

## An Integrated AHP-PROMETHEE Method for Selecting the most Suitable Ethylene Propylene Diene Termonomer

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### ABSTRACT

This paper considers the problem of selecting the most appropriate ethylene propylene diene monomer (EPDM), which is a polyolefin with a variety of usages in different areas. The metallocene catalyst, bis(2-phenyl indenyl) zirconium dichloride ((2-PhInd)<sub>2</sub>ZrCl<sub>2</sub>) was synthesized by a modified method and applied to the terpolymerization of ethylene, propylene, and 5-ethylidene-2-norbornene (ENB). The methylaluminoxane (MAO) was used as a cocatalyst. It showed an appropriate activity, a high incorporation ability of the comonomers, and good performance in terpolymerization. The compounded EPDM showed good thermal stability with time. Proper criteria were chosen for the selection of the best EPDM, and a hybrid of the analytical hierarchy process (AHP) and preference ranking organization method for enrichment evaluations (PROMETHEE) was used for prioritizing 15 different synthesized EPDM species. The sensitivity and Genetic Association Interaction Analysis (GAIA) analysis were also performed. Finally, one of the polymers, which had a very high quality and moderate yield, cost, and curing time was selected.

**Keywords:** AHP, PROMETHEE, MCDM, EPDM, Catalyst, Metallocene

### INTRODUCTION

More than 60 years has passed since the discovery of Ziegler-Natta catalysts. The increasing use of synthesized polyolefins with these catalysts has been very significant and is expected to reach about 160 million tons in 2018 [1-3]. Nowadays, research in the field of catalysts has been concentrated on innovation in the production of polyolefin with special features and usages, taking a major share of the investment of the polyolefin firms. In this regard, ethylene propylene diene monomer has a variety of usages in building, electric insulation, and automotive industries as well as products such as roof insulation, wire and cable coating, and sealant

due to its unique features. Consequently, most efforts are focused on the production of vanadium catalysts to produce EPDM, which is highly considered in different industries; most catalysts used for many years are in the soluble form of compounds like VCl<sub>4</sub> and VOCl<sub>3</sub> [4]. Metallocene catalysts have found more applications in the industrial polyolefin production. High comonomer incorporation, homogenous distribution of comonomer in the polymer chains, and the polymer structure are some of the advantages of metallocene catalysts compared to conventional Ziegler-Natta catalysts [5-6]. Regarding these advantages, tendency to using metallocene instead of Ziegler-Natta catalysts for producing EPDM has

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been increased [7-9]. Other advantages which can be mentioned are the more homogenous distribution of propylene and ethylene in the chains of polymers, a wide range of feed ratios, decreasing the consumption of diene monomer, and better curing behaviors [8-10]. Despite the large efforts made by researchers, which led to thousands of published articles and patents related to coordination catalysts as well as the identification of their produced polymers, sensible weaknesses in the analysis of the catalyst parameters affecting the final properties of products can be seen. A large number of researches has focused on the role of catalyst such as activity, type of catalyst, and polymerization conditions [4, 8, 9, 11], but the quality of the manufactured product, economic aspects, and their interaction have not been evaluated. In other words, a comprehensive analysis of catalyst roles and process conditions on the final properties of the product through using different criteria has never been performed. Therefore, multiple criteria decision making (MCDM) methods can be utilized in order to select the appropriate polymer. Bagla et al. [12] reported that in MCDM problems, the best alternative is chosen through the analysis of all facing alternatives given the various and different criteria. Approximately, most MCDM problems are various, multiple, and complicated set of social, actual, and tangible factors and are very difficult to be solved using pure intuition. Opricovic et al. [13] stipulated in their study that MCDM is a dynamic and complicated process, which includes two managerial and engineering levels. They have stated that the management level specifies the objectives and selects the final optimum alternatives. Decision-makers in this level are able to accept or reject the proposed solution of the engineering level; so, the multiple natures of decision criteria are emphasized on this level. The engineering level defines the alternatives and implies the election outcomes of each alternative based on different criteria. Furthermore, on this level the alternatives are ranked on the basis of multiple criteria. MCDM analysis is widely used for decision-making problems with multiple criteria to select alternatives.

Numerous methods such as preference ranking organization method for enrichment evaluations (PROMETHEE) and analytical hierarchy process (AHP) are developed to solve the MCDM [14]. In this study, criteria for selecting the best polymers resulting from  $(2\text{-Ph-Ind})_2\text{ZrCl}_2$  metallocene catalyst is determined by a decision maker and then the polymers are ranked using AHP and PROMETHEE methods. In the following, first a brief introduction to these methods are explained and then, according to what are gathered and obtained, calculations are conducted: The integrated AHP-PROMETHEE for selecting the most suitable polymer, data gathering, AHP and PROMETHEE combinations, and sensitivity and GAIA analysis are reported as well. Finally, concluding remarks are given in section 4.

## EXPERIMENTAL PROCEDURES

The chemicals, polymer characterizations, and the polymerization procedure are explained elsewhere [8-9].

### The Proposed Method

In this section, for those who are not acquainted with MCDM methods, basic fundamentals of AHP and PROMETHEE methods are introduced.

### AHP Method

AHP is an analytical hierarchy process for multiple criteria decision-making, which is described elsewhere [15]. The applied nature of this method has resulted in its applications in many practical fields and in solving the large size and complicated decision-making problems in recent two decades.

Dagdeviren et al. [16] suggested that AHP method should initially convert the complicated multiple criteria decision-making problems to a hierarchy of decision elements (objectives, criterion, and alternatives similar to a family tree). There are at least three levels in the hierarchy: the overall objective, which is placed at the first level, multiple criteria which evaluate the alternatives at the middle level, and the alternatives at the third level.

The second step is to compare the criteria and alternatives. Once the problem is disintegrated and its hierarchy is made, prioritization procedures in order to determine the relative importance of each level criteria are initiated. Paired analysis begins at the second level (i.e. criteria) and ends at the last level. At each level, a couple of criteria are compared according to their levels of impact weight and on the basis of the criterion specified at the higher level.

Bogdanovic et al. [17] have asserted that the paired comparisons should be made by asking from decision-makers. To this end, a number from 1 to 9 should be assigned to the importance of each criterion relative to each other. The tables of the paired comparisons of the elements in AHP are completed and the weights of the criteria and sub-criteria are computed from these tables. Finally, the overall priority and ranking of the alternatives 1 to  $n$  is determined by combining the results of all the levels.

### PROMETHEE Method

PROMETHEE is an outranking method to rank a limited set of alternatives. PROMETHEE methods including PROMETHEE-I (partial ranking) and PROMETHEE-II (complete ranking) were developed by Brans et al. [18]. This method, which is used to analyze the multi-criteria problems, is simpler than the other methods in terms of concept and application [19]. Later, different versions of PROMETHEE methods were developed. For more information one may refer to Behzadian et al. [20].

### Fundamentals of PROMETHEE Method

Evaluation table is the starting point of PROMETHEE method in which the alternatives are evaluated according to different criteria [21]. Two types of additional information are needed to implement the PROMETHEE method. The first category is the information about the relative importance of the criteria (i.e. weights) and the

second one is the information about the decision-maker preference function, which is used to compare alternatives separately given the different criteria [22]. Suppose that there is a multiple criteria problem as given below:

$$\text{Max } \{f_1(a), f_2(a), \dots, f_n(a) \mid a \in A\}$$

where,  $A$  is a finite set of possible alternatives,  $f_j(a)$  means the evaluation of the alternative ( $a$ ) based on the criteria ( $j$ ) [22].

### Determining Criteria Weights

Now the weight of criteria should be determined. This work can be performed according to different methods. PROMETHEE does not provide a specific guideline to determine these weights, with the assumption that the decision-maker is able to weight the criteria appropriately [21]. The weights are non-negative numbers which are independent of the criteria units and the sum of the weights equals 1. The higher the weight is, the more important the related criterion becomes [23]. As mentioned above, in this paper, AHP has been used for weighing the criteria.

$$\sum_{j=1}^k w_j = 1 \quad (1)$$

### Preference Function

Comparing two criteria  $a, b \in A$ , the results of these comparisons should be stated based on a preference [21]. In PROMETHEE method, the preference function of each criterion is usually determined through the nature of the criterion and the viewpoint of the decision-maker [19]. The preference function,  $P_j(a, b)$ , convert the quantity difference of ( $a$ ) and ( $b$ ) alternatives in a special criterion into a preference degree which varies from 0 to 1 [22].

$$P_j(a, b) = F_j[d_j(a, b)] \quad \forall a, b \in A \quad (2)$$

where,

$$d_j(a, b) = f_j(a) - f_j(b) \text{ and } 0 \leq P_j(a, b) \leq 1 \quad (3)$$

There are six predefined functions, including usual

criterion, quasi-criterion, criterion with linear preference, level criterion, and criterion with linear preference and indifference area, and Gaussian criterion for  $F_j[d_j(a, b)]$  that cover most of the applications [19].

In the next step, the overall preference index is calculated as follows:

$$\pi(a, b) = \sum_{j=1}^k P_j(a, b) \cdot w_j \quad (4)$$

where,  $\pi(a, b)$  is the weighted sum of  $P_j(a, b)$  for each criterion and  $w_j$  is the weight associated with criterion ( $j$ ) [20].

Bogdanovic et al. [17] in an explanation of the next step stated that the preference positive (output) flow is calculated as follows:

The preference negative (input) flow is also calculated with following equation:

$$\Phi^-(a) = \frac{1}{m-1} \sum_{x \in A} \pi(a, x) \quad (5)$$

The method of PROMETHEE-I provides the partial ranking of alternatives, while the PROMETHEE-II method, by the calculation of the net flow, provides the full ranking of the alternatives. The following equation is used to calculate the net flow:

$$\Phi(a) = \Phi^+(a) - \Phi^-(a) \quad (6)$$

In PROMETHEE-I, comparing the out-ranking flows is done as follows:

$$\left\{ \begin{array}{l} aP^I \text{ bif } \left\{ \begin{array}{l} \Phi^+(a) > \Phi^+(b) \text{ and } \Phi^-(a) < \Phi^-(b) \\ \Phi^+(a) > \Phi^+(b) \text{ and } \Phi^-(a) = \Phi^-(b) \\ \Phi^+(a) = \Phi^+(b) \text{ and } \Phi^-(a) < \Phi^-(b) \end{array} \right. \\ aI^I \text{ bif } \Phi^+(a) > \Phi^+(b) \text{ and } \Phi^-(a) = \Phi^-(b) \\ aR^I \text{ otherwise} \end{array} \right. \quad (7)$$

where,  $P^I$ ,  $I^I$ , and  $R^I$  are respectively preference, indifference, and incomparable. Then, this partial preorder is given to decision-maker to make decision about the problem. If the decision-maker needs overall order, the full ranking method (PROMETHEE-II) is used. Ranking of alternatives is performed easily in this method [18].

$$\begin{array}{l} a \text{ outranks } b (aP^{II}b) \text{ if } \Phi(a) > \Phi(b) \\ a \text{ is indifferent to } b (aI^{II}b) \text{ if } \Phi(a) = \Phi(b) \end{array} \quad (8)$$

## AHP-PROMETHEE Approach for Selecting the most Suitable Polymer

Macharis et al. [21], by investigating the advantages and disadvantages of both AHP and PROMETHEE approaches, stated that AHP approach by the appropriate structuring of the problem and breaking it into simpler parts as well as weighting the criteria can assist PROMETHEE method, which does not provide any special techniques to weight criteria. On the other hand, PROMETHEE method has advantages such as the need for less input and computing and better software capabilities can be used along with AHP to rank alternatives. Therefore, in the current work, the weights will be calculated by AHP and ranking is done by PROMETHEE method to utilize both benefits.

### The Integrated Method

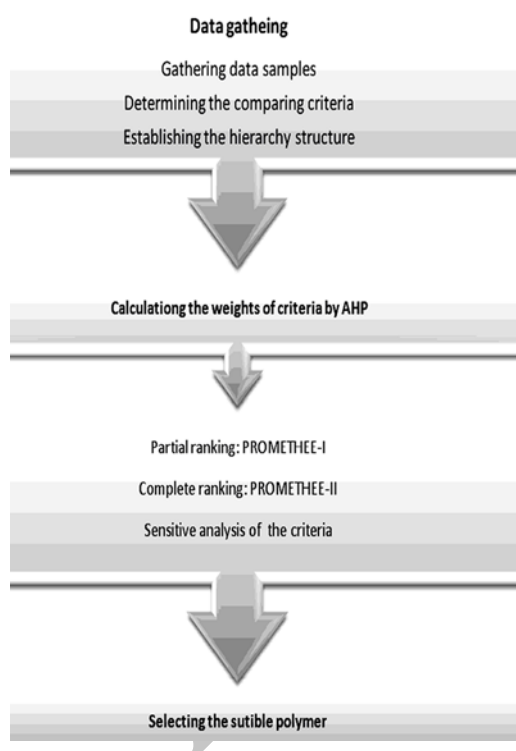
In the following flowchart (Figure 1), the various steps to reach the proper polymer, according to different criteria, using the integrative approach of AHP-PROMETHEE are provided. In the first step, after gathering data, the criteria are determined by decision-makers and to explain the status of the different criteria and alternatives, the hierarchical structure is plotted.

In the second step, the weights of the criteria are determined by a decision maker using AHP method. Then, weights calculated in the previous step are used to rate the options by the PROMETHEE method, the analysis of the GAIA diagram, and the sensitivity analysis is conducted, and finally the appropriate polymer is selected. Below, each part will be discussed in more detail.

## RESULTS AND DISCUSSION

As mentioned earlier, one of the problems existed in selecting the proper polymer is the lack of a suitable method to consider multiple criteria, either qualitatively or quantitatively. In this paper, the synthesized EPDM polymers

with the  $(2\text{Ph-Ind})_2\text{ZrCl}_2$  metallocene catalyst were analyzed, which was prepared in different polymerization conditions such as polymerization temperature, monomers total pressure, different feed ratios, catalyst concentrations, and the ratios of cocatalyst to catalyst. In order to find the proper product, the quantitative and qualitative analyses of the samples have been employed to specify the best process situations for producing EPDM rubber. Four parameters of polymers, weight of product, quality, cost of laboratory scale, and curing time were determined by a decision-maker, who is an expert in polymer and chemical sciences as the key criteria influencing the final products.



**Figure 1: Steps of the research.**

Due to the complexity of EPDM polymers and the

**Table 1: The criteria and their description.**

Criterion	Scale	Maximum or Minimum	Description
Quality	5-Point	Max	Propylene and ethylene uniform distribution as a symbol of quality of polymer has been determined by the decision-maker
Cost	\$	Min	The total cost of polymer estimated per gram of polymer was produced in laboratory scale
Yield	gr	Max	It is a measure of the weight of the polymer obtained from the polymerization catalyst.
Curing time	Min	Min	This is the basis for the rubber curing process. Curing time down economically for production of consumer rubbers is preferred.

existence of three different monomers in the main chain structure, decision-making and selecting the criteria is carefully carried out. As it is shown in Table 1, the polymer yield is considered as a criterion for catalyst performance and its quality is considered as a criterion for the proper distribution of propylene and ethylene in polymer chains based on the priorities. The cost of laboratory scale was considered as a criterion for the economic cost and the curing time as a symbol of the diene monomer presence in polymer chains. Among these parameters, the yield of polymers, cost, and curing time are quantitative amounts and can be analyzed and the polymer quality is specified as a qualitative criterion by the decision maker. This qualitative criterion has been measured by asking some questions from decision-maker about the polymer quality and by using a 5-point scale (Tables 1 and 2). As it is obvious, quality and yield should be maximized and cost and curing time must be minimized. Thus, in this combined decision-making method, the polymer which is the best in all the criteria will be selected. The number of evaluated polymers is 15 and their polymerization conditions are completely provided in Table 3. The amounts of ethylene, propylene, and diene monomer are specified using the CNMR technique and curing time is determined by a Rheotech model rheometer. In order to better understand the structure of decision-making, the criteria and alternatives are displayed hierarchically in Figure 2. The first level shows the goal, the second shows the criteria, and the last one lists the 15 polymer grades, which must be prioritized.

Table 2: 5-point qualitative scale.

1	2	3	4	5
Very low	Low	Medium	High	Very high

Table 3: The polymerization conditions for different polymers.

No.	Temperature(°C)	Pressure (bar)	E/P feed ratio	Cat. (mol.)	ENB (mol.)	MAO (mmol.) (mol.)	Yield
Ph1	60	1	80/20	4×10 <sup>-5</sup>	0.15	5	20
Ph2	60	1	80/20	4×10 <sup>-5</sup>	0.15	7.5	26.2
Ph3	60	1	80/20	4×10 <sup>-5</sup>	0.15	10	27.4
Ph4	50	1	80/20	4×10 <sup>-5</sup>	0.15	7.5	24.6
Ph5	40	1	80/20	4×10 <sup>-5</sup>	0.15	7.5	43.1
Ph6	60	1	67/33	4×10 <sup>-5</sup>	0.15	7.5	33.1
Ph7	60	1	50/50	4×10 <sup>-5</sup>	0.15	7.5	10.8
Ph8	60	1	33/67	4×10 <sup>-5</sup>	0.15	7.5	7
Ph9	30	1	80/20	4×10 <sup>-5</sup>	0.15	7.5	33.8
Ph10	60	1	80/20	4×10 <sup>-5</sup>	0.15	7.5	23.5
Ph11	60	1	80/20	4×10 <sup>-5</sup>	0.10	7.5	22.6
Ph12	60	1	80/20	4×10 <sup>-5</sup>	0.05	7.5	27
Ph13	40	4	67/33	4×10 <sup>-5</sup>	0.15	7.5	47.7
Ph14	40	2	67/33	4×10 <sup>-5</sup>	0.15	7.5	42.6
Ph15	40	4	50/50	4×10 <sup>-5</sup>	0.15	7.5	39.4

### AHP Computations

The AHP decision-making table (Table 4) was accomplished in order to specify the weights of these criteria and thus AHP matrix was imported into “Expert Choice 11” software after determining the criteria by the decision-maker. After running the software, the weights were determined for cost, quality, yield, and curing time to be 0.09, 0.364, 0.342, and 0.204 respectively. Thus quality is the most important criteria in decision maker’s point of view and cost is the least one. The calculated inconsistency coefficient is 0.02, which is significantly lower than the critical value of 0.1. Hence it can be concluded that the decision-maker has reasonably determined the weights to the importance of the criteria and no more comparing is needed.

Table 4: Decision making AHP matrix.

Criterion	Cost (\$)	Quality	Yield	Curing time (Min)
Cost	1	4	3	3
Quality	0.25	1	1	2
Yield	0.33	1	1	2
Curing time	0.33	0.5	0.5	1

### PROMETHEE Computations

To do the computations and evaluations of the PROMETHEE method, “Decision Lab” software is used. The decision-makers are able to improve the decision-making processes by using this software due to its structured process, reliability, and contribution for qualitative computations and analysis [20].

As seen in Table 5, the alternatives and criteria along with the relevant data have been imported into software. The calculations relating to  $\Phi^+$ ,  $\Phi^-$ , and the net  $\Phi$  are shown in Table 6. The ranking was carried out in the first step as it can be seen in Figure 3, in which ph6 polymer was evaluated as the best and ph3 polymer as the worst one according to the specified criteria. However, as it can be seen, the alternatives such as ph1, ph5, and ph7 are incomparable; thus full ranking or PROMETHEE II was used. As you can see in Figure 4, all the alternatives are arranged and be continued respectively from ph6, ph2, and ph4 to ph3 and ph12.

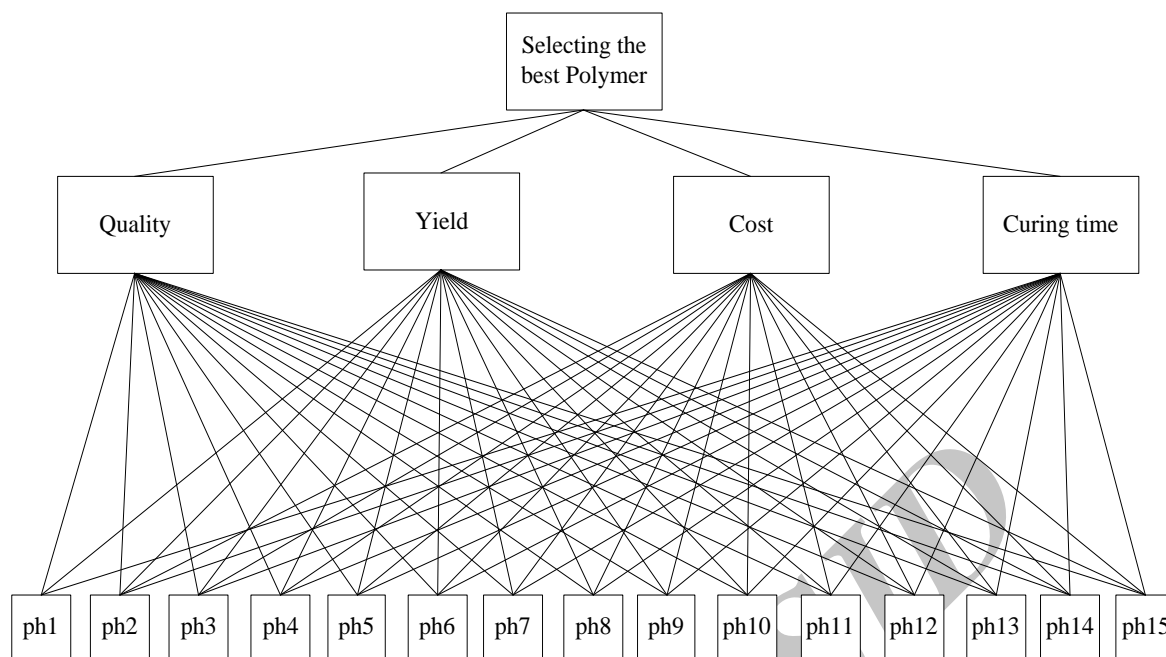


Figure 2: The hierarchical structure of selecting the best polymer.

Table 5: The evaluation matrix.

Criterion	Quality	Yield	Cost	Curing Time
Unit	5-point	-	(\$)	(Min)
Preference Function	Usual	V-Shape	V-Shape	V-Shape
Ph1	Very high	20	6.34	7.5
Ph2	Very high	26.2	8.34	6.5
Ph3	High	27.4	10.34	7.8
Ph4	Very high	24.6	8.34	7
Ph5	High	43.1	8.34	8
Ph6	Very high	33.1	8.34	6.5
Ph7	Very high	10.8	8.34	5
Ph8	Very high	7	8.34	4.5
Ph9	High	33.8	8.34	7.8
Ph10	High	23.5	8.61	6.3
Ph11	Very high	22.6	8.06	8.5
Ph12	High	27	7.79	11
Ph13	Average	47.7	8.34	10
Ph14	High	42.6	8.34	8
Ph15	High	39.4	8.34	8

The alternatives can be graphically displayed using GAIA diagram (Figure 5), while the status of each alternative can be seen given the intended criterion. This plane is the result of principal component

analysis (PCA), which projects the 4-dimensional space of criteria into a two-dimensional plane, i.e. the 4 original variables are transformed to the two new variables obtained by two linear combinations

of the original variables.

Table 6: PROMETHEE flows.

Polymers	$\Phi^+$	$\Phi^-$	$\Phi$
Ph1	0.4518	0.3806	0.0712
Ph2	0.5083	0.2253	0.2830
Ph3	0.2533	0.5147	-0.2614
Ph4	0.4633	0.3071	0.1560
Ph5	0.3818	0.3394	0.0424
Ph6	0.5864	0.1605	0.4259
Ph7	0.4347	0.3514	0.0833
Ph8	0.4249	0.3613	0.0636
Ph9	0.3228	0.3952	-0.0667
Ph10	0.2741	0.5280	-0.2539
Ph11	0.3876	0.4430	-0.0554
Ph12	0.2659	0.5439	-0.2780
Ph13	0.3694	0.5727	-0.2033
Ph14	0.3757	0.3455	0.0302
Ph15	0.3513	0.3882	-0.0369

By using the PCA, the related criteria are handled by these combinations and double counting never occurs [19]. Those axes, which end up with the square, represent four criteria and the points

displayed with the triangle represent the alternatives. As shown in Figure 5, the alternatives, which are closer to the axis of a criterion, mean a better alternative in terms of that special criterion. There is also an axis, which is a decision-making index; an alternative closer to this axis represents a better alternative in terms of the decision-making overall objectives [17]. As it can be seen in Figure 5, ph6 has this status.

### Sensitivity Analysis

One of the features that Decision Lab provides is sensitivity analysis. How the variation of 4 criteria weights will affect the ranking is the question that should be answered in this part. The sensitivity analysis has been performed and the resulting values are given in Table 7. If the weight of each criterion varies between those intervals, no changes will occur in PROMETHEE II ranking.

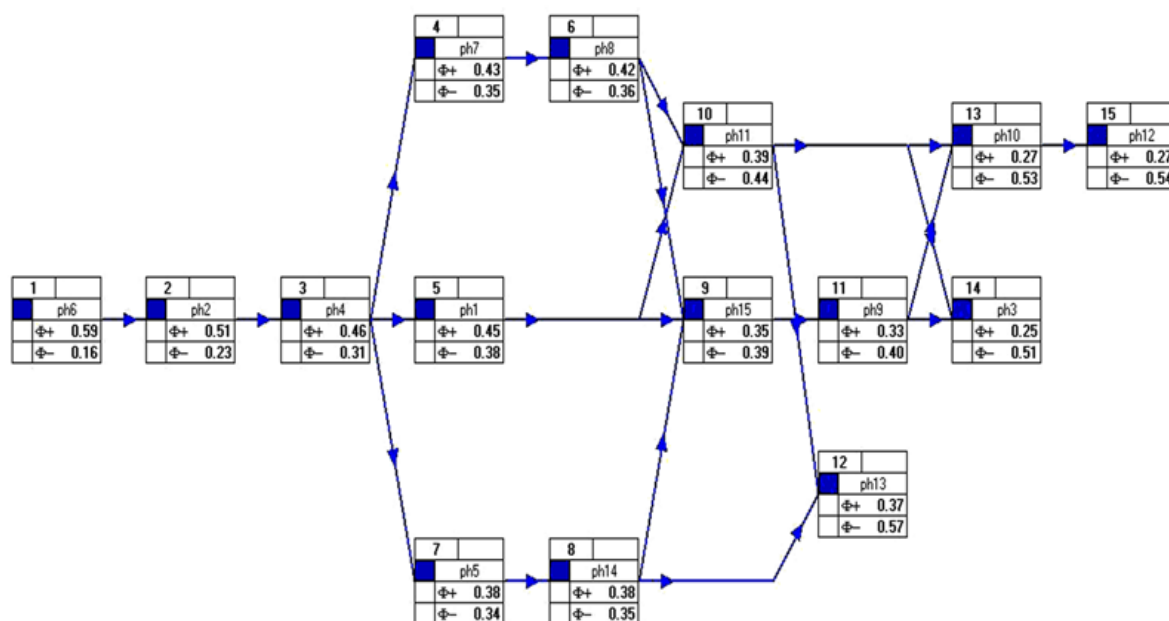


Figure 3: The partial ranking of polymers.

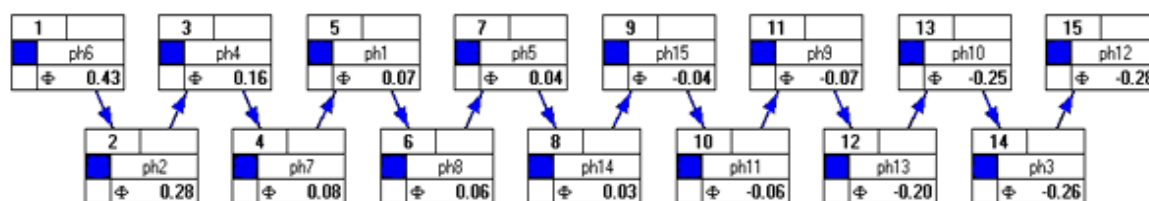


Figure 4: The complete ranking of polymers.



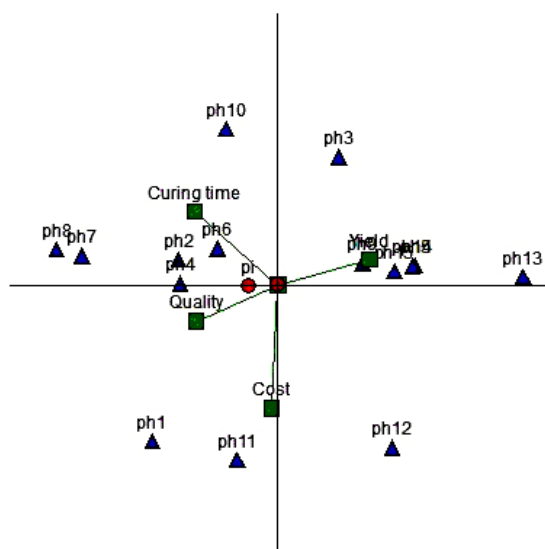


Figure 5: The polymers and criteria on the GAIA diagram.

Table 7: Stability intervals.

Criteria	Max.	Min.
Cost	0.0829	0.0989
Yield	0.3253	0.3537
Curing time	0.1946	0.2123
Quality	0.3527	0.3825

## CONCLUSIONS

In the present work, AHP-PROMETHEE approach was used to select the appropriate polymer. As previously mentioned, the polymers have been investigated only with respect to one or two criteria. However, herein, 15 polymers were ranked by employing the PROMETHEE method and considering the various quantitative and qualitative criteria using an MCDM approach. These criteria were weighted by the decision-maker using AHP method. As explained, the polymer No. 6 (ph6), which has a very high quality and moderate yield, cost, and curing time was selected. Finally, the GAIA and the sensitivity analysis were performed. In future studies, other decision-making methods and other combinations of weighting methods can be used to prioritize the alternatives and the results can be compared. Other criteria can also be investigated by this method.

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