

Thermal Effects on the Percolation Behavior of Polyvinylidene Fluoride/Nickel Composites

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ABSTRACT: Percolation theory predicts the ideal percolation threshold (P_C) for insulator/conductor composites (ICC) to be at 0.16 of the conductor volume fraction in the composite. In this article, we have investigated the percolation behavior in polyvinylidene fluoride/nickel (Ni) composites by varying the Ni concentration. It is observed that the thermal effect/time of heat treatment play a crucial role in changing the value of P_C in a simple random continuum percolative ICC. The effect is attributed to decrease in: (i) intercluster distance, (ii) viscosity of the polymer, and (iii) wetting of the polymer to metal. The heat energy helps the polymer matrix to be melted as a result the metal particles/clusters come closure, that causes an increase in the cluster size of the metal particles.

The overall effect is lowering of P_C mainly due to decrease in intercluster distance. A drastic enhancement in the dielectric permittivity with increase of metal content is explained using boundary layer capacitive effect arising due to Maxwell–Wagner–Sillars interfacial polarization of accumulated charges at the metal–polymer interfaces and blocking of charge carriers at the insulating boundary. The substantial enhancement of ac conductivity at the P_C is attributed to leakage of charge carriers across the insulating barrier. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3023–3028, 2010

Key words: composites; conducting polymers; dielectric properties; dispersions; molding

INTRODUCTION

Conductive polymer composites have received considerable attention due to their technological importance in a wide variety of applications, such as, microwave absorbing materials, electromagnetic shielding materials, impedance matching, antistatic materials, self-regulating heaters, etc.^{1–5} In addition, they are also considered to be important in many other applications, such as, printed circuit boards, embedded capacitors, high-charge storage capacitors, high electric energy density materials, electrostriction artificial muscles, smart skins for drug reduction, micro fluidic systems for drug delivery, etc.^{6–10} Normally, the conductivity in a polymer is imparted by incorporation of electrically conductive fillers into the polymer matrix. The various conductive fillers, such as, metal fillers,^{4–8,11–13} carbon fibers,^{1,14–17} conductive carbon black,^{2,3,18–22} graphite nanoplates,^{23,24} and other types of conductors^{25,26} have been used in practice. These composites are of recent interest because of their high dielectric constant, easy processing, flexibility, ability to absorb mechanical shock, etc.^{1–26} It is well-known that these random insula-

tor/conductor composites (ICC) undergo a metal–insulator transition (MIT) at a critical concentration of the metal (conductor) in the composite. The percolation theories (for these random continuum percolation systems^{27,28}) predict the ideal percolation threshold (P_C) i.e., the critical volume fraction for any 3D random percolative ICC to be at 0.16^{29–31} (where the fillers are assumed to be of hard spheres), where as experimentally the P_C value is found to be at variance.^{1–8,11,12,14–26} The focus of research in polymer/conductor composites is on P_C and the critical behavior in the vicinity of MIT. Although half a century has passed since the initial development of the standard percolation theory,^{29–31} yet a consensus has not been reached so far as the calculation of P_C for a given material that exhibits a conductor–insulator transition is concerned. Still a lot of controversy exists which requires serious attention. Previous reports in literature showed that the value of P_C depends on various parameters, such as, size, shape, spatial distribution, adhesiveness, viscosity, wetting of the polymer, polymer matrix, process conditions, etc.^{1–8,11–26} This has motivated us to consider a systematic study to optimize P_C as a function of various parameters, such as, materials processing conditions, shape and size of the fillings, rheological properties of the matrix, etc.

A P_C of 0.17³² for silver-coated-glass-Teflon composites and 0.16¹³ for hot molded (200°C) polyvinylidene fluoride (PVDF)/micron-sized nickel (Ni)

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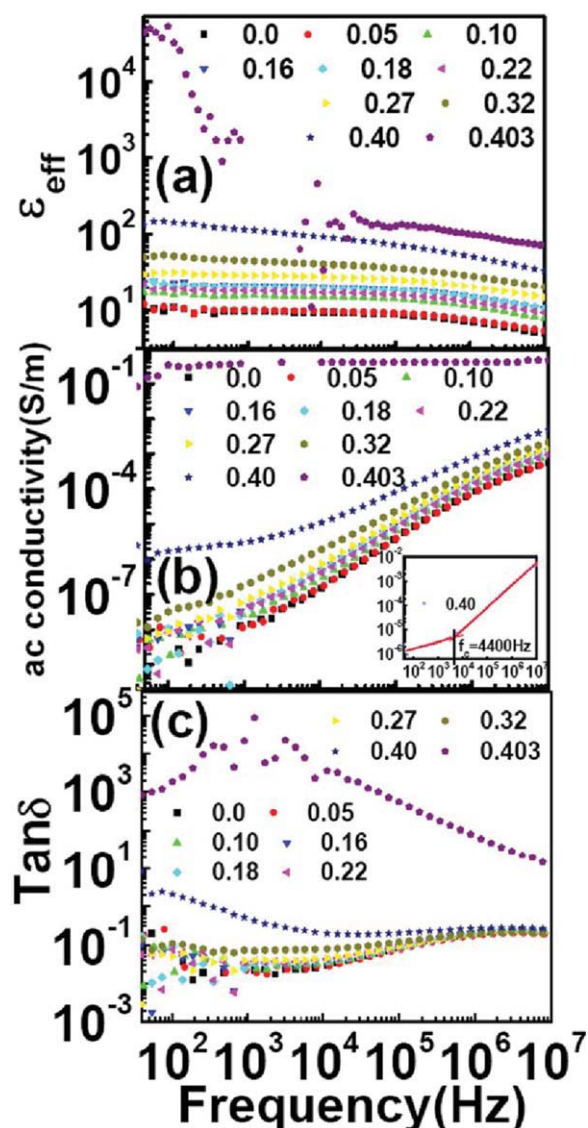


Figure 1 The variation of (a) effective dielectric constant, (b) effective conductivity, and (c) loss tangent as a function of frequency for all the composites with different f_{Ni} . The solid line for the sample $f_{Ni} = 0.40$ in inset of Figure 1(b) shows the fits to Equation 1 in evaluating f_c value, which is found to be 4400 Hz. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

composites has been reported experimentally, which coincides with the ideal P_C , whereas composites prepared through cold compact method exhibited a P_C value of 0.57.⁷ These results suggest that the thermal effects do play an important role in lowering the P_C . It is important to lower the P_C using various processing conditions, so that the flexibility of the polymer matrix can be retained and at the same time additional functionality could be introduced in the composite through the fillers, which can serve as candidates for multifunctional applications. In this work, we aim to investigate the effect of heat treat-

ment and its duration on tailoring of the P_C in a metal-dispersed polymer matrix composite.

EXPERIMENTAL

The composites of PVDF/Ni were prepared with different volume fractions of Ni (f_{Ni}) in the composite. The constituents were thoroughly mixed with the help of agate mortar and pestle for 90 min. The samples with different f_{Ni} were hot molded at a temperature of 200°C and 10 MPa pressure for 12 min. Alternatively, we have studied isothermal effects on one of the compositions $f_{Ni} = 0.22$. This is done by increasing the cure time during hot molding of the cold compacted sample under same temperature and pressure conditions. The electrical properties were measured using a precision impedance analyzer (Agilent 4294A) in the frequency range of 40 Hz to 10 MHz with Agilent 16451B dielectric test fixture. The micrographs were taken with the help of a polarized optical microscope (model no: Nikon Eclipse E 400 POL).

RESULTS AND DISCUSSION

Figure 1 shows the variation of effective dielectric constant, ac conductivity and loss tangent of all the composite samples of $f_{Ni} = 0.0, 0.05, 0.10, 0.16, 0.18, 0.22, 0.27, 0.32, 0.40, 0.403$ molded under 200°C and for 12 min. We can see from the Figure 1(a) that there is a sudden increment in dielectric constant for the sample 0.40 as compared with 0.32. The static dielectric constant increases from 50 for $f_{Ni} = 0.32$ to 133 for $f_{Ni} = 0.40$. The dielectric constant at 0.40 is 13 times the dielectric constant of the pure polymer matrix. As this is a macroscopically heterogeneous system consisting of two components of very different permittivity and conductivity, because of Maxwell,³³ Wagner,³⁴ and Sillars³⁵ interfacial polarization due to the accumulation of charges at the interface of metal and insulating polymer, the charge is blocked,²⁴ i.e., suffer resistance to flow and indirectly leads to the storage of charge and there by increases the capacitance and hence the dielectric constant. This increase continues with increase in more number of interfaces with an increase in metal content in the composite. Below the critical concentration of the filler loading, the interparticle distance is large enough so that neighboring local fields apparently do not interact. Thus, dielectric factor in this region increases slowly. But as the filler loading increases, the Maxwell–Wagner–Sillars effect increases due to reduction in the interaggregate/cluster/particle distance giving rise to high dielectric properties. The increase in dielectric constant can also be explained with the help of “boundary layer capacitor effect,”^{6,7,14,24} i.e., as with increase of metal

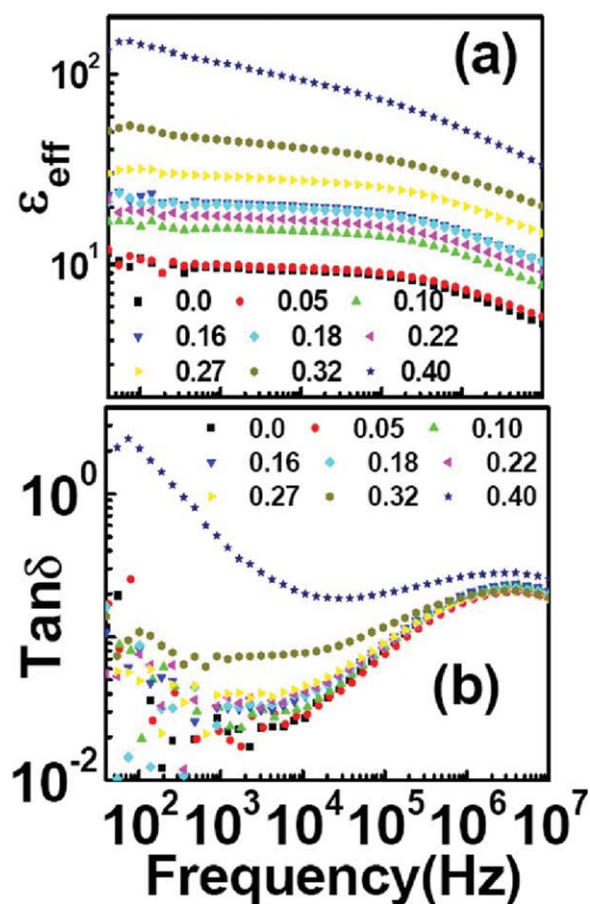


Figure 2 (a) The dispersion of dielectric constant and (b) the dipolar relaxation with frequency for pure polymer and all the composites below and above percolation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

content the intercluster/particle distance decreases and at a particular concentration, the clusters/particles are separated by a thin dielectric insulating layer forming large number of microcapacitors and thereby increase the capacitance and hence the dielectric constant. The contribution to dielectric constant for the pure PVDF and as well as for all other samples below percolation from dipolar polarization becomes negligible at high frequencies, i.e., above 10^5 Hz [Fig. 2(a)] which is attributed to the dipolar relaxation within that frequency range and can be observed from Figure 2(b) that there is also a relaxation peak in loss tangent versus frequency over that frequency range for all the samples below 0.32, i.e., in the insulating side. The 0.40 sample does not show any dipolar-relaxation peak because it is in the deep metallic region and it becomes a charge carrier dominated system, and when it becomes a charge carrier dominated system, there is no dipoles in the system. As it is a charge carrier dominated system, 0.40 shows anomalous low frequency dispersion³⁶ in its dielectric constant and loss tangent as a function

of frequency [See for 0.40 sample in Fig. 2(b)]. The dipolar relaxation³⁶ occurring for all the samples below 0.32, i.e., below percolation is attributed to the presence of polar groups ($-F$) and MWS dipoles formed at the interfaces of metal-polymer in the composite. The dispersion of dielectric constant becomes prominent for composites with high-metal content due to high leakage current.^{5-8,14,24} Thus, at percolation there is a divergence in real part of dielectric constant. As it is undergoing an MIT, 0.32 is in the insulating region, whereas 0.40 is in the metallic region. The dielectric constant for 0.403 sample shows negative value over a certain frequency range as it is towards the deep metallic region. The static dielectric constant for this sample is also very high,

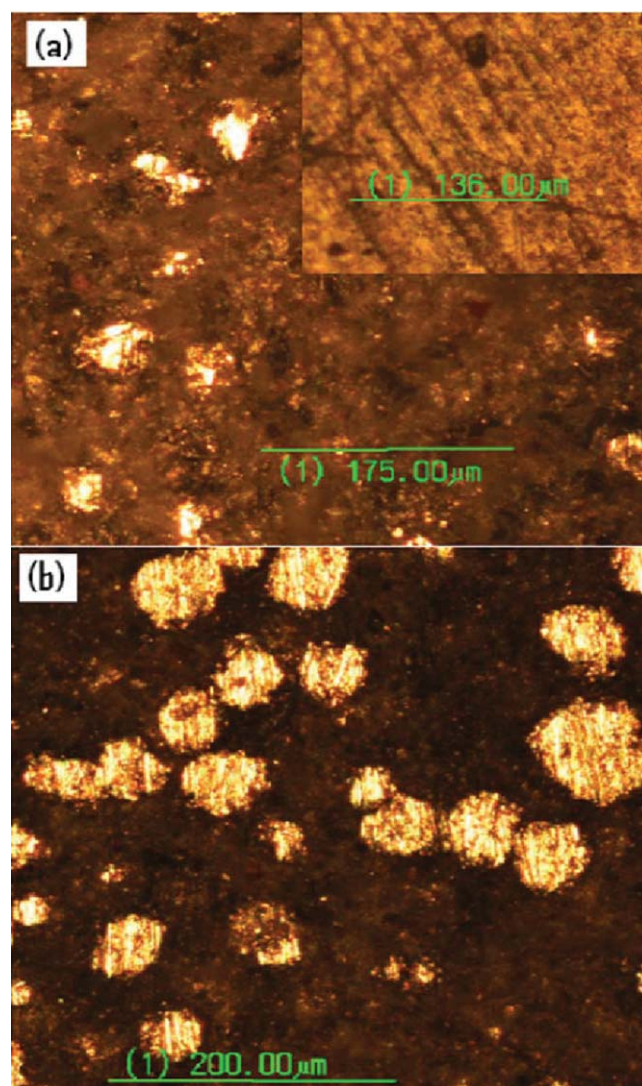


Figure 3 Optical micrographs of the composites with different f_{Ni} molded at 200°C for 12 min (a) $f_{Ni} = 0.22$ (b) $f_{Ni} = 0.32$. Inset: $f_{Ni} = 0.0$, i.e., pure polymer sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

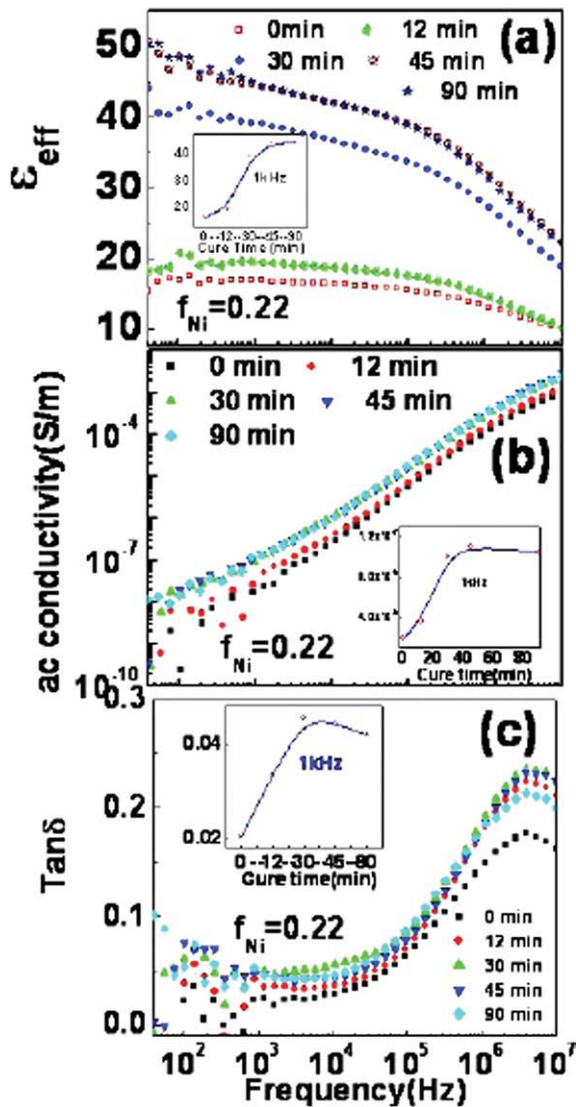


Figure 4 The variation of (a) effective dielectric constant, (b) effective ac conductivity, and (c) loss tangent for the sample with $f_{Ni} = 0.22$ molded for different timings as a function of frequency. Inset: (a) effective dielectric constant, (b) effective ac conductivity, and (c) loss tangent versus molding time at 1 kHz for $f_{Ni} = 0.22$ sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

i.e., $>50,000$ which is normally observed for conductors only.

From the ac conductivity graph [Fig. 1(b)], it can be noticed that there is an abrupt increase in dc conductivity at low frequencies for $f_{Ni} = 0.40$ as compared with $f_{Ni} = 0.32$ which is also consistent with the percolation theory.^{29–31} Thus from this data, it is obvious that P_C lies in between 0.32 and 0.40. One can observe for the sample 0.40 that ac conductivity is independent of frequency up to a limiting frequency beyond which the ac conductivity increases with frequency obeying Johnson's universal dielectric response law.³⁶ The dc conductivity independent

of frequency is coming due to long range connectivity across the bulk resistance of the composite due to the occurrence of physical contacts among the filler clusters, whereas the increase in ac conductivity after certain frequency is explained due to the hopping of localized charge carriers within the localized sites. The Johnson's universal dielectric response law is given by,

$$\sigma_{ac} = \sigma_0 + A\omega^n \quad (1)$$

where σ_0 is the dc conductivity and ω is the angular frequency. From the fitting of above eq. (1) to the conductivity data for 0.40 sample shows that the value of n was found to be 0.78 which is well within the Johnson's universal value of between 0 and 1.³⁶ The frequency which separates the region of ac and dc conductivity region is called critical frequency or hopping frequency (f_c).²⁵ The critical frequency is normally determined by locating the intersection of the lines that are tangent to the frequency-dependent and frequency-independent regions. Above f_c , the conductivity increases according to the power law $\sigma(\omega) \propto \omega^x$, where ω is the angular frequency. The f_c value is found from the fits is 4400 Hz [Inset, Fig. 2(b)], which separates the region of ac and dc conductivity. For other samples, i.e., from 0.0 to 0.32 the dc conductivity value is very less as there is no physical contact between the filler clusters. For the sample 0.403, the conductivity is completely of dc conduction and there is no effect of frequency on the conductivity which is because of development of complete physical connectivity among the filler clusters and that is also toward the deep metallic region.

The sudden increment in loss which is also a feature of percolation can be observed for the sample 0.40 as compared with 0.32 sample [Fig. 1(c)]. For the sample 0.403, very high loss of >1000 is observed as it is in the deep metallic region. The difference in microstructure and how the filler clusters are approaching closure with increase of concentration of the metallic filler can be observed from the optical micrographs as shown in Figure 3. The bright portions are the Ni clusters and the background is the polymer matrix.

Thus, we conclude from above discussion that the P_C found under this condition of sample preparation was between 0.32 and 0.40. Recently, under the similar processing conditions, the P_C was found at 0.16 for the same composites.¹³ With the idea that time of hot molding may change the P_C of the sample, i.e., 0.22 just above 0.16, i.e., the ideal P_C was hot molded for different cure time.

The composite 0.22 shows a value of static dielectric constant of 15 for the room temperature compacted sample. With increase of heat treatment for

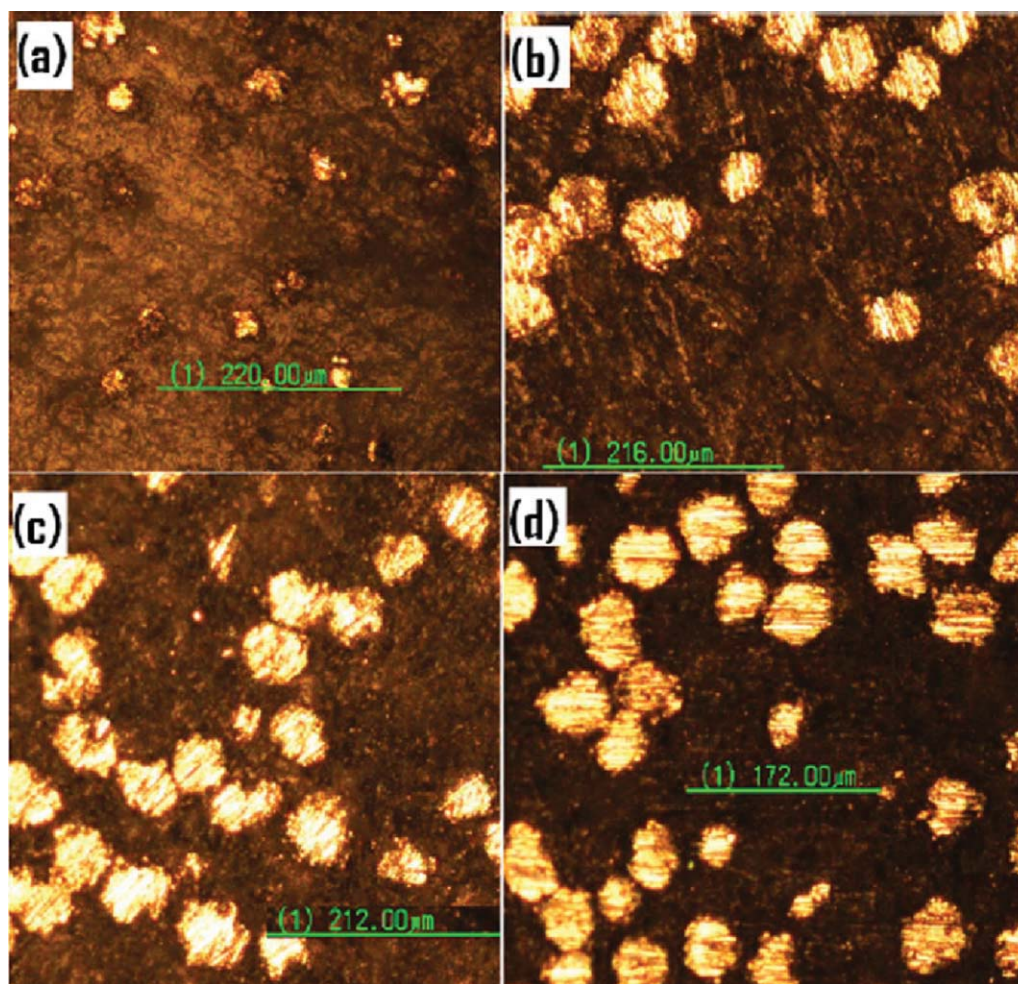


Figure 5 Optical micrographs of the composite sample with $f_{Ni} = 0.22$ molded at 200°C for different timings (a) 0, (b) 30, (c) 45, and (d) 90 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

different timings, the value of static dielectric constant increases slowly to 18 for the samples with cure time of 12 min, 43 for 30 min, 50 for and 45 min, 50 for 90 min [Inset, Fig. 4(a)]. The dielectric constant for all the samples decrease at above 10^5 Hz due to the noncontributing of dipolar polarization because within that frequency range the samples are undergoing dipolar relaxation. We observe that the thermal effects do play a role up to a certain limiting time (for a particular concentration of the conductor) and after that there is no impact of time on percolation and on interparticle distance. We can observe also from Figure 4(b,c) that the value of ac conductivity and loss tangent also increases with increase of cure time for the composite sample 0.22. The ac conductivity are found to increase from $10^{-8} \Omega^{-1} \text{m}^{-1}$ to $10^{-7} \Omega^{-1} \text{m}^{-1}$ at 1 kHz for $f_{Ni} = 0.22$ [Inset, Fig. 4(b)]. The value of loss tangent also increases from 0.02 to 0.04 at 1 kHz for $f_{Ni} = 0.22$ for different hot molding timings [Inset, Fig. 4(c)]. The overall mechanism what it governs is that the interfacial area and interparticle distance are likely the key parameters in controlling the properties of the

composites. The increase in dielectric constant is due to the decrease in intercluster/particle distance and decrease in viscosity of the polymer leading to less adhesiveness of the polymer with metal such that it helps in increase of accumulation of charges at the metal/polymer interface. The increase in ac conductivity and loss tangent is due to more probability of tunneling with decrease in interfiller cluster distance and increase in overlapping of the effective tunneling range of the two filler clusters^{37,38} and decrease in viscosity of the polymer with increase of heat content leading to less adhesiveness of the polymer¹¹ with metal which can be observed from the optical micrographs [Fig. 5]. But the effect of increment occurs up to a certain extent and after that heat treatment cannot lower down the percolation if the concentration of filler and spatial distribution connectivity is not there. This is evidenced by invariant values of dielectric constant, ac conductivity and loss tangent for the sample molded for 45 min and 90 min. In fact, these values tend to saturate instead of undergoing MIT as a function of molding time. Thus, we conclude that the effective range of metal

concentration for percolation lies above 0.22 and below 0.40, i.e., ($0.22 < P_C \leq 0.40$). Previous reports on identical systems give $P_C = 0.16$ ¹³ and $P_C = 0.57$ observed by us.⁷ The large change in P_C from 0.57 to <0.40 , i.e., ($0.22 < P_C \leq 0.40$) is explained as due to the heat energy, the polymer matrix melts; as a consequence the cluster size of the metal particles increases. Due to increase in cluster size, more physical contacts are developed giving rise to long range dc conductivity which is a typical feature of percolation. Due to the increase in heat treatment viscosity of the polymer decreases leading to decrease in intercluster distance and wetting of the polymer to metal also. Thus, we observed P_C in metal–polymer (conductor–polymer) composites is predominantly controlled by processing conditions. The results in this article have clearly confirmed out the initial idea of process conditions on tailoring of P_C . Thus, it seems getting ideal P_C is a matter of coincidence only as it depends completely on the interparticle distance, spatial distribution of the composite components and is controlled simultaneously by a number of parameters as discussed earlier.

CONCLUSIONS

The P_C found in the case of PVDF/Ni composites molded for 12 min is in between 0.32 and 0.40, whereas with increase of timing of hot molding the P_C is found to be in between 0.22 and 0.40. These results are in strong deviation from the earlier reported values. Thus in addition to the parameters like size, shape, spatial distribution, connectivity of the filler, interfacial interaction, which controls the P_C , we have observed that the heat treatment/time of heat treatment strongly alters the value of P_C in a random polymer/conductor continuum composite. The experimental validation of ideal P_C is a matter of coincidence only as it is controlled simultaneously by a number of parameters, such as, size, shape, interfacial interaction, wetting, adhesiveness, spatial distribution, time of mixing, time of heat treatment, temperature, diffusivity, viscosity, etc. and a slight change in one parameter strongly alters the P_C .

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