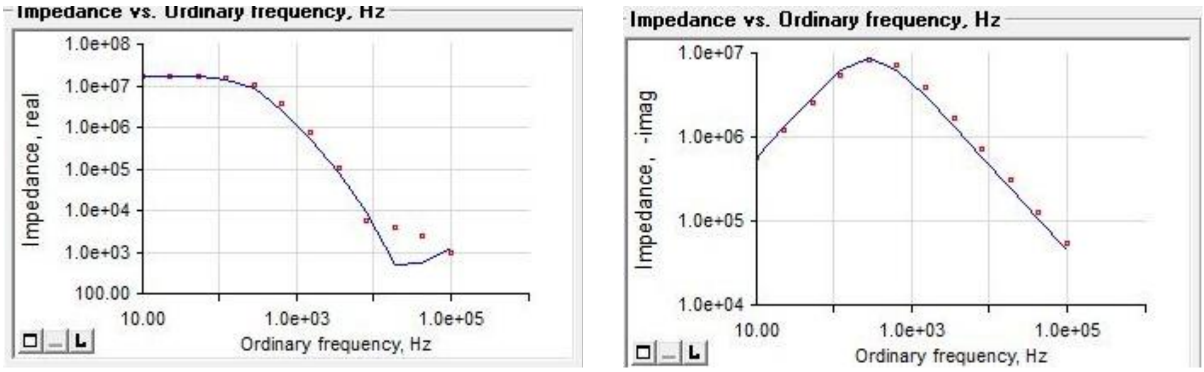
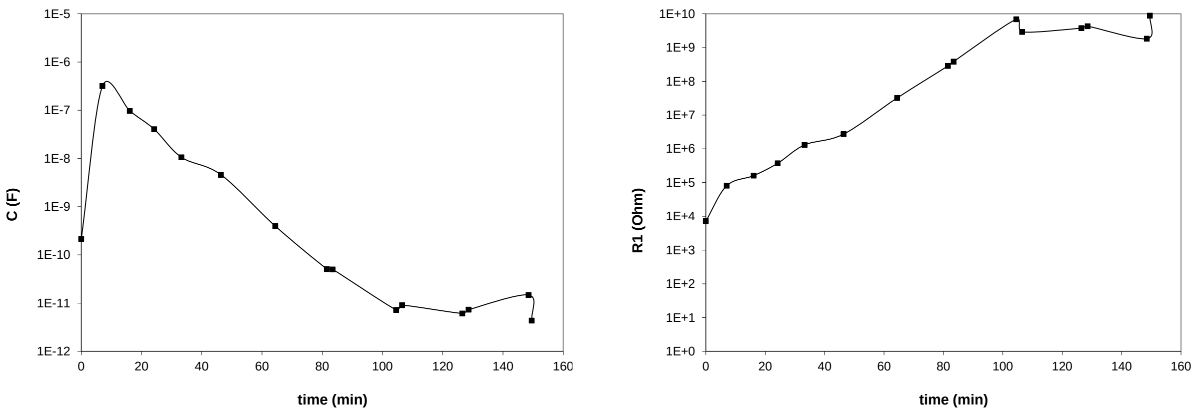


FIGURE 6. Comparison between data (points) and circuit model prediction (continuous line) for the real and imaginary impedance after the execution of the fitting routine.

In the following description the values of the parameters of the equivalent circuit of Figure 3 are presented and the significance of the changes during the dispersion process is discussed.

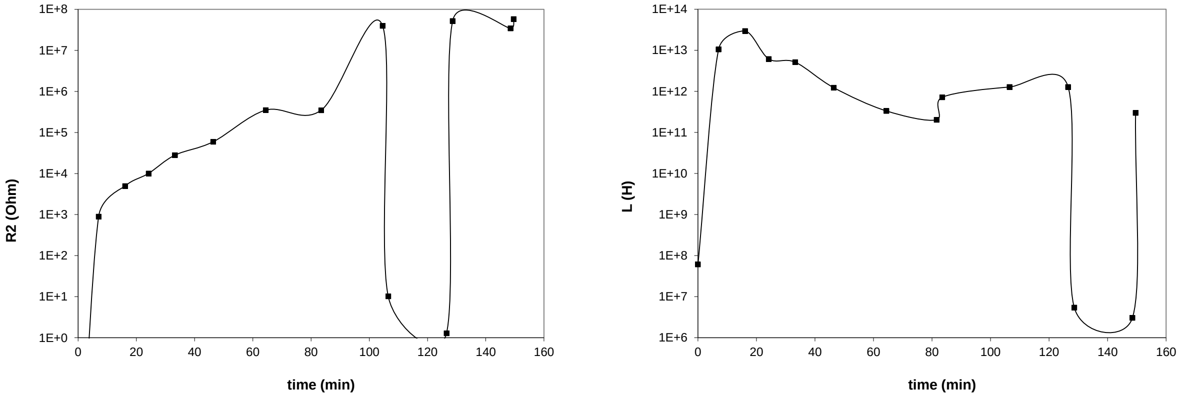


(a) (b)

FIGURE 7. Values of (a) C(t), capacitance vs. dispersion time and (b) R_1(t), resistance vs. dispersion time.

Figure 7 shows the values of the circuit elements in the branch representing the main relaxation and the charge separation in the material. There is a progressive change in the fitted values for both capacitance C and resistance R1. As far as the capacitance is concerned (Figure 7a), there is an initial sharp increase at the start of the dispersion process, which is followed by a gradual drop in values up to 100 min in the process. At that time the capacitance value approaches the order of magnitude of capacitance in air showing that there are no significant relaxation processes in the signal any more. This levelling signifies the stability of the dispersion and an indication of the completion of the process. It is worth mentioning the high values of capacitance at the start of the process, which implies that the particular material structure at this stage is suitable for the development of energy storage devices. A potential freeze of the nanostructure at the specific formation would lead to an efficient capacity in charges separation.

As far as the resistance R1 is concerned (Figure 7b), the plot demonstrates similar gradual change, which is an increase for this element up to 100 min in the process. The starting value is around 10 kΩ, a low figure, as a result of low apparent viscosity of the resin under the initial conditions of the dispersion process (presence of few but large agglomerates of CNTs). As the dispersion proceeds, the agglomerates are breaking and the apparent viscosity increases causing the rise in resistance. The final level of the element R1 (corresponding to the resin component) in the order of GΩ indicates the reduced mobility of ions in the resin system. The time of levelling off is identical for both capacitance and resistance circuit elements.



(a) (b)

FIGURE 8. Values of (a) $R_2(t)$, resistance vs. time and (b) L(t), inductance vs. time.

Figure 8 shows the values of the circuit elements in the branch representing the conductive and inductive behaviour of the CNT structure within the liquid resin. There is a progressive change in the fitted values for both resistance R2 and inductance L. As far as the resistance is concerned (Figure 8a), there is an initial sharp increase at the start of the dispersion process, which is followed by a gradual increase in values. The final level is reached at 100 min in the process, but a disturbance in the behaviour is observed when the final level is reached. The disturbance has the form of very low values for a period of 20 min. The above changes are explained by the dispersion procedure, which breaks the nanoparticles agglomerates into smaller entities, thus increasing the length of conductive paths in the system. An effective dispersion process is expected to result in a significant increase of this resistive component. The increase in resistance is around four orders of magnitude. As far as the observed disturbance in resistance is concerned, this can be attributed to the occurrence of a 'conductive spike' in the system observed only at the CNT components of the circuit model.

As far as the inductance L is concerned (Figure 8b), the plot demonstrates also a sharp increase at the start of the process and then a gradual drop towards the final level at 100 min in the process. The starting value is around 100 MH and the final level is at 1 TH. As the dispersion proceeds, the agglomerates are breaking, the average distance between individual CNTs is increasing and the inductive effect is also increasing. A similar disturbance is observed in inductance.

The above description shows clearly how dielectric measurements in the dispersion process can be used to detect the main stages of the process and indicate its completion.

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CONCLUSIONS

The dispersion of carbon nanotubes (CNTs) in a typical epoxy resin was monitored on line via the employment of impedance spectroscopy. The system used interdigital sensors which allowed for in situ process monitoring during the dispersion process. The sensors were immersed in the epoxy/carbon nanotubes system which was subjected to dispersion. The real and imaginary parts of the impedance were recorded during frequency scans at regular intervals in the course of the sonication of the mixture. The equivalent circuit analysis of the sensor signal assisted in the detection of the gradual progress of the process and also the indication of time of completion.

The dispersion process is significant for the effective use of CNTs in modern technological products, such as those used in marine applications. Currently nanotechnology products are used for surface protection of principal structures, such as hulls, and also effective coating for the prevention of algae growth in submerged surfaces. The preparation of these products involves dispersion of CNT structures in the carrying liquid. Monitoring the dispersion process ensures high quality of products and facilitates optimal material selection in the product formulation.

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