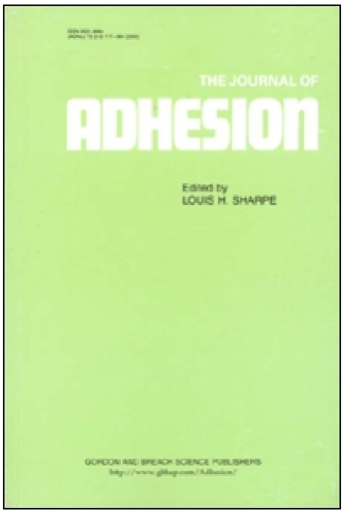

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Diffusion Aided Joint Healing in Polymers at Interfaces

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This article reports the results of diffusion studies of 4,4′-diphenyl methane diisocyanate (MDI) at 40°C into different kinds of thermoplastic materials, and, thereafter, application of the same concept in polymer joint healing at interfaces. Two categories of samples were used for adhesion studies: (1) aged at 40°C for 100 h and (2) non-aged samples. The adhesion/failure strength at the interface was measured using a peel test method. The thermoplastic materials used were a copolymer and/or blends of the following polymers: polystyrene-co-maleic anhydride (SMA), polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS), and silicone-acrylate rubber (SAR). A gravimetric method was used to measure the mass uptake and the optical microscopy was employed for the determination of the diffused layer of MDI into the thermoplastic materials. In two of the thermoplastic blends, glass fiber (GF) was also blended along with the copolymers. MDI was found to have no diffusion in neat/pure SMA copolymer, whereas the diffusion coefficient for PC/ABS was the highest for the samples investigated. The results are discussed in terms of functional groups present in the different interacting materials. In general, the aged samples showed higher adhesive strength than the non-aged samples.

Keywords: 4,4′-Diphenyl methane diisocyanate (MDI); Adhesion by diffusion; Aging; Interfaces; Peel test; Thermoplastics

1. INTRODUCTION

Diffusion of small liquid molecules into polymer systems has been the subject of a number of studies over the years [1–4]. Diffusion of liquid molecules in the polymer matrix plays an important role in a wide

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variety of areas of scientific and technological importance, such as adhesion, drying of paint, etc. The diffusion of molecules depends on the solubility of the two materials and it is related to the adhesion strength at the interface [5]. Since diffusion and adhesion in polymers at interfaces are closely related to each other, fundamental understanding of the behavior of polymer solid surface is crucial in optimizing the interfacial strength. The schematic mechanism of the diffusion process in polymers at interfaces is shown in Fig. 1 [6]. The interface boundary/layer contains both materials, *i.e.*, the liquid molecule and the polymer. The composition of the interface layer depends upon the specific liquid molecule and the polymer system. In the figure below (Fig. 1) A represents a liquid, whereas B is a polymer matrix. After A and B are brought into contact with each other, an interface boundary/layer develops [7,8]. With the passage of time, the thickness of the interface layer becomes wider and wider depending on whether or not the liquid component is exhausted. The thickness of the interface layer depends on the spatial arrangement of the atoms in the molecule and their polarity (molecular structure) of both interacting substances. The composition of the two interacting materials changes with time in the interface [9,10]. Therefore, if interdiffusion phenomena are involved in the joint healing, the strength/adhesion should depend on different factors, such as contact time, temperature, nature, and molar masses of polymers, etc. For example, when two miscible or partially miscible polymers are brought into contact at temperatures above the glass transition temperature, the initial macroscopic interface gradually disappears, and the strength of adhesion increases with time. Such a phenomenon has been attributed to the intermingling of

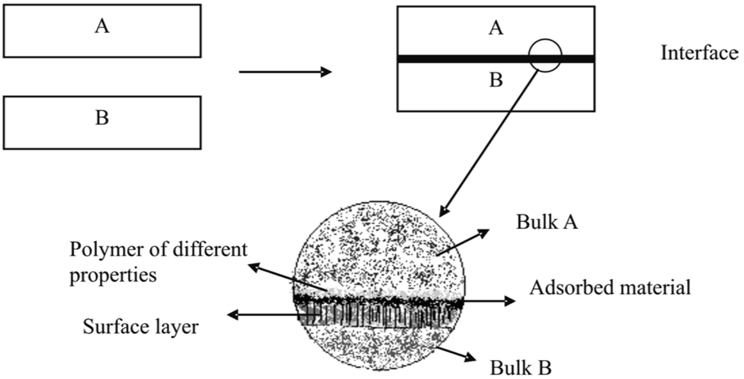

FIGURE 1 Schematic representation of interdiffusion process of material, A and B. The interfacial area is explained in the enlarged image.

the surface macromolecules followed by a mass transfer of polymer chains across the interface [11–15]. Finally, it can be summarized that diffusion phenomena do actually contribute greatly to the adhesive strength in many cases involving polymer-polymer joints. Nevertheless, the interdiffusion of macromolecular chains requires both polymers to be sufficiently compatible and the chains to possess a sufficient mobility [16]. These conditions are obviously fulfilled for autohesion, healing, or welding of identical polymers. In order to follow such diffusion processes at polymer-polymer interfaces different spectroscopic techniques have been employed. The most popular ones include transmission FTIR spectroscopy [17], dynamic light scattering [18], neutron scattering [19–22], etc.

To enhance the joint strength at the interface between two different materials, approaches such as using a primer or performing plasma treatment can be applied, but for industrial processes it is of interest to reduce the number of production steps. Polyurethane (PU) foams are directly synthesized on different thermoplastic materials and these are used for insulation purposes [23,24]. In this study, we have investigated the diffusion of a liquid PU foam component (4,4′-diphenyl methane diisocyanate, MDI) into thermoplastic materials and its correlation with the adhesion. To follow the diffusion process, first a gravimetric method was used and later samples were microtomed for optical image analysis. This was carried out to measure the thickness of the transient interface layer which is related to the diffusion coefficient using the model published in the literature [25]. The diffusion coefficient determined in this study is related to the interfacial failure strength. In order to establish a relationship between the diffusion and the interfacial strength, the thermoplastic material was adhered to PU foams. The following thermoplastic material systems were chosen as polymer matrices for the present investigation: (a) polycarbonate/acrylonitrile butadiene styrene (PC/ABS) with polystyrene-co-maleic anhydride (SMA), (b) PC/ABS, (c) polycarbonate/silicone acrylate rubber with glass fiber (PC/SAR-GF), and (d) PC/ABS-GF. Polyurethane foam components used were polyether polyol, *i.e.*, a mixture of polyethylene and propylene oxide and 4,4′-diphenyl methane diisocyanate (MDI). The blowing agent used in the PU foam formulation was water.

2. EXPERIMENTAL

2.1. Materials

All the chemicals for the PU foam were obtained from Bayer AG, Dormagen, Germany and used without further purification. MDI with an isocyanate index of 88 (isocyanate index is the molar ratio of isocyanate *versus* active hydrogen bearing groups, *i.e.*, hydroxyl and amino groups) was used. The –OH terminated polyethers were polypropylene and polyethylene oxide based on a weight ratio of 80:20 (PPO:PEO). The PU foam was synthesized by reacting polyol and MDI with a polyol:MDI ratio of 100 g:45 g and a water content of 2.6 g as blowing agent. The five types of thermoplastic material plates were prepared by compression molding with a size of 10.5 × 15 × 0.3 cm for the experiments. The thermoplastic materials used were neat SMA (Cadon DMC250), a blend of PC with ABS (PC/ABS, Bayblend T65), a blend of PC with ABS and SMA (PC/ABS-SMA), and two samples reinforced with glass fibers, based on a blend of PC with ABS (PC/ABS-GF, Bayblend T88-2 N, includes 10% glass fiber) and a blend of PC with SAR (PC/SAR-GF). All of the above materials were obtained from Bayer AG and were used without further purification.

2.2. Gravimetric Analysis

The purpose of this test was to find out how much MDI diffuses into different thermoplastic materials as a function of time. The mass gain of the test samples was recorded at different time intervals. The progress of the diffusion of MDI, one of the foam components, was studied using five different thermoplastic material systems at 40°C (foaming temperature). Small thermoplastic strips having dimensions of $2 \times 5 \times 10\,\text{mm}^3$ were cut from each thermoplastic material plate which was compression molded. Each strip was weighed and then dipped into the MDI, removed from the MDI after certain time intervals (5, 20, 45, 70, and 100 h), dried with tissue paper, and weighed. The final weight gain was obtained by weighing the samples after 100 h.

2.3. Optical Microscopy

The diffused layer thickness was measured from the optical microscope images. Liquid nitrogen cooled samples were microtomed with a thickness of 10 μm using a Rotationsmicrotom HM 360 microtome (Leica Microsystems, Nussloch, Germany). The samples were fixed on glass slides by using silicone oil and then the images were acquired using a research microscope RM DX (Leica Microsystems, Nussloch, Germany). In the present study all the images were acquired at a magnification of 16×.

2.4. Preparation of PU Foam Samples

To prepare the samples with PU foam adhered to the thermoplastic material plate, 100 g of polyol were mixed with 45 g of MDI and mechanically stirred for 10 s. Finally, the reacting mixture was transferred to a heatable quadratic foaming tool (size: $20 \times 20 \times 2\,\mathrm{cm}^3$), which already contained the thermoplastic material plate (size: $18 \times 10 \times 0.5\,\mathrm{cm}^3$). The tool was then closed to allow the process to progress for 10 min at 40°C. After that the foamed plate was removed from the foaming tool. The amount of the PU educts was chosen depending on the composition to obtain a final product with a foam density of $0.16 \pm 0.02\,\mathrm{g/cm}^3$.

To simulate the effect of diffusion process at the PU foam and thermoplastic interface, the samples were divided into two sets. One set was placed in an oven at 40°C for 100 h. These samples are referred to as aged samples. The other set of samples was kept at room temperature and peel tests were conducted 20 ± 5 min after preparation. These samples are referred to as non-aged samples.

2.5. Peel Test

The peel test samples were prepared by cutting the thermoplastic plate after the foaming process into rectangular strips of dimensions of $120 \times 18\,\mathrm{mm}^2$ with a 5-mm thick PU foam layer on it. The peel test was carried out on a computerized Zwick 1120 Werkstoffprüfmaschine (Zwick Roell, Ulm, Germany) by peeling the PU foam layer from the thermoplastic material at a peel angle of 90° and at room temperature conditions. The peeling rate used was 10 mm/min. The testing machine provides a constant rate of peel and continuously measures the force of detachment during the test. The peeling force, P, required for separating the PU foam layer from the thermoplastic material substrate was recorded continuously. The normalized total force, G, is related to the applied steady state peel load, P, the width, b, of the specimen, and the peel angle, y, by Eq. (1) [26]:

$$G = \frac{p}{b}(1 - \cos\theta). \tag{1}$$

The value of G includes the interfacial adhesion strength, and any plastic work done in bending the peel arm. The reported results were calculated by subtracting the plastic work done in bending the peel arm (PU foam layer). The value of interfacial adhesion strength is assumed to be a characteristic of the particular interface, and ideally independent of the geometrical details of the peel test specimens such as the thickness of the peel arm and the peel angle. For each TP material system, five samples strips were measured to calculate a statistical error.

3. RESULTS AND DISCUSSION

3.1. Gravimetric Analysis

The data of MDI mass uptake at 40°C by the thermoplastic materials is shown in Fig. 2. All the test samples show generally a similar trend of MDI sorption; initially the slopes of the curves are steep and as the time increases the slopes of the curves decrease. This trend means the rate of MDI sorption to the polymer substrate is initially high and decreases with the passage of time. This trend is in accord with the well-known Fick's law which is mathematically written as [27]:

$$J = -D\frac{\partial C}{\partial d}, \tag{2}$$

where J is the flux, or diffusion current density, the amount of material diffused in a unit time per unit area perpendicular to the interface, D is the diffusion coefficient, C is the concentration, and d is the distance along the direction of diffusion.

At the beginning of the experiment, there is no sorbed material in the polymer matrix, and, therefore, the concentration gradient at the

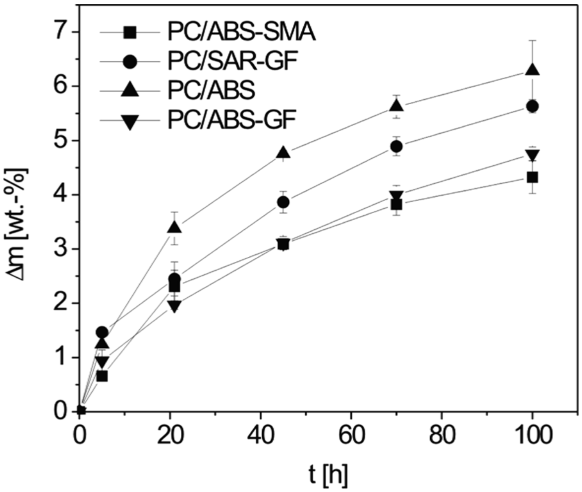

FIGURE 2 Mass uptake (wt.%) of MDI curves for different thermoplastic materials inversed in MDI at different time intervals at 40°C.

interface is high and, hence, the diffusion is fast. In other words, the mass uptake of MDI is higher initially. As time passes, some of the MDI is already taken up by the polymer matrix and, therefore, the concentration gradient now is less; therefore, less mass diffuses in a similar time interval. With time, the concentration gradient keeps on decreasing and, thereby, less and less MDI is being taken up by the polymer matrix.

The mass uptake (Δm) is the amount of MDI sorbed per unit weight of the thermoplastic materials and it is expressed in terms of wt.%. The mass uptake of MDI by the thermoplastic materials ranges from 4.5 to 6.5 wt.%. All the thermoplastic materials show qualitatively similar behavior of MDI mass uptake as a function of time.

However, quantitatively different MDI masses were sorbed into different thermoplastic materials. The experiments were continued for long times to ensure the maximum MDI sorption. As given in Fig. 2, the PC/ABS sample shows the maximum mass uptake of MDI, while the minimum sorption is observed for the PC/ABS-SMA sample. The lower sorption in PC/ABS-SMA might be due to the SMA content in the sample, as neat SMA did not show any MDI uptake (data not shown). This indicates that MDI does not diffuse into SMA component of the blend. Samples such as PC/SAR-GF and PC/ABS-GF show intermediate results; the mass uptake (Δm) values of these samples are between the mass uptake values of the two samples discussed above. The data show that the sample PC/ABS-GF (70 wt.% PC and 20 wt.% ABS) shows significantly less MDI uptake as compared with PC/ABS (60 wt.% PC and 40 wt.% ABS). This observation reveals that the MDI uptake is strongly enhanced by increasing the ABS content of the samples from 20 to 40 wt.%. However, due to the different compositions of the samples, it is very difficult to explain the influence of individual content of the samples on the MDI mass uptake. For the pure SMA plastic material there was no MDI sorption and, therefore, these results are not shown in Fig. 2.

To gain further insight into the MDI sorption mechanism, the sorption results were fitted to Eq. (3) [1]:

$$d = At^{\alpha}, \tag{3}$$

where d is diffusion length, A is the proportionality factor, t is time, and α is the diffusion exponent.

The diffusion exponent (α) is a parameter related to the diffusion mechanism. The least-squares estimate of α was obtained at the >95% confidence limit for the different thermoplastic materials at

40°C. For all the thermoplastic materials the value of α is 0.50 ± 0.05, which indicates the diffusion in all the investigated samples follows the Fickian Model.

3.2. Optical Microscopy

In order to check the depth of the diffused MDI layer in the thermoplastic materials, optical microscopic studies were conducted on samples without glass fiber. Images were acquired of the thermoplastic materials at different time intervals. Representative microscopic pictures for the PC/ABS-SMA sample are shown in Fig. 3 in which the arrows indicate the MDI diffusion direction. The depth of the diffused MDI layer was directly calculated from the images by excluding the swelling area above the surface of the thermoplastic material. It is evident from the images that the thermoplastic samples swell with the MDI diffusion. Moreover, a sharp front of the MDI diffusing layer can be seen in the images (Fig. 3b).

The diffused MDI layer clearly indicates the extent of diffusion. This obviously contributes to joint healing. The image acquired after 100 h shows less swelling for PC/ABS-SMA in MDI as compared with PC/ABS (images are not shown here). MDI diffused to a longer distance in the PC/ABS sample as compared with the PC/ABS-SMA sample. The longer is the diffused length of MDI in the plastic material the higher the mass being taken up by the plastic material. As similar trend was observed for these two samples in mass uptake experiments, *i.e.*, a higher mass uptake of MDI by the PC/ABS sample in comparison with the PC/ABS-SMA sample (see Fig. 2). From these results it can be assumed that the diffusion of MDI to the SMA phase of the thermoplastic material is very limited and, therefore, less

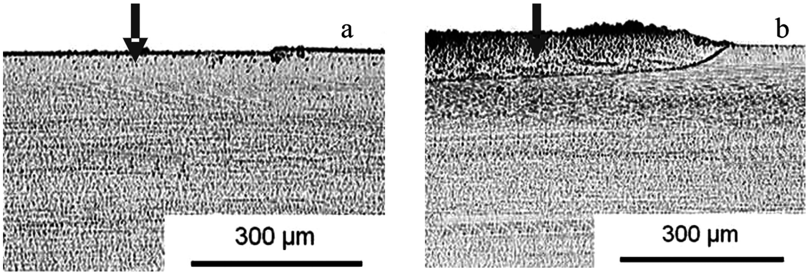

FIGURE 3 Representative optical microscopic images acquired from thin sections of PC/ABS-SMA thermoplastic materials after MDI diffusion at 40°C, (a) 5 h and (b) 100 h diffusion time.

diffusion takes place in the PC/ABS-SMA sample as compared with the PC/ABS sample. This result is in accord with the results discussed for the mass uptake (gravimetric) experiment. In the gravimetric experiments it was found that there was no mass uptake of MDI by the pure SMA sample and it is, presumably because of the polarity of the maleic anhydride group.

3.3. Determination of Diffusion Coefficients

There are various procedures described in the literature [28] to measure the diffusion coefficient, D, from the diffused length d *vs.* t plot. In this study, the diffusion coefficients for PC/ABS-SMA and PC/ABS were calculated using the data obtained from optical micrographs [Eq. (4)]:

$$d = \sqrt{Dt}, \tag{4}$$

where d is diffusion length, t is time, and D is the diffusion coefficient.

The experimental results are plotted in Fig. 4 as d *vs.* $t^{1/2}$, and a straight line is observed for both the systems, *i.e.*, PC/ABS-SAM and PC/ABS. The diffusion coefficients calculated from Fig. 4 for MDI in PC/ABS-SMA and PC/ABS are $1.5 \times 10^{-10} \pm 0.01 \times 10^{-10}\,\text{cm}^2/\text{s}$ and $2 \times 10^{-10} \pm 0.06 \times 10^{-10}\,\text{cm}^2/\text{s}$, respectively. The results show that MDI has a higher value of diffusion coefficient for the thermoplastic material without SMA and with a high PC content (PC/ABS, 60 wt.% PC). This is also obvious from the visual inspection of Fig. 4.

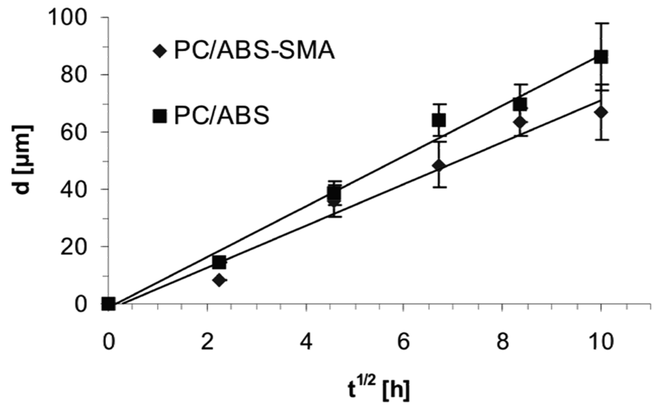

FIGURE 4 Plot of the diffusion distance, d, of MDI in thermoplastic materials *vs* $t^{1/2}$, along with a linear fit. The result of the fitting procedure gives the diffusion coefficient.

A close comparison exists between mass uptake *vs*. time and diffusion *vs*. time trends. If the results of Fig. 2 are plotted as Δm *vs*. $t^{1/2}$ straight lines for all the systems under study can be observed, like the plot of d *vs*. $t^{1/2}$ shown in Fig. 4. These plots of Δm *vs*. $t^{1/2}$ are shown in Fig. 5. Comparison of Figs. 4 and 5 indicates that the mass uptake and the diffusion follow similar mechanisms.

3.4. Peel Test

In order to simulate the effect of diffusion on joint healing at the interface between the thermoplastic materials and the PU foam, the samples were characterized using a peel test. The composition of the thermoplastic materials was the same as those used for the gravimetric analysis.

3.4.1. Analysis of Peel Test Results

The adhesion force measured in the peel test is demonstrated in Fig. 6. The y-axis represents the force required to peel off and deform the PU foam from the thermoplastic material and the x-axis represents the peeled length of the PU foam from the thermoplastic material. The adhesion strength per unit width of the sample strips was calculated by dividing the measured force by the width of each sample using Eq. (5):

$$F = \frac{P}{W}, \tag{5}$$

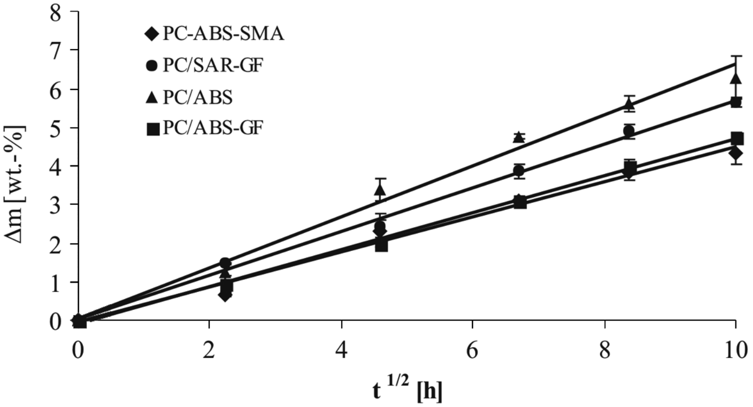

FIGURE 5 Mass uptake of MDI (wt.%) by different thermoplastic materials inversed in MDI at different time intervals at 40°C, plotted as mass uptake (Δm vs. $t^{1/2}$).

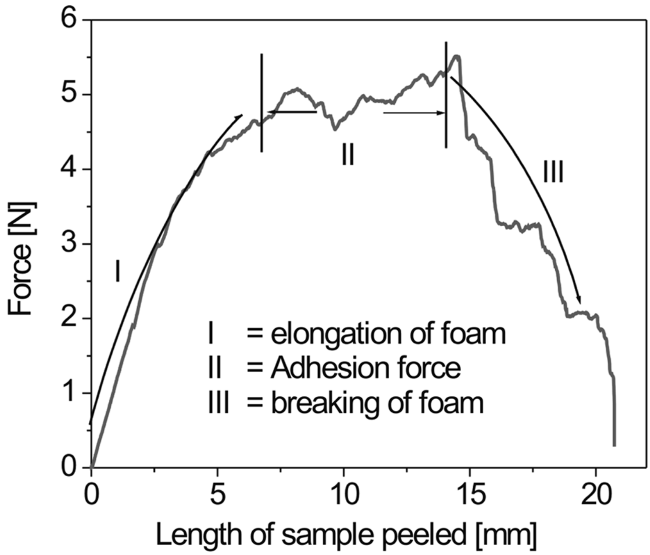

FIGURE 6 Plot of peel test data obtained when an 18-mm wide sample with a 2-mm thick PU foam layer was peeled off at a peeling rate of 10 mm/min from a PC/ABS-SMA sample.

where F is force per unit width of the peeled strip, P is measured force, and W is the width of the sample strip.

The force due to the stretching and the breaking of the foam (Region I and III in Fig. 6) was excluded in order to minimize the error in the reported failure strength. Normally, the force measured due to the breaking of the foam was higher when compared with the peeling off force. For each thermoplastic material plate, five samples were tested and an average value was reported as the interfacial adhesion/failure strength of a particular PU foam/thermoplastic material system.

In Fig. 6, the regions indicated by I–III positions represent the elongation of the foam, the adhesion/failure force at the interface, and the breaking of the foam, respectively.

The investigated PU foam systems have shown very strong adhesion to the thermoplastic materials after aging at 40°C for 100 h and the peeling off forces are as high as 5–6 N/mm (depending on the nature of the thermoplastic material).

It is not necessary that the failure would occur at the interfacial joint between the PU foam and the thermoplastic material. The PU foam could break within the bulk material in the peel test, depending on whether it is cohesive or adhesive failure. In the former case, the PU foam would break within the bulk phase as opposed to the interface.

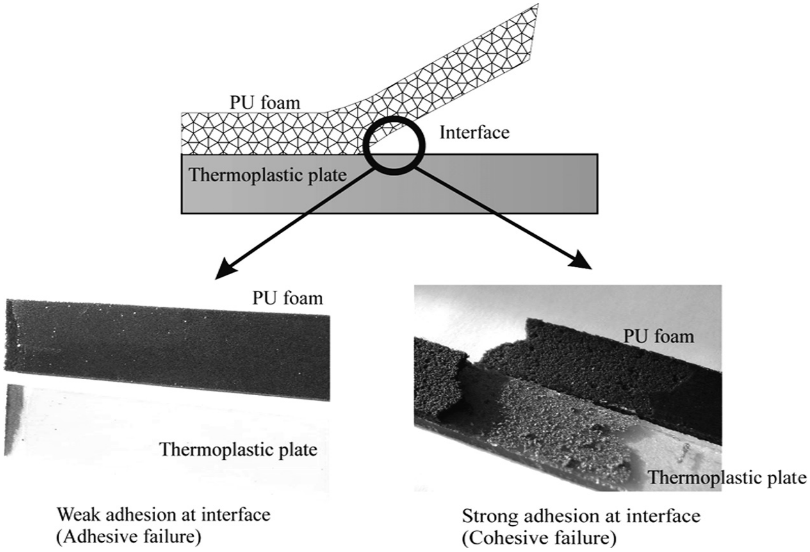

FIGURE 7 Schematic representation of PU foam/thermoplastic materials at the interface (top) and the pictures of the surfaces formed after separating the components (bottom).

In order to differentiate between the two types of peeling behavior of the test samples, the observed failure modes are shown in Fig. 7.

The plane surface of the two materials (bottom left) represents weak adhesion at the interface (adhesive failure) and the rough surface (bottom right) indicated the strong adhesion at the interface (cohesive failure).

A marked difference was observed for the two categories of the samples, namely, aged and non-aged samples. The aged samples were kept at 40°C for 100 h before conducting the peel test. Figure 8 shows a comparison of the two samples, one aged and the other unaged. The sample without any aging shows an adhesive kind of failure, *i.e.*, the PU foam peels off of the thermoplastic material smoothly. In the case of aged samples, a strong peak in the force *vs*. peel length profile can be seen which is factor of two (more than 6 N) higher than for the non-aged sample. The visual observation of the corresponding test samples showed that the failure was not smooth and a rather rough surface resulted, which means a cohesive failure occurred.

The peel test results of the PU foam system with five different thermoplastic materials before and after aging at 40°C are reported in Fig. 9. As can be observed from the figure, a lower peel off strength of the PU foam with all thermoplastic materials was found before aging

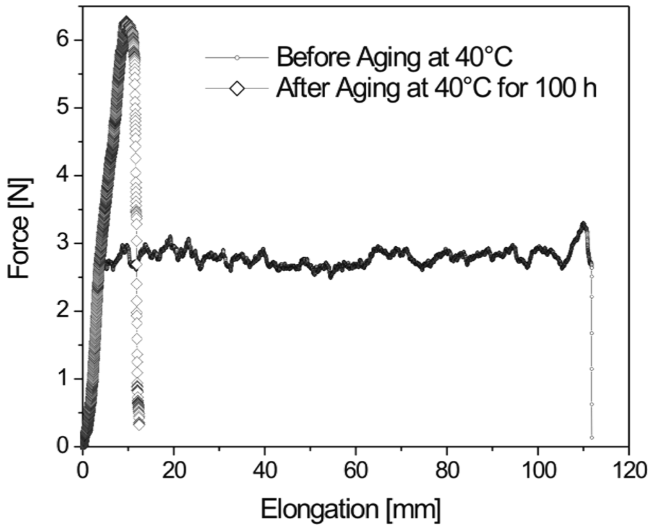

FIGURE 8 Plot of peel test data obtained when an 18-mm wide sample with a 2-mm PU foam layer thickness was peeled off at a peel rate of 10 mm/min from PC/ABS-SMA samples. (a) Before aging at 40°C, (b) after aging at 40°C for 100 h.

at 40°C. After aging at 40°C for 100 h the peel off strength increased significantly. Due to aging, diffusion occurs at the interface between the PU foam and thermoplastic materials, thereby resulting in an increase in adhesion. However, the changes are different for each sample indicating the extent of the diffusion and/or the chemical reactions occurring during the aging process. These results confirm that, due to the aging of such materials, the diffusion of unreacted moieties takes place at the interface, which greatly contributes to the joint healing.

On the contrary, a higher peeling off force was observed for the SMA thermoplastic material compared with all of the other samples, whereas the lowest peel strength was for the PC/SAR-GF samples. The other three thermoplastic materials show comparable peel strengths. The strong adhesion between SMA and the PU foam may be explained as follows. The SMA thermoplastic material is a copolymer of styrene and maleic anhydride. Maleic anhydride is a strongly polar molecule, whereas styrene is non-polar. When these two monomers copolymerize the orientation of the anhydride group on the maleic anhydride molecules will be away from the bulk of the polymer and towards the surface of the SMA copolymer. MDI molecules are polar and when applied to the SMA thermoplastic material first they adhere to it, as polar molecules have an affinity for other polar

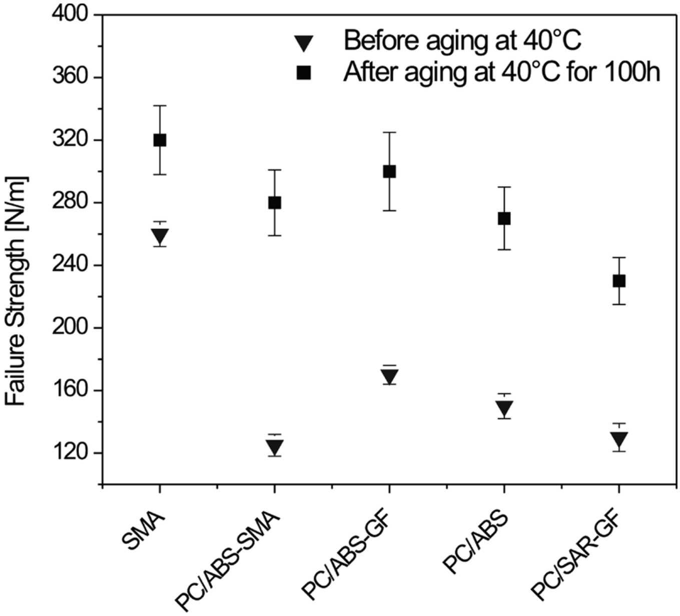

FIGURE 9 Failure (peel) strength of PU foam with five different thermoplastic materials as measured by the peel test method before and after aging for 100 hours at 40°C.

molecules. Furthermore, a chemical reaction occurs between the anhydride groups of maleic anhydride and the isocyanate groups of MDI, to form an imide bond. As a result of this reaction, a distinct peak appears in the infrared spectra at $1713\,\text{cm}^{-1}$, confirming the reaction between maleic anhydride and MDI [28]. Due to a chemical reaction a the interface of strong adhesion results, this gives higher failure strength (cohesive) when subjected to a peel test. Comparing the result of SMA and PC/ABS-SMA, the ABS is a polar substance and so is SMA. A blend of these copolymeric systems will result in the orientation of the SMA polar groups towards the PC/ABS polar groups, therefore, essentially canceling the polar effect of SMA alone or PC/ABS alone. The net result is that the PC/ABS-SMA system has a lower adhesion/peel strength than SMA or PC/ABS alone.

4. CONCLUSIONS

The mass uptake and diffusion behavior of MDI in four different thermoplastic materials has been studied. The diffusion of MDI in the thermoplastic materials was found to follow a Fickian model of diffusion. The mass uptake of MDI ranged from approximately 4.5 to 6.5 wt.% of the thermoplastic materials in 100 h at 40°C. This uptake of the MDI mass gradually increased from the beginning of the experiment to the end (100 h), though the rate of mass uptake decreased gradually with time.

Peel tests showed that samples aged at 40°C for 100 hours have higher peel off strengths than samples that are not aged. When the samples are aged, a certain extent of MDI diffusion takes place which causes the increase in the peel off strength which, in turn, implies better joint healing at the interface.

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